APPLICATION OF SODIUM DEOXYCHOLATE FOR SEPARATION OF HEAVY METALS

A thesis presented in partial fulfilment of the requirements for the degree of
Doctor of Philosophy
in
Environmental Engineering
at Massey University, Palmerston North, New Zealand.

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2003

ABSTRACT

Sodium deoxycholate (NaDC) and sodium taurodeoxycholate (NaTDC) have been used to bind and subsequently remove nickel, copper and zinc ions from aqueous streams by ultrafiltration.

The mixture of metal and NaDC solutions forms a precipitate of insoluble metal deoxycholate. This precipitate can be removed from the solution in most cases by conventional techniques such as filtration and centrifugation. Ultrafiltration membranes made of polyethersulphone can also retain the precipitate effectively, producing an environmentally accepted effluent. The exception is the high copper and NaDC mixture where none of the operations works at room temperature because of the gelatinous nature of copper deoxycholate.

The removal of metal ions by precipitating them as metal deoxycholate is affected by such parameters as equilibration time, surfactant-to-metal (S/M) ratio, feed concentration, temperature and pH. An equilibration time of 3 hours or greater is required to have a major part of precipitation completed. A S/M ratio of 2.5 is sufficient, except in the case of low nickel concentration when a higher S/M ratio is necessary. A higher temperature (e.g., >40^{0}C) does not significantly affect the metal removal, but increases the process flux markedly. The high copper and NaDC mixture can also be operated with reasonable flux at a higher temperature. The use of NaDC to precipitate metal ions is inappropriate below or above the neutral pH value because DCA starts to precipitate as the pH is lowered to around 6, and metal ions precipitate as metal hydroxide at a high pH.

Because different metal ions have a differential affinity for the deoxycholate ions, NaDC can potentially separate one metal from mixtures of metals. The separation of individual metals from copper/nickel mixture is good compared to poor separations for copper/zinc, zinc/nickel and copper/zinc/nickel mixtures. This is evident from the molar ratios of two metals of 1:67, 1:2.5 and 1:7 respectively in the respective permeates.

The mixture of metal and NaTDC solutions is homogeneous and metals are removed by micellar-enhanced ultrafiltration (MEUF). Since NaTDC is expensive and difficult to recover, its application may not be economically feasible.

Based on the present research, two NaDC-mediated processes are proposed: (1) a process for removing metal ions from single-metal systems, and (2) a process for separating copper/nickel mixtures.

ACKNOWLEDGEMENTS

I would like to express my deep sense of gratitude to my supervisors, Associate Professor Robert Chong and Professor Rao Bhamidimarri of Massey University, for their valuable advice, guidance, suggestions and encouragement towards the successful completion of this research. This required a mixture of their knowledge and expertise in chemistry, environmental engineering and chemical engineering. Their patience in discussing my work over the period of my research, and reading and commenting on various drafts of my written work, and finally the thesis in its present form, is deeply appreciated.

My special thanks go to Associate Professor John Mawson of Massey University for his invaluable suggestions in several sections of this thesis.

Professor Srikanth Chatterjee advised me in various aspects of my research and this thesis, which I gratefully acknowledge.

The assistance of Mrs. Ann-Marie Jackson, Mr. Michael Sahayam and Mr. John Sykes in securing for me some obscure chemicals and equipment that I needed during the experimental work is gratefully acknowledged. Mr. Mike Stevens provided the safety measures for the laboratory and the use of hazardous chemicals, which I deeply appreciate.

My thanks go also to the staff and senior postgraduate students in the department who have always been ready to help me out in times of need.

I would like to gratefully acknowledge the help of New Zealand Pharmaceuticals Limited in supplying me, as a gift, the deoxycholic acid powder that I needed in my experiments.

Massey University Postgraduate Students Fund has provided the financial support for this project. Without this funding, this research would not have been possible. I acknowledge this support with thanks. Massey University also awarded me a Doctoral Scholarship for 3 years, which helped me financially, and enabled me to concentrate on my research with fewer anxieties. I remain grateful to the University for this.

My father-in-law, Sree Satish Chandra Howlader was the first to show an interest in my PhD research, and he has continually encouraged me to complete the work. I am grateful for his affection and his encouragement. My parents and relatives also always encouraged me to complete this research. A big thanks of course goes to my wife Urmi who took over with patience all the responsibilities of our family so that I could devote my time and energy to the research. Our baby son Indraneel Udoy, who was born during the course of my research, made me forget, with his sweet smiles, all my anxieties and tiredness. I am deeply appreciative of the support of my family.

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NOMENCLATURE

AA	atomic absorption
BOD	biochemical oxygen demand, mg/L
C_0	initial solute concentration in the sample, mg/L
C_p	solute concentrations in the permeate, mg/L
C_r	solute concentration in the retentate, mg/L
C_f	solute concentration in the feed, mg/L
C_G	solute concentration in the gel layer, mg/L
C_B	solute concentration in the bulk feed, mg/L
c_i	ionic concentration, M
cmc	critical micelle concentration, mM
CA	cellulose acetate
CIP	clean-in-place
COD	chemical oxygen demand, mg/L
CP	concentration polarization
CTAB	cetyltrimethylammonium bromide
D	diffusion coefficient, m^2/s
DCA	deoxycholic acid
EDTA	ethylenediaminetetra-acetic acid
EHPNA	2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester
I	ionic strength, M
J_w	pure water flux, $L/m^2/h$
LM	ligand-modified
LIX 54	1,3-isodecanedione, 1-phenyl
LIX 63	5,8-diethyl-7-hydroxy-6-dodecanone oxime
LIX 64N	2-hydroxy-4-nonylbenzophenone oxime
LIX 84	1-(2-hydroxy-5-nonylphenyl)ethanone oxime
LIX 860	5-dodecyl-2-hydroxy-benzaldehyde oxime
MEUF	micellar-enhanced ultrafiltration
MWCO	molecular weight cut-off

MF	microfiltration
NaC	sodium cholate
NaDC	sodium deoxycholate
NaTDC	sodium taurodeoxycholate
NF	nanofiltration
PONPE10	polyoxyethylene nonyl phenyl ether with 10 ethylene oxide units
PS	polysulphone
PEI	polyethylenimine
PES	polyethersulphone
PEG	polyethylene glycol
P_T	applied transmembrane pressure, kPa
R	solute rejection coefficient
RC	regenerated cellulose
RO	reverse osmosis
R_M	intrinsic membrane resistance, kPa/LMH
R_G	resistance due to concentration polarization, kPa/LMH
R_F	resistance due to fouling, kPa/LMH
SDS	sodium dodecyl sulphate
S/M	surfactant-to-metal ratio
TCA	taurocholic acid
TDCA	taurodeoxycholic acid
UF	ultrafiltration
V_0	initial volume, L
V_p	permeate volume, L
V_r	retentate volume, L
V_f	feed volume, L
z_i	valency of the ion
ρ	density, kg/m^3
μ	viscosity, cP
α	separation factor

Chapter 1

INTRODUCTION

Heavy metals present a continuous threat to all living organisms because of their high toxicity and detrimental effects on the health and environment even at very low concentrations. Many industrial wastewaters contain heavy metals that can contaminate the environment upon their disposal. Therefore, the treatment of such wastewater to reduce the heavy metal content to an acceptable limit has become a primary concern to minimise the damage to the environment. Upon demand, various treatment and separation techniques have been developed. Conventional techniques such as evaporation, chemical precipitation, ion exchange and solvent extraction can remove significant amounts of heavy metals from waste streams, but they are subjected to such limitations as slower kinetics, lower capacities due to heterogeneous reactions and interface transfer resistances (Uludag *et al.* 1997). Separation of heavy metals employing membranes is a relatively new technique that shows a number of potential advantages over the conventional methods.

Ultrafiltration (UF) is a pressure-driven membrane separation process, which is effective in separating, concentrating and fractionating macromolecular aqueous solutions. UF has become more effective after the introduction of polymeric membranes that give high water permeabilities and high solute rejections (Palmer *et al.* 1973).

The majority of heavy metal salts are dissociated into ions in aqueous solutions at appropriate pH. These metal ions easily pass through the tightest ultrafiltration membrane available. Thus, the UF membranes will not retain or reject them unless they are bound with larger impermeable particles. Surfactants, which produce larger particles called "micelles" are employed for this purpose. Ultrafiltration using surfactant micelles is known as micellar-enhanced ultrafiltration (MEUF) (Huang *et al.* 1994, Jones and Chapman 1995). MEUF is one of the latest innovations to the heavy metal removal technology and is still in the development stage.

In MEUF, a surfactant of opposite charge to that of a target metal ion is added to aqueous solutions. The surfactant molecules will aggregate into macromolecules or micelles at a concentration above the critical micelle concentration (cmc). The multivalent metal ions become electrostatically adsorbed or bound onto the charged micellar surface and form larger metal-surfactant complexes (Huang *et al.* 1994; Scamehorn *et al.* 1994). A compatible membrane with pores smaller than these complexes is employed to retain them, while the unbound species pass through the membrane. Thus, the target metal ions are separated from the aqueous solution. The process produces high quality permeates in which the concentrations of the metal ions and the surfactant are very low. This permeate can be disposed of or reused for other purposes. The small volume of the concentrated retentate stream can be treated further as required.

At a concentration below the cmc and even above the cmc, surfactants molecules may form small aggregates (e.g., dimers and trimers), which can be transported with the permeate through the membrane. When discharged to the ecosystem, these surfactant aggregates can cause secondary pollution. Therefore, the use of natural surfactants, which are biodegradable and less toxic than the chemically synthesised conventional surfactants, can obviate this problem (Hong *et al.* 1998).

The bile acids, which are derivatives of cholesterol, form a group of natural surfactants. This group includes deoxycholic acid (DCA), taurocholic acid (TCA), taurodeoxycholic acid (TDCA) and so on. The bile acids are water-insoluble, but their sodium salts are water-soluble and function as biological surfactants. Huang *et al.* (1994) utilised the sodium salt of DCA to successfully remove copper, cadmium, zinc, nickel and lead from waste streams. However, the effects of the key parameters such as equilibration time, temperature, pH and membrane material on the MEUF performance of heavy metals using DCA as the surfactant were not previously investigated. Moreover, the utilisation of TDCA as a surfactant has not yet been reported.

The aim of this research was to investigate the separation of three heavy metals (copper, nickel and zinc) by using sodium salts of DCA and TDCA. DCA was used to study the mechanism of metal removal and the effects of variables such as equilibration time, surfactant-to-metal (S/M) ratio, membrane type/material, temperature and pH. The selectivity of DCA in separating individual metals from mixtures of two or three metals was also investigated. TDCA was used to investigate its potential as a surfactant to remove individual metal ions and, to separate individual metals from their binary and ternary mixtures.

Structure of the thesis

Chapter 1 provides the general background information and the objectives of this research.

Chapter 2 includes the detailed literature review. It begins with an overview of heavy metal sources and their effects, and then discusses the conventional methods of metal removal. Recently introduced pressure-driven membrane processes, particularly ultrafiltration (UF) and microfiltration (MF) are then reviewed. UF, being the focus of this research, has been discussed in more detail. The chapter also deals with various aspects of surfactants and surfactant assisted UF. It concludes with the scope of this research based on the reported literature.

Chapter 3 contains the general methodology used throughout this research.

Chapter 4 expansively investigates the ultrafiltration separation of copper, nickel and zinc from aqueous solutions by using sodium salt of DCA as the surfactant. It provides the effects of equilibration time, S/M ratio, feed concentration, membrane type/material, temperature and pH. It also investigates the separation of individual metals from mixtures by using sodium salts of DCA and NaOH.

Chapter 5 describes the application of sodium taurodeoxycholate as the surfactant. It investigates the effects of S/M ratio, feed concentration and membrane material and, separation of mixtures.

Chapter 6 discusses the applications of this research and suggests a process for metal separation using the sodium salt of DCA. It also includes the recommendations for future work.

Chapter 7 concludes the research with the summary.

Chapter 2

LITERATURE REVIEW

2.1 Heavy metals in wastewater

2.1.1 Definition of heavy metals

A metal is a type of solid mineral substance that is usually hard and shiny, and can be characterised by lustre, ductility, malleability, high electric and thermal conductivity, and chemically, of forming bases (Russell 1978; Vouk 1979). It has also been suggested that metals tend to exist as cations under biologically significant conditions (Phipps 1981). In general, a heavy metal can be defined as a metal of high specific gravity (5 g/cm^3 or greater) (Rudd 1987[a]; Russell 1978). Sixty-nine elements fall into this category, but all of them are not considered as 'heavy metals' in the context of environmental pollution. Pollutant 'heavy metals' are selected by chemistry and toxicological criteria (Martin and Coughtrey 1982; Phipps 1981).

From an environmental perspective, the group of heavy metals generally includes cadmium, chromium, copper, mercury, nickel, lead, zinc, and the metalloids arsenic and selenium. Lighter metals such as aluminium and beryllium are also included in this group in terms of their environmental context. Heavy metals are often termed as "toxic elements" because most of them are very toxic to human health (Rudd 1987[a]).

Heavy metals are usually classified by their chemical or biological properties. Chemical classifications are based on the traditional concepts of acids and bases. Biological classifications are based on the essentiality and/or toxicity of individual metals (Rudd 1987[a]).

The toxicity of a metal is largely a function of its concentration. Certain elements such as arsenic and selenium may be beneficial at low doses, but become hazardous in excess of physiological requirements. Hence, caution should be used when defining a metal as toxic (Rudd 1987[a]).

Any metal can be toxic when present in excess. Though iron, copper, cobalt, etc. are very essential elements, they can be deadly poisons. Highly toxic elements like cadmium, arsenic and lead, though dangerous even at low doses, are thought to have essential physiological roles at more minute concentrations (Berman 1980).

2.1.2 Sources of heavy metals

Heavy metals may be present in wastewater in various forms. Stephenson 1987 grouped the sources into four major areas: domestic, industrial, runoff and landfill leachate.

Domestic sources

Human wastes such as faeces contribute a significant amount of heavy metals in domestic wastewater. Zinc, copper, lead, nickel and cadmium are the major metals from human wastes. Wastes from hotels, restaurants, car washes and garages, automobile repair shops warehouses and shopping centres are not usually handled as industrial wastes, but they contain heavy metals. A wide variety of products made for household use such as toothpastes, cleaners, cosmetics, shampoos, medicines and polishes contain aluminium, copper, iron, lead and zinc, and these metals thus may appear in domestic wastewater (Stephenson 1987).

Industrial sources

Heavy metals have numerous applications in various types of industries. Some industries use heavy metals directly for products. Others use process equipment and chemicals made up of or containing heavy metals. Hence, wastes from these industries contribute a major portion of heavy metals in wastewater (Stephenson 1987). Two major contributing industries are electroplating and metal finishing industries.

Electroplating

Electroplating is the formation of a thin metal coating upon the surface of another metal by electro-deposition. Chromium, nickel, cadmium, zinc, copper, silver, gold and rhodium are usually used in plating (National Occupational Health and Safety Commission 1989; Waste management guide 1988).

The electroplating process consists of two major operations. Firstly, the metal surface to be electroplated is properly cleaned and rinsed prior to the plating process because the electroplating process is very sensitive to impurities. A number of procedures and solutions are used for this purpose. The work-piece is rinsed after each step of cleaning. Secondly, metal ions in acid, alkaline or neutral solutions are applied to the desired metal surface and this process is known as plating. After plating, the work-piece is rinsed to remove excess material and attached contaminants (Waste management guide 1988).

Wastewaters generated from cleaning and plating processes contain cadmium, hexavalent chromium, copper, nickel, zinc, silver, cyanide, acids, alkalies and solvents (Waste management guide 1988). Hence, this wastewater is highly toxic (Stephenson 1987).

Metal finishing

Wastewater from metal finishing industries contains mainly iron, copper, zinc, aluminium, chromium, lead and nickel (Stephenson 1987). These may be present as cyanide complexes as finishing baths often contain cyanide.

The major industrial sources of heavy metals are listed in Table 2.1.

Table 2.1

Industrial sources of heavy metals (Stephenson 1987)

Heavy metals	*Major industrial sources*
Cadmium	Electroplating and coating, paint, battery manufacture, plastic manufacture, alloys, fungicides, rubber curing, photographic chemicals.
Chromium	Transport, building and machinery-construction industries, electroplating and metal finishing, chemical manufacture, ink, pigment, rust inhibitors, preservatives, dyeing and tanning industries.
Copper	Electroplating and metal finishing, electronics, fungicides, fertilizers, and rayon manufacture
Mercury	Electrical equipment, paint
Nickel	Alloys, electroplating, pigments, batteries
Lead	Battery manufacture, pigments, cable
Zinc	Brass and bronze alloys, galvanizing, paints, electroplating and metal finishing, plastic, rubber, battery, fertilizer, light, television, tire manufacturing
Aluminium	Building construction, electrical and mechanical engineering, metal finishing, powder, paste and metal alloys manufacturing
Beryllium	Manufacturing of nuclear reactors, electrical appliances
Arsenic	Manufacturing of insecticides, herbicides, ammonia and sulphuric acid
Selenium	Manufacturing of semiconductors, rectifiers, and photoreceptors for the electrical and electronics industries, ceramic, glass, pigments, alloys, lubricants, pesticides, pharmaceuticals, and rubber industry.

Runoff

Rural runoff generally contains lower metal concentrations, but runoff from industrial sites is usually rich in heavy metals. Runoff from roads of relatively impervious material contributes varying amounts of heavy metals, depending on vehicle lubricant loss, load loss, tire degradation, exhaust emission, road-surface degradation, road cleaning and atmospheric precipitation. The heavy metal transported by road runoff is mainly lead, but zinc and copper may also be present (Stephenson 1987).

Landfill leachate

When hazardous and heavy metals are discharged to landfill, soluble heavy metals may be transported to streams through uncontrolled leachate. The concentration of heavy metals depends upon the management of the site (Howard 1985). The metals from landfill leachate are mainly iron, manganese, cadmium, copper, lead, mercury, chromium, nickel and zinc.

2.1.3 Toxicity of heavy metals on human health

Heavy metals pose various degrees of toxicity to human health, which are outside the scope of this thesis. However, a few of the serious effects are listed in Table 2.2.

For public awareness and safety, the maximum permissible limit of each heavy metal in drinking water was set by European Standards (ES), World Health Organization (WHO) and Guidelines for Drinking Water Quality (GDWQ). The U.S.S.R. also has limited the concentration of heavy metals in the watercourses used for hygienic and domestic purposes (Kirk 1987). All the permissible limits are presented in Table 2.3.

Table 2.2

Effects of heavy metals on human health

(Berman 1980; Cory-Slechta 1993; Dept. of the Environment, London 1974; Hogan 1993; Rudd 1987[a]; Russell 1978; Sittig 1979; Squibb and Snow 1993; Steinberger 1993; Sunderman 1992;)

Heavy metals	*Health effects*
Cadmium	Heart enlargement, damages in kidney, lung, endothelium and testis leading to cancer
Chromium	Renal damage, kidney necrosis, chrome ulcers in the skin and corrosive holes in the nasal septum, lung cancer, pulmonary malignancy
Copper	Ulceration and turbidity of the cornea, gastric ulcer, renal damage, hepatic necrosis, genetic diseases, leukaemia in children
Mercury	Serious and irreversible brain damage, inflammation of gums with black line, teeth loss, bronchitis, memory loss
Nickel	Severe lung damage, insomnia, retrosternal pain, cyanosis, carcinogen to pulmonary tract and nasal passages
Lead	Burning abdominal pain, encephalopathy, abnormal body functions, cancers of the respiratory tract, gastrointestinal tract, renal and kidney
Zinc	Severe anaemia, electrolyte imbalance, muscular incoordination, eye swelling, corneal ulceration
Aluminium	Cornea necrosis, eczema, dermatoses, conjunctivitis and irritation of upper respiratory system, pulmonary fibrosis, brain disease and behavioural disorders
Beryllium	Substernal pain, skin and mucous membrane damages, weak carcinogen
Arsenic	Renal damage, skin and lung cancer, hair loss, prevents DNA repair, inhibits cellular metabolism
Selenium	Eye and stomach irritation, loss of hair, discoloration, dental caries, pulmonary oedema, brittleness of finger nails, skin destruction

Table 2.3

Limits of heavy metals in water (Kirk 1987).

Metal	WHO(mg/L)	ES (mg/L)	GDWQ(mg/L)	USSR(mg/L)
As	0.05	0.05	0.05	0.05 [d]
Cd	0.01	0.01	0.005	0.01
Cr	-	0.05[a]	0.05 [b]	0.1 [a]
Hg	0.001	PC	0.001	0.005 [d]
Pb	0.1	0.1	0.05	0.1 [d]
Se	0.01	0.01	0.01	0.001 [d]
Be	PC	PC	-	0.0002 [d]
Al [c]	-	-	0.2	-
Cu [c]	1.5	0.05	1.0	0.1
Zn [c]	15.0	5.0	5.0	1.0
Ni	-	0.05	-	0.1

Note: PC : presence should be controlled

a : Cr(VI)

b : total Cr

c : values based on aesthetics, corrosion, deposit formation, etc.

d : toxicology based

2.1.4 Effects of heavy metals on the environment

Heavy metal species have a strong attraction to biological tissues and are slowly eliminated from biological systems (Oehme 1978).

Heavy metals tend to pose extreme toxicity to all human, animal and plant life. The human body can tolerate low concentrations of some heavy metals such as copper and cobalt, which are essential components of various enzyme systems. However, these metals are toxic when present in larger amounts. Other heavy metals are toxic at any amounts. They can give rise to carcinogenic, mutagenic and teratogenic effects (Howard 1985; Rudd 1987[a]).

The heavy metals are persistent, nonbiodegradable and remain for a long period once in a system unless otherwise removed or adsorbed. Some metals such as mercury and cadmium can be bioaccumulated in the food chains (Oehme 1978; Rudd 1987[a]).

When the treated waste effluent containing heavy metals is discharged, it creates problems to the receiving environment. Disposal at sea can have great impacts on aquatic and plant life directly, and human beings indirectly. If disposed of on land, plants may absorb heavy metals and accumulate them in stems and fruits. Human beings as well as animals can be affected when using these plants as food sources. Heavy metals can also reach and pollute the groundwater (Rudd 1987[a]).

If heavy metals are present in municipal wastewater, they can cause difficulties in treatment. The metals cause system failure in biological wastewater treatment as most organisms cannot tolerate and survive in the presence of toxicity posed by heavy metals (Shanks 1982).

2.1.5 Removal of heavy metals from wastewater

Previously, attempts were made to precipitate heavy metals by allowing the wastewater to settle in a sedimentation tank prior to the actual treatment, but this was dependent on the presence of metals in a settleable form. Metals existing in insoluble forms or bound to other settleable solids are usually removed by settling. Up to 50% metal load can be reduced by primary sedimentation (Lester 1987; Rudd 1987[b]).

Considerable amounts of heavy metals come to municipal wastewater from industries that make the whole treatment system costly and ineffective. Hence, these wastewaters should not directly be discharged to the municipal sewers without some pretreatment. Pretreatment would reduce the loading of industrial wastewater to such a level as to render it harmless. Hence, a separate pretreatment plant should be set up for each or similar industries.

There have been various methods to treat wastewater containing heavy metals. Some important ones are discussed here.

Evaporation

The wastewater is boiled to vaporize the water. The metal salts and other mineral salts are concentrated in the residue, which are treated further for safe disposal (Nemerow and Dasgupta 1991).

Solar evaporation and mechanical evaporation are the two types of techniques employed for evaporation. Solar evaporation usually uses surface ponds exposed to the sunlight. The advantages of selecting solar evaporation are that it conserves energy and resources, requires low capital cost, and releases minimal pollutants to the environment. Solar evaporation depends on climatic conditions (humidity, precipitation, wind velocity and solar radiation), requires large land areas, attracts waterfowl, and needs bottom lining to prevent the migration of hazardous constituents into the ground water. Other than the cost of land area required, solar evaporation is inexpensive (Delaney and Turner 1988). Nevertheless, it is a very slow process and takes much longer time to complete the operation.

Mechanical evaporaton uses equipment known as “evaporators” to provide the means to transfer heat to the liquid and to allow the vaporisation process to occur. Thus, mechanical evaporation requires minimal land area and takes less time for operation compared to solar evaporation. However, mechanical evaporation requires significant instrumental and operating costs, and suffers from scale formation, corrosion, foaming and salting (Delaney and Turner 1988).

In spite of few limitations, evaporation is a proven, well-developed and flexible process. It is usually used as pretreatment method to reduce the volume of wastewater for final treatment or shipment off site. However, it can be used for industries producing very small quantities of wastewater or where no other practical treatment method is available (Nemerow and Dasgupta 1991; Woodland 1978).

Chemical precipitation

Heavy metals can be removed by precipitation as metal hydroxides or carbonates at elevated pH values by adding lime, limestone, caustic, magnesium hydroxide or soda ash. Sulphide precipitation of metals is obtained by using organic or inorganic sulphides (Cort 2003; Nemerow and Dasgupta 1991). Soluble metal substances are converted to insoluble forms by chemical reactions or composition changes, which precipitate upon standing. The separated precipitated solid is disposed of after further treatment (Chung 1988).

Lawn *et al.* (1980) used FeS to remove residual heavy metals from a zinc phosphatising rinse water after an initial precipitation with lime. The removals of Cr6+, Ni and Zn were 71%, 87% and 99% respectively under alkaline conditions from an initial concentrations of 0.07 mg/L, 0.77 mg/L and 24 mg/L respectively. Whang *et al.* (1982) obtained Pb, total Cr, Zn, Cd, Cu and Ni removals of 77%, 92%, 76%, 90%, 85% and 78% from electroplating wastewaters by soluble-sulphide precipitation using $Na_2S_2O_5$. Hoell *et al.* (1991) demonstrated that over 99% of Cu, Cd and Zinc, and over 96% of Ni would be precipitated from pure solutions by using magnesium bicarbonate. Peters and Bennett (1989) attained Cu, Pb and Zn removals of about 94% from industrial wastewaters by using hydroxide precipitation.

Chemical precipitation is widely applicable to remove and recover heavy metals from wastewater. It is economical, easy to operate and requires less energy (Chung 1988; Dohnert 1978). Heavy metals may form complexes with organic substances that interfere with normal precipitation processes. Occasionally, precipitate forms very small particles that remain in suspension and do not settle. Heavy metals are not totally removed in such cases. Moreover, when heavy metals are precipitated by lime, large amounts of calcium also precipitate (Dohnert 1978). Precipitation is usually not effective to remove low concentrations of metal ions (Gould and McCready 1994). Due to these limitations, chemical precipitation is not entirely suitable for total removal of heavy metals.

Ion exchange

Ion exchange is used for both general and selective removal of heavy metals from wastewater by exchanging undesirable metal cations (Valentine 1978[a]). To separate the heavy metal ions from other cations in the mixture, the resin should be selected carefully. Though strong acid resins favour the uptake of polyvalent cations, weak acid resins show higher affinity for metal ions. Heavy metal ions in a complexed form must be dealt with using a chelating resin capable of competing with the ligands in the wastewater so that the stability constant for the resin complex is greater than that of the complexes existing in the wastewater. Recovery of metal ions from wastewaters containing a high level of alkali metal ions needs further refinements (Bolto and Pawlowski 1987).

The major applications of ion exchange are removing chromium from the rinse solution of electroplating operations, treatment of metal-cyanide complexes, removal or recovery of valuable metals such as copper, zinc, mercury, molybdenum, cobalt and nickel from industrial aqueous streams (Bolto and Pawlowski 1987; Valentine 1978[a]). Sugo *et al.* (1993) passed an electroplating plant effluent containing 0.3-0.4 mg/L Co through an ion-exchange resin bed having acrylic acid-ethylenediamine copolymer functional groups at a flow rate 10 m/h for 100 min and the Co removal was greater than 96%. Chrifova *et al.* (1990) used granulated peat as an ion-exchanger to remove Cu, Ni and Zn where they obtained metal removals of 92-99%.

Ion exchange involves complex chemical reactions. Moreover, it uses some chemicals that are themselves hazardous and produces some chemical wastes that need further treatment before disposal (Nemerow and dasgupta 1991; Valentine 1978[a]; Brown 1988).

Ion exchange has limitations for the wastewater containing a mixture of two or more heavy metals because it needs resins having differential selectivity for the heavy metals which are very expensive (Bolto and Pawlowski 1987). Hence, ion exchange is suitable for wastewater containing low levels of heavy metals (Brown 1988).

Liquid ion exchange (Solvent extraction)

Liquid ion exchange (more commonly known as solvent extraction) is a well-established technique for general and selective separation of free and complexed metal ions. In this process, an aqueous solution (or organic solution) containing metal ions is placed in contact with an organic solvent (immiscible phase) containing a ligand in which the metal-ligand complexes are more soluble than in water. Then the metal ions will be partitioned or extracted into the organic solvent as an ion (complexed or solvated), an ion pair, or as a unionised compound. The loaded organic phase is then regenerated for metal recovery or treated further for disposal. Metals can be extracted as cations with cationic reagents such as 2-ethylhexylphosphoric acid, and as complex chloride anions with anionic or neutral reagents such as quaternary ammonium salts. Liquid ion exchange can treat much higher concentrations than conventional ion exchange (Ibrahim *et al.* 1994; Valentine 1978[b]). It is applicable for removing and/or recovering copper, nickel, cobalt, cadmium, zinc, molybdenum and chromium (VI) from mines and waste streams (Valentine 1978[b]).

From a mixture of metals, all metals can be recovered separately by solvent extraction. Each metal can be selectively separated at a time using an extractant or resin that is selective only for one metal over others and such an extractant or resin is often very expensive. After extraction of a metal, the extractant containing the metal is stripped with dilute acid to recover the metal as its salt. Each extraction or stripping usually takes a number of stages (Monhemius 1980; Valentine 1978[b]).

For example, copper was selectively extracted from aqueous ammoniacal solutions of copper and nickel having a pH of over 9. More than 90% copper was extracted in four stages using a water immiscible organic extractant (a mixture of an oxime with kerosine). Suitable oximes were 2-hydroxy-4-nonylbenzophenone oxime (LIX 64N) and 5,8-diethyl-7-hydroxy-6-dodecanone oxime (LIX 63) (Anon 1974)

From a solution of deep-sea manganese nodules, iron, copper, nickel and cobalt were extracted and recovered separately. Recoveries of these metals varied from 80% to 99%, depending upon various processes by a number of organizations (Monhemius 1980). There are numerous examples of such selective separation of metals.

Solvent extraction can produce environmentally accepted effluent by removing toxic metals from wastewaters, but sometimes, low metal concentrations can occur in the effluent requiring further treatment. When the relative volume of the extractant employed becomes high, no useable phase separation will occur. Usually the available extractants are suitable for heavy polyvalent metals and it becomes difficult to find the suitable extractant for alkali metals (Anderson and Reinhardt 1983; Ritcey 1983; Valentine 1978[b]).

Membrane separations

Membrane processes have been recently used for removing heavy metals from wastewater (Mulder 1991). They are described in more detail in the following section.

2.2 Membrane separations

2.2.1 General

Membranes are employed to remove one or more components from gas or liquid mixtures. Membranes primarily act as barriers in the flow path of the feed. They allow the components smaller than the membrane pores to pass through, but retain the larger components. The material that passes through the membrane is called the 'permeate' or 'filtrate' and the portion remaining is called the 'retentate' or 'concentrate'. Therefore, after membrane filtration, the concentrations of components will be different in the permeate and the retentate (Cheryan 1998; Mulder 1991).

Some kind of driving force is required for the flow of feed through a membrane. This driving force can be generated by a pressure difference, a concentration difference, an electrochemical potential difference or a temperature difference across the membrane (Mulder 1991). The basic principle of membrane separation is shown in Fig. 2.1.

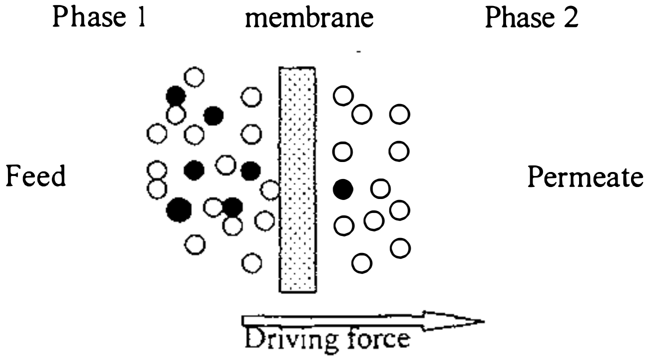


Fig. 2.1 Schematic of membrane separation (Mulder 1991).

Membranes are usually inert to the permeating components, but sometimes, can change or modify some of their physical or chemical properties such as with ion-exchange or biofunctional membranes (Cheryan 1998).

Membranes can significantly reduce the volume of wastewater without any phase change. The wastewater is allowed to pass through a module containing the membrane. Water with very small amounts of solutes passes through the membrane and the residue becomes more and more concentrated with the target solutes. The original volume of the wastewater is thus reduced to a smaller volume that can be reused or treated easily by various methods (Huang *et al.* 1994; Mulder 1991).

2.2.2 Advantages of membrane separation processes

Membrane separation processes have a number of advantages. The main advantages are discussed here (Caetano 1995; Cheryan 1998; Mulder 1991; Scott 1980):

- There is no change in the phase or state of the solvent as required by evaporation or freeze concentration. Hence, less energy is required to operate a membrane separation process.
- Their operation is simple, using only electrical energy, and no heat-transfer or heat-generating equipment is required. Thus, they are relatively cheap and need low maintenance.
- Membranes are available in a variety of sizes and can be used in various modules. They can also be operated in a batch or continuous mode. Hence, their operation is flexible.
- Membranes are usually operated at ambient temperatures, but they can also be operated at lower or higher temperatures when required. For example, higher temperatures may be used to lower the viscosity of the retentate or to minimise microbial growth and lower temperatures to prevent microbial growth.

Membrane separation processes have some drawbacks however. The solutes cannot be taken to dryness. Sometimes, the retentate becomes too viscous and its collection or pumping becomes difficult (Cheryan 1998). The membrane life is limited and the rate of permeation usually decreases with time (Mulder 1991).

2.2.3 Types of membrane separation processes

A number of membrane separation processes have been in use, depending on various driving forces. Mulder (1991) lists the following:

Concentration-driven membrane processes : Gas separation, pervaporation, Dialysis liquid membrane

Pressure-driven membrane processes : Reverse osmosis (RO), ultrafiltration (UF) microfiltration. (MF)

Eelectrochemical potential-driven membrane processes : Electrodialysis

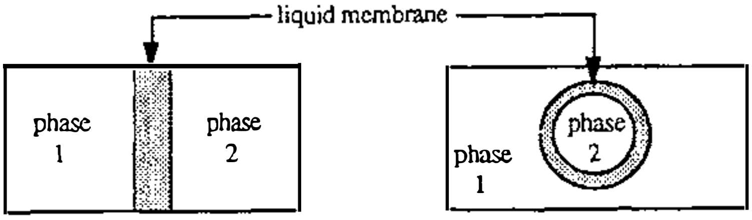
Temperature-driven membrane processes : Membrane distillation

Pressure-driven processes are mostly applicable for wastewater treatment (Mulder 1991).

2.2.4 Liquid membrane

Removal and recovery of heavy metal ions from aqueous solutions by the liquid membrane process is a relatively new approach. In such a process, the solute is transported from one liquid phase to another across a thin liquid film with a concentration difference across the membrane being the driving force (Gutman 1987). Separation occurs because of differences in solubility and diffusivity of solutes in the liquid film (Mulder 1991).

Liquid membranes are basically of two types (Fig. 2.2): supported liquid membrane (SLM) and emulsion liquid membrane (ELM).



(a) SLM system (b) ELM system

Fig. 2.2 Basic principles of SLM and ELM systems (Mulder 1991)

In the SLM system (Fig. 2.2a), an organic liquid film is supported within the pores of a microporous membrane interposed between two aqueous solutions, one of which acts as the feed solution (phase 1) and the other as the stripping solution (phase 2). The microporous membrane may be made of any type of membrane material that is compatible with the liquid membranes used such as polypropylene, polytetrafluoroethylene, polysulphone and cellulose acetate. Examples of some of the organic liquid films employed are o-dichlorobenzene, 1-octanol, dibutylphthalate, o-nitrophenyl octyl ether and o-nitrophenyl phenyl ether (Majumdar and Sirkar 1992; Mulder 1991). The transport of a salt through these organic solvents is usually very low because of its low-solubility in the organic phase. However, the transport of salt can be increased by adding a carrier molecule (e.g., oximes, tertiary amines and crown ethers) to the organic liquid, which is then called 'facilitated transport' (Mulder 1991). The metal species is extracted from the feed solution into the liquid membrane at the interface between the feed solution and the membrane; it then diffuses to the other side of the membrane where it is back extracted into the strip solution at the interface between the strip solution and the membrane. The metal becomes highly concentrated in the strip solution, which is then recycled to recover the metal (Guha *et al.* 1994; Majumdar and Sirkar 1992).

The SLM system can be highly selective for particular species because of the properties of its reacting chemical extractants or absorbents. The selectivity can be increased further by selecting a carrier molecule that has a high affinity for one of the solutes in the feed phase. The solute removal capacity of the SLM improves as the solute concentration in the feed decreases since the solute permeability increases due to facilitated solute transport. SLMs can reduce the feed solute concentration to a very low level; reduction of metal concentration in a dilute feed by two or more orders of magnitude has been demonstrated (Kemperman *et al.* 1993; Majumdar and Sirkar 1992; Mulder 1991).

The advantages of the SLM system include high separation efficiency, low capital, operating and maintenace costs, low inventory of extractants (or membrane liquid) and no extractant loss due to poor coalescence as occurs in solvent extraction (Majumdar and Sirkar 1992). However, the SLM suffers from instability resulting from loss of membrane liquid by its solubilisation in the feed and strip solutions, progressive wetting of support pores by surface-active carriers molecules, osmotic flow of water across the membrane, and the pressure differential across the membrane (Guha *et al.* 1994; Majumdar and Sirkar 1992; Yun *et al.* 1993). The SLM also has a low permeability (Mulder 1991; Teramoto 1993). However, SLMs can be stabilised by filling the support membrane pores with gels (i.e. gelled supported liquid membrane) (Teramoto 1993). To retain the inherent SLM advantages, new liquid membrane structures are being developed. The hollow-fiber contained liquid membrane is such a recently developed liquid membrane system (Majumdar and Sirkar 1992).

The ELM is prepared by first forming an emulsion by mixing two immiscible phases (e.g., water and oil), which are stabilised by a surfactant. This emulsion is then dispersed by mechanical agitation into a third phase (phase 1, Fig. 2.2b) containing the metal ions or other solutes. The liquid phase separating the encapsulated internal droplets is the liquid membrane. Usually, the internal encapsulated phase (phase 2) and the feed phase are aqueous solutions and are miscible. The liquid membrane contains a water-immiscible organic solvent and an extracting agent. It may contain a surfactant and an additive as stabilising agents that control selectivity and permeability. The aqueous receiving phase (phase 2) contains a stripping reagent. The separation of mixtures is achieved by selective diffusion of one component through the membrane phase into the receiving phase of lower equivalent concentration. The component is thus trapped and concentrated in the internal phase. After the separation is achieved, the emulsion is separated by settling, as in solvent extraction, and broken, usually by applying high voltage. The metal-enriched receiving phase is then processed to recover the metal and the organic liquid is recyled for further emulsification (Gutman 1987; Ho and Li 1992; Ho *et al.* 2001; Mulder 1991; Raghuraman *et al.* 1994; Reis and Carvalho 1994; Sznejer and Marmur 1997).

ELMs are highly selective. They are advantageous because of their high interface area for mass transfer and high diffusion rate of metal ions through the membrane. The extraction (at the outer interface) and stripping (at the inner interface) operations can be carried out in one single stage (Reis and Carvalho 1994; Sznejer and Marmur 1997). However, the ELM suffers from swelling instability of the emulsion since the volume of the inner phase increases because of the co-transport of water (osmosis) and hence, the internal receiving phase is diluted. It also requires both emulsification and demulsification operations to be performed, and the latter step is difficult. Another limitation is the leakage of the internal phase due to rupture of the membrane. However, the development of new surfactants should increase the membrane stability, permeability and permselectivity (Guha *et al.* 1994; Reis and Carvalho 1994; Teramoto 1993).

A number of successful applications of both supported and emulsion liquid membranes for removing heavy metal ions from aqueous streams have been reported in the literature. Yang *et al.* (2001) investigated the removal and recyle of copper, zinc and chromium from plating rinse water using flat-sheet SLMs in series with specific extractants. The liquid membrane phases were 10% (v/v) LIX 984N (50% oxime in kerosene, 1% 1:1 mixture of 5-nonylsalicylaloxime and 2-hydroxy-5-nonyl-acetophenone oxime) in kerosene for copper, 20% di(2-ethylhexyl) phosphoric acid in kerosine for zinc, and 0.5 M tri-n-octylamine in kerosene for chromium. The stripping solutions were 2 M sulphuric acid for copper, 2.5 M sulphuric acid for zinc and 1-2 M NaOH for chromium. After 3 consecutive SLM treatments, the removals of Cu, Zn and Cr from the wastewater (with initial concentrations of 350 mg/L, 90 mg/L and 54 mg/L respectively) were over 99.9%, 99.8% and 98.7% respectively.

Yun *et al.* (1993) developed a hollow fiber contained liquid membrane permeator where the usual limitations of SLMs were absent. They used a feed solution containing 200-500 mg/L of Cu and 100 mg/L of Cr(VI). Cu concentration was reduced to 1 mg/L (i.e. over 99.5% removal) and simultaneously concentrated in the strip to 1700-7000 ppm using

LIX84 in n-heptane. Cr concentration was lowered to 1-2 mg/L (i.e. over 98% removal) using trioctylamine in xylene.

Sznejer and Marmur (1997) demonstrated the removal of cadmium ions from an aqueous solution by an ELM system by using an emulsion with a water to oil phase ratio of 0.5. The oil phase consisted of 90% (v/v) paraffin oil (Bayol 92), 5% emulsifier (Span 80) and 5% carrier (diethyl hexyl phosphoric acid), and the aqueous (stripping) phase contained 3 M nitric acid. The authors concluded that the main resistance to mass transfer might lie at the outer oil-water interface. From a initial cadmium concentration of 1000 mg/L, the final concentration after 3 stages was less than 0.5 mg/L (i.e. over 99.9% removal).

Wang *et al.* (1992) applied an ELM process to zinc-containing acidic wastewater from viscose fiber manufacture. The zinc concentration of 500 mg/L was reduced to less than 5 mg/L (i.e. over 99% removal).

Kumar *et al.* (1994) reported Cr and Hg removals from aqueous solutions by using an ELM system containing 28% (v/v) Alamine 336 as an extractant, distilled kerosene as a diluent and Span 80 as a surfactant. The efficiency of the system for simultaneous removal of Cr and Hg was maxium at the feed pH of 2 and strip solution pH of 9. The removals of Cr and Hg were over 96% and 86% respectively.

Guha *et al.* (1994) used a hollow-fiber-contained liquid membrane technique to successfully remove Cu, Cr(VI) and Hg from wastewater where Cr(VI) and Hg were present as anions and Cu as cation. Using cotransport, Cr(VI) and Hg in the feed were transferred individually through the liquid membrane containing tri-n-octylamine in xylene and concentrated in an alkaline strip solution. Cu was removed and concentrated by countertransport by using a liquid membrane containing LIX84 in n-heptane. The removals obtained for Cu, Cr(VI) and Hg from initial concentrations of 500 mg/L, 100 mg/L and 200 mg/L respectively in the feed were 99.9%, 99.5% and 99.9% respectively.

2.2.5 Pressure-driven membrane separation processes

The choice of using RO, UF or MF depends on the particle sizes to be separated because these processes are related to the particle size of the solute and, consequently, to the membrane structure (Mulder 1991). The principle of these processes is shown in Fig. 2.3, Fig. 2.4 and Fig. 2.5. Their main characteristics are compared in Table 2.4.

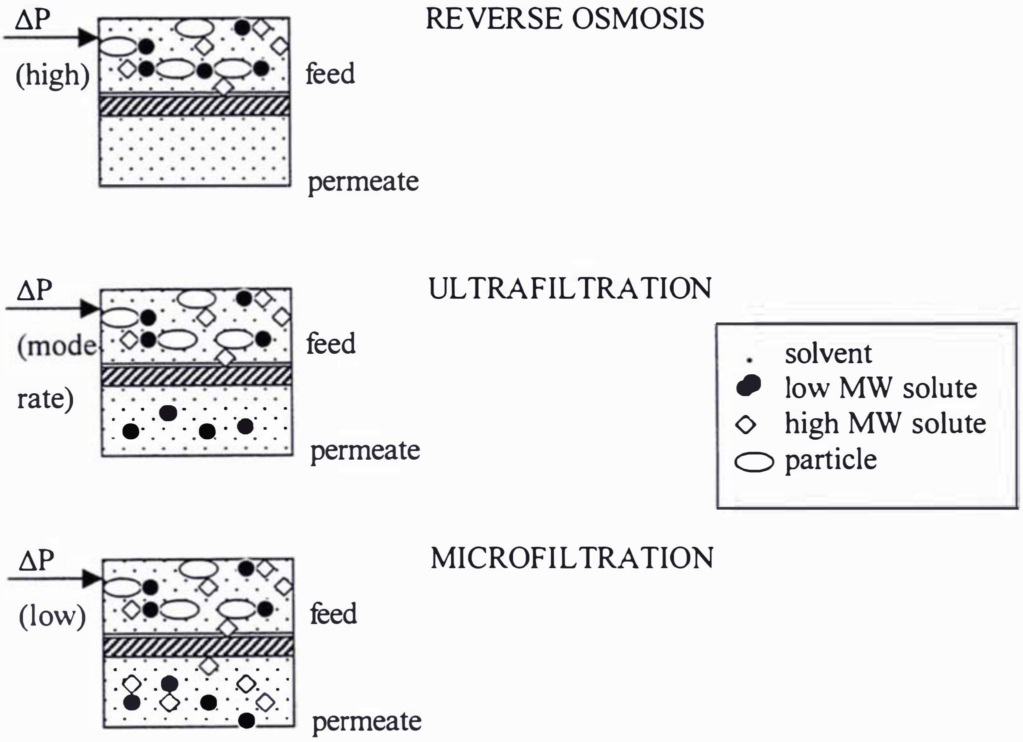


Fig 2.3 Schematic of RO, UF and MF (Mulder 1991)

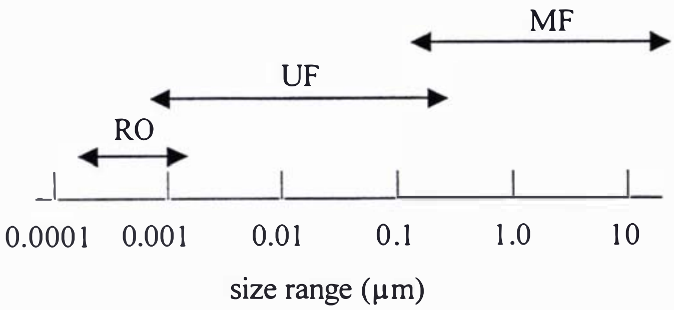


Fig. 2.4 Separation ranges of RO, UF and MF (Mulder 1991)

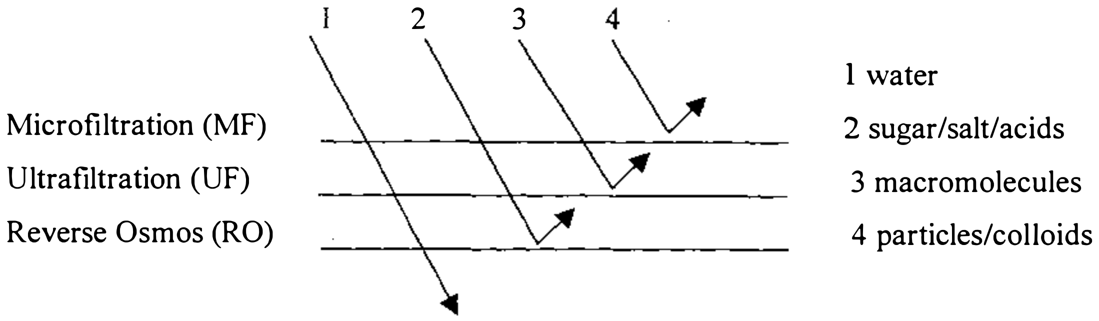


Fig. 2.5 Separation Characteristics of RO, UF and MF (Cheryan 1998)

Table 2.4

Comparison of main characteristics of reverse osmosis, ultrafiltration and microfiltration (Cheryan 1998; Mulder 1991; Vyas 1999)

Reverse osmosis	***Ultrafiltration***	***Microfiltration***
Separation of low molecular –weight solutes (e.g., salts)	Separation of macro-molecules (e.g., proteins)	Separation of particles (e.g., bacteria, yeast)
Osmotic pressure high (500 – 2500 kPa)	Osmotic pressure negligible	Osmotic pressure negligible
Applied pressure high (2000 – 6000 kPa)	Applied pressure low (100 – 1000 kPa)	Applied pressure low (<200 kPa)
Asymmetric membrane	Asymmetric membrane	Usually symmetric membrane
Thickness of actual separating layer: 0.1-1.0 μm	Thickness of actual separating layer: 0.1-1.0 μm	Thickness of separating layer: 10-150 μm
Pore size:<0.002 μm	pore size: 0.001 – 0.1 μm	pore size: 0.05 – 10 μm
Separation based on differences in solubility and diffusivity	Separation based on particle size	Separation based on particle size

Nanofiltration (NF) is a more recent modified RO process that uses membranes with pores smaller than the UF membrane pores. NF behaves as an ultratight UF or a loose RO process. NF membranes allow greater transmission of salts with the solvent and thus, accomplish some demineralisation or desalting as well. Its mass transfer mechanism is based on both the diffusion and the pore flow models (Jelen 1991; Cheryan 1998; Mulder 1991).

Though the main distinction between MF, UF, NF and RO is the applied pressure (<200 kPa for MF, 100-1000 kPa for UF, 1000-3000 kPa for NF and 2000-6000 kPa for RO), the nature of the membrane is also important to control the permeation or rejection of any species. An ideal RO membrane retains all components other than the solvent (e.g., water). UF membranes retain macromolecules, while MF membranes retain colloids or particles in the size range shown in Fig. 2.3. Thus, RO is essentially a dewatering process, while UF is suitable for simultaneously purifying, concentrating and fractionating macromolecules, and MF is mainly a clarification technique that separates suspended particles from dissolved substances. Compared to RO, UF and MF both require low operating pressures, which greatly reduce their equipment and operational costs (Cheryan 1998).

Heavy metals remain in the aqueous solution as ions, which easily pass through the UF and MF membranes, but can be retained by RO or NF membranes. Since the usual permeate fluxes of RO and NF processes are very limited, their industrial applications are expensive (Renner and El-Salam 1991; Sadaoui *et al.* 1998). If the metal ions are attached to surfactant macromolecules, UF membranes can retain them. With relatively larger pores, MF membranes offer a higher process flux, but usually cannot retain most of these surfactant macromolecules. UF has the ability to operate with a fairly steady permeation rate and without the need of an external device for cleaning (Renner and El-Salam 1991).

When removing heavy metals from an aqueous system, unlike the systems used for producing pure water, other non-hazardous components are not removed and hence, using RO or NF may not be economical.

From these considerations, UF should be more suitable for removing heavy metal ions. Therefore, UF is the main focus of this study and has been described in more detail than MF in the following sections.

2.3 Ultrafiltration

2.3.1 General

Ultrafiltration is a pressure-driven filtration separation process occurring on a molecular scale where a liquid having small dissolved molecules is forced through a semi-permeable asymmetric membrane. Large dissolved molecules, colloids and suspended solids usually can not pass through the ultrafiltration membrane pores and are, therefore, retained. UF membranes have little or no permselectivity for inorganic salts and other low molecular-weight solutes. Trnasport through UF and also MF membranes is based on the membrane being a porous medium and the mechanism is described by the pore-flow model in contrast to the solution-diffusion model for reverse osmosis. In UF, the osmotic pressure to be overcome is smaller than that in RO and therefore, UF operations are performed at low pressures (200-1000 kPa) compared to quite high pressures (2000-6000 kPa) for RO operations (Brock 1983; Howe-Grant 1993; Lonsdale 1972; Mulder 1991; Stewart 1983).

2.3.2 Membranes for ultrafiltration

Early UF membranes were amorphous in composition with nearly equal pore openings on both sides. Hence, they had very low fluxes and possibilities of clogging easily due to entrapment of partially permeating species (Blatt 1976; Brock 1983).

Modern UF membranes are usually anisotropic consisting of a thin skin on the surface. The thickness of the skin-layer is usually 0.1 μm or less when the total membrane thickness is 200-250 μm. The skin-layer is dense and consolidated, and has the minimum pore size. It comprises of a series of well-ordered pores having a relatively narrow distribution of mean pore diameters. Since the skin-layer of the membrane faces the feed solution, it shows a unidirectional flow with higher flux and lower tendencies for clogging. If any solute particle can enter into a pore of the skin-layer, it will easily pass through the membrane giving less possibility for its entrapment in the pore (Blatt 1976; Porter 1990^{a}).

Molecular weight cut-off (MWCO) is an important parameter for characterizing ultrafiltration membranes; it is one of the retention characteristics of the membrane expressed in terms of molecules of known sizes. The MWCO of a membrane is defined as the weight of a spherical uncharged molecule when more than 90% of components with weight greater than or equal to that molecular weight (MW) are rejected. Linear molecules having MW greater than the MWCO of the membrane can still pass through it and charged molecules with MW less than the MWCO can be retained. Available MWCO ranges from about 500 to 300,000 (Brock 1983; Porter 1990^{a}). MWCO is useful to separate molecules from other molecules or particles according to size (McGregor 1986).

UF membranes can be prepared from a wide range of polymers. The most important polymers are polysulphone or polyethersulphone, cellulose acetate and polyamide. Polymeric asymmetric membranes are prepared mainly by a phase-inversion process (Cheryan 1998; Mulder 1991).

Polysulphone

Membranes from polysulphone and its family are widely used in UF applications. Polysulphone contains repeating diphenylene sulphone units. The $-SO_2$ group in polymeric sulphone is very stable. Due to repeating phenylene rings, membranes from polysulphone and its family show higher molecular immobility, stability, rigidity, strength, and creep and heat resistance (Cheryan 1986). Presently, polysulphone (PS) and polyethersulphone (PES) are widely used for manufacturing UF membranes because of the following properties (Cheryan 1986):

- PS and PES membranes can withstand very high temperature ranges. The usual upper temperature limit is 75^{0}C, but it can go up to 125^{0}C for membranes from some manufacturers. The high temperature can help to lower the viscosity of many solutions and, for sterilisation by heat treatment in some fermentation and biotechnology processes.
- PS and PES membranes enjoy wide pH limits ranging from 1 to 13.
- They show reasonably good resistance to chlorine. The limits of tolerance are up to 200 mg/L for short-term and up to 50 mg/L for long-term uses.
- They can easily be fabricated in various configurations and modules.
- They are available in a wide range of pore size. MWCOs from 1000 to 50,000 are common.

In spite of so many advantages, PS and PES membranes have some limitations. Their pressure tolerance is limited: only 690 kPa (100 psi) for flat-sheet and 172 kPa (25 psi) for hollow fibre membranes. Due to their hydrophobicity, they tend to interact with many solutes and enhance membrane fouling (Cheryan 1986).

Cellulose acetate membranes

Cellulose acetate (CA) is prepared from cellulose, which is a high polymer of ß-1, 4 linked glucose units. Cellulose is usually linear, rod-like and inflexible. CA is made by reacting the cellulose with acetic anhydride, acetic acid and sulphuric acid. The optimum degree of polymerisation of cellulose is 100–300 that results in molecular weights of about 25,000 to 80,000 (Cheryan 1986).

CA membranes have a permselective layer on one side known as the 'active side'. This side of the membrane faces the feed solution on the high-pressure side during separation operations. For membranes having total thickness between 50μm to 150 μm, the active layer or skin is about 0.25 μm thick, but this thickness varies with drying time and concentration of the swelling agent in the casting solution. When the concentration of swelling agent increases in the casting solution, void volume increases and the skin thickness decreases. The layer below the skin layer is termed as the 'porous substructure' that extends to the bottom surface in most cases. The void diameter usually increases from the minimum at the top surface to the maximum at the bottom surface. Sometimes, there exists a transition layer between the active layer and the porous substructure that shows a density intermediate between those two layers (Kesting 1977).

CA membranes are mostly used in flat sheet (spiral elements) and hollow fibre configurations for commercial basis because they are economical with the required degree of perfection. The tubular configuration has limited applications mainly due to its low effective area per unit volume, making the module large and costly (Kesting 1977).

CA membranes offer higher flux and higher rejection for salts and organic species of various molecular weights. Their manufacture is relatively easy and cheap with a broad range of renewable raw materials (Cheryan 1986; Mulder 1991).

The use of CA membranes has a number of limitations (Cheryan 1986; Mulder 1991):

- The membranes cannot be operated at a temperature over 30^0C and at any pH outside the range of 3.0-7.5; otherwise the cellulose matrix will be hydrolysed.
- They have poor resistance to chlorine that makes the membranes unsuitable for using in the food industry since chlorine is most commonly used for sanitising.
- They lose their properties gradually under pressure over their operating lifetime.
- They are highly biodegradable and this limits their life since microbial growth is most prominent within their operating temperature range.
- They show poor rejections for low molecular-weight solutes.

Polyamide membranes

Polyamide membranes are prepared from materials having an amide bond (-CONH-) in their structures. Examples of polyamide membranes are cross-linked aromatic polyamide, aryl-alkyl polyamide, polybenzimidazole and polyacrylamide. They can withstand higher temperatures (up to 35^0C) and a wider pH range (4-10) than CA membranes. They can reject a wide range of low molecular-weight organics such as phenols and amines, which are not readily rejected by cellulose acetate membranes. The major limitations of polyamide membranes are that they show lower flux and lower chlorine tolerance than cellulose acetate membranes (Cheryan 1986).

Other polymeric membranes

Other common UF membranes include polyacrylanitryl, cellulose triacetate, cellulose nitrate, regenerated cellulose, polyvinyl chloride copolymer, polyvinylidene fluoride, polypropylene, nylon and polytetrafluoroethylene (Cheryan 1986; Huang *et al.* 1994; Paulenova *et al.* 1996; Scamehorn *et al.* 1994).

Inorganic membranes

Inorganic UF membranes were developed after polymeric membranes. They are also known as ceramic or mineral membranes. They possess a number of well-defined properties, which allow their use in many new areas where polymeric membranes are not suitable (Cheryan 1998). Zirconium oxide membranes and microporous glass membranes are two examples of inorganic membranes. For zirconium oxide membranes, a thin skin layer of zirconium oxide is deposited onto a porous carbon support tube. Microporous glass membranes are prepared by heating sodium borosilicate glass between 450^0C to 600^0C (Cheryan 1998).

The available configurations of inorganic membranes are tubular and flat sheet. Tubular membranes can be single-channeled, or multi-channeled with 7 to 37 individual circular channels called 'lumens'. The feed flows through the inside of the channels, but the permeate passes through the support layers around the lumens (Cheryan 1998).

Inorganic membranes have the following useful properties (Cheryan 1998):

- They are inert to most of the common chemicals and solvents.
- They can withstand high temperatures and pressures. The upper limits are 350^{0}C for temperature and 150 psi (1,035 kPa) for pressure.
- They have a good operating pH range of 0.5-13.
- They can tolerate high chlorine doses (up to 2000 mg/L in certain cases).
- They can be operated for a very long time (10-14 years).

The main drawbacks of inorganic membranes are that they are brittle and more expensive (due to higher initial cost) than polymeric membranes (Cheryan 1998).

2.3.3 Modules for ultrafiltration membranes

A module is the smallest unit into which the membrane area is packed and it is the core of a membrane installation (Mulder 1991). Four basic module designs are available for industrial uses. Their configurations are given in Fig. 2.6, Fig. 2.7, Fig. 2.8 and Fig. 2.9.

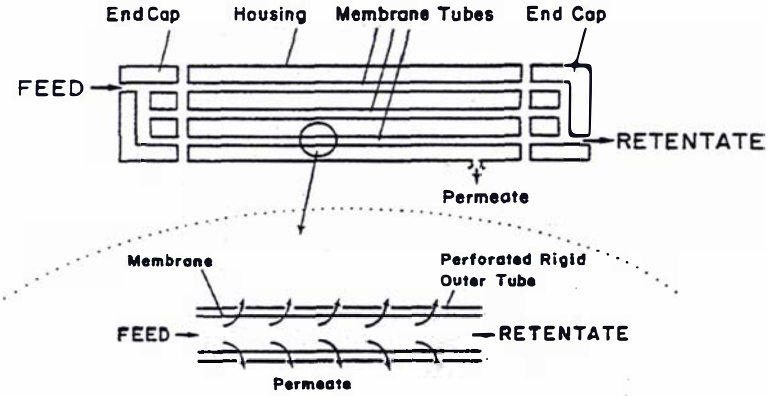


Fig. 2.6 Schematic of a tubular membrane for UF (Cheryan 1998)

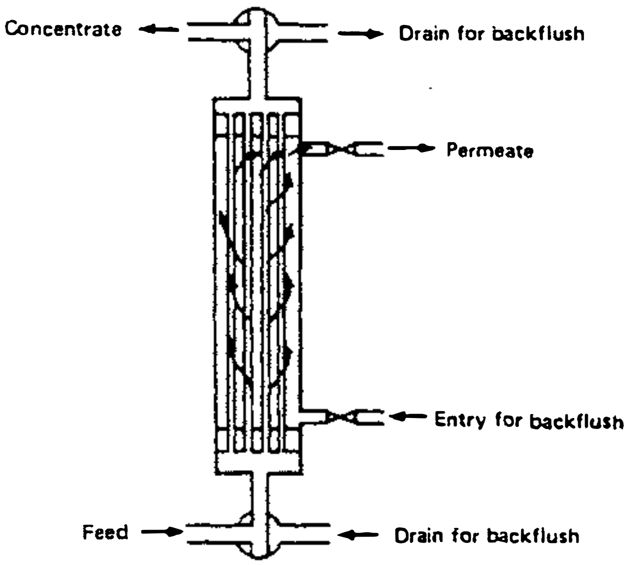


Fig. 2.7 Typical Hollow fibre unit for UF (Gutman 1987)

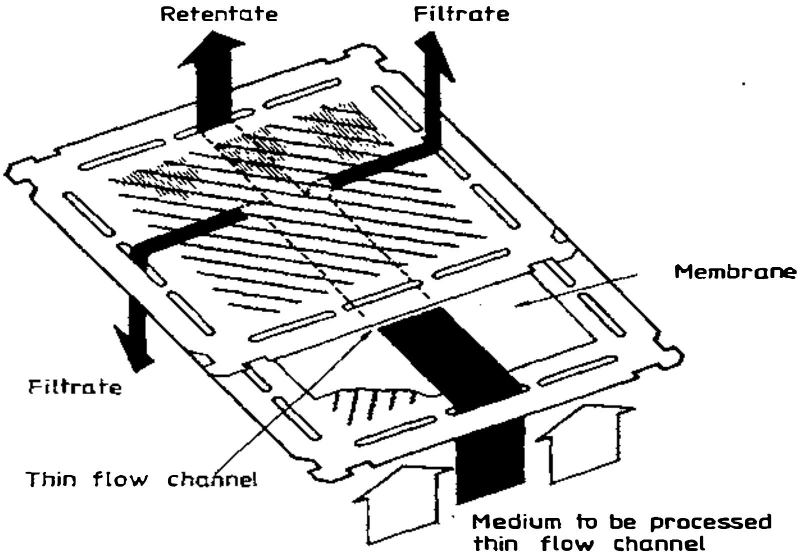


Fig. 2.8 Typical plate and frame unit (Gutman 1987).

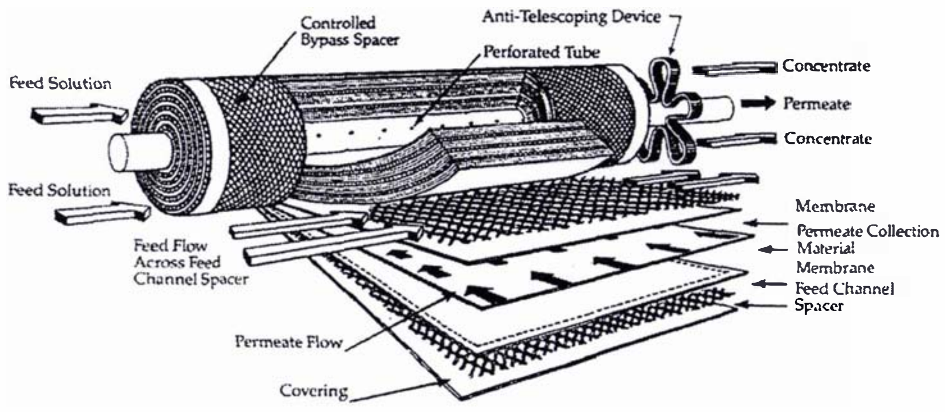


Fig. 2.9 Spiral wound module (Cheryan 1998).

Comparison of conventional UF membrane modules

The operational parameters, cost and a few other characteristics of the conventional modules are compared in Table 2.5.

Table 2.5

Comparison of conventional UF membrane modules (Mulder 1991; Porter 1990[a]).

	Tubular	*Plate-and-frame*	*Spiral-wound*	*Hollow fibre*
Cost/area	higher	high	low	lower
Replacing cost	high	low	low/moderate	moderate
Operating cost	higher	high	moderate	low
Packing density	low	moderate	moderate/high	very high
Fold-up volume	high	medium	medium	low
Flux	good	good/excellent	good	poor/fair
Energy used	high	medium	medium	low
Fouling tendency	low	moderate	moderate	high
Cleaning	good	good	fair	poor

The choice of a specific module depends, mainly, on the type of application and also on the cost particularly when more than one module is applicable. In MEUF applications where fouling tendency is high, the tubular module is well suited because of its good process control and ease of membrane cleaning, although the cost is high. The relatively cheap hollow fibre module is avoided in such a case because of difficulty in its cleaning since it is very susceptible to fouling (Mulder 1991).

2.3.4 Feed flow pattern

The flow of feed to the ultrafiltration membrane may be in two patterns: dead-end flow and cross-flow. The flow patterns are shown in Fig. 2.10.

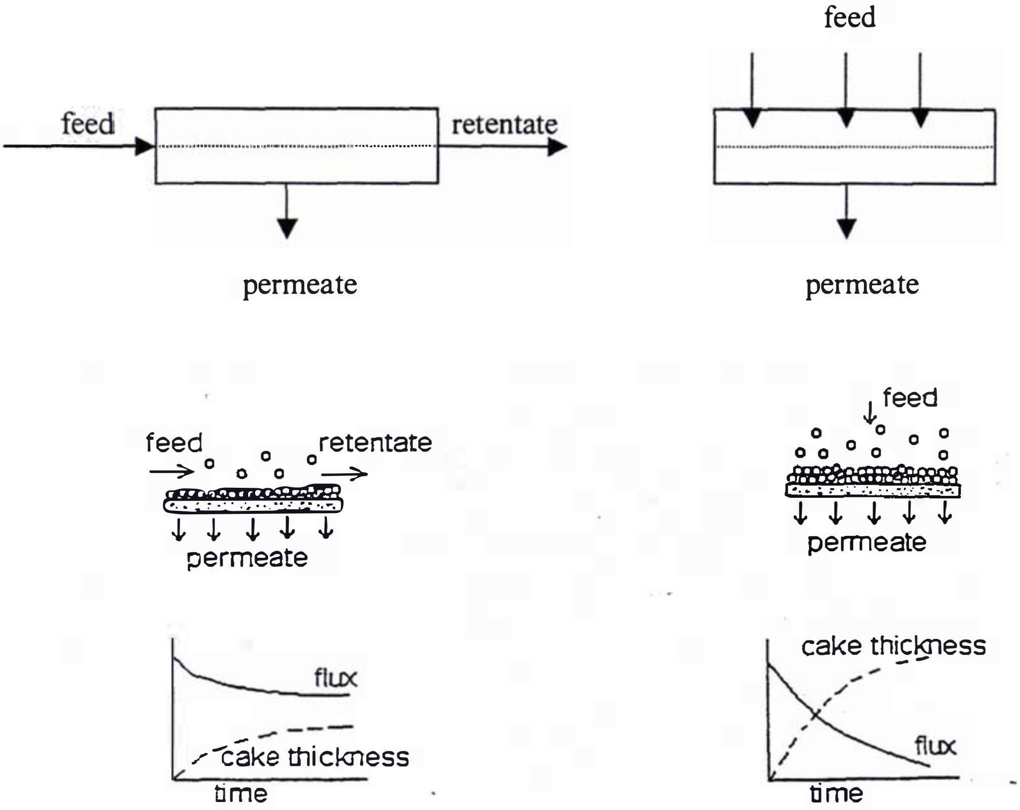
Dead-end flow

In dead-end operation, the feed flows perpendicularly to the membrane surface. The rejected solute molecules accumulate continuously on the membrane surface and forms solid cakes that increase with time. Since the solute particles are forced towards and through the membrane, portions of larger particles are trapped into the membrane pores and cause membrane fouling. Thus, the permeate flux in dead-end operation gradually decreases with time. The membrane needs regular cleaning to restore the flux (Mulder 1991). Hence, dead-end flow is not suitable for large-scale or industrial applications.

Cross-flow

In cross-flow operations, the feed flows parallel to the membrane surface. A portion of the feed flows through the membrane that becomes the permeate. The rest of the feed becomes the retentate that is collected separately or recyled to the feed tank. Shear forces prevent the rejected solute molecules to be readily accumulated on the membrane surface. Thus, the flux decline with time is small and there is no significant cake formation. The flux increases if the cross-flow velocity increases (Mulder 1991).

Thus, cross-flow operation is usually suitable for industrial applications because of its comparatively smaller concentration polarisation and fouling effects (Mulder 1991).



Cross-flow

Dead-end flow

Fig. 2.10 Cross-flow and dead-end flow patterns (Vyas 1999)

2.3.5 Modes of operation

There are three basic modes of operation for ultrafiltration. They are batch, single-pass, and feed and bleed operations. Another operational technique, sometimes associated with UF, is diafiltration (Cheryan 1998).

Batch operation

In batch operation, the feed is pumped from the feed tank to flow over the membrane. The retentate is recycled to the feed tank. The feed volume decreases as the permeate is removed. Hence, the decreased feed solution becomes more concentrated. The run is over when the feed volume becomes too small to pump, or the desired concentration or volume reduction of the feed is achieved. The initial flux is high, but it decreases with an increase in feed concentration (Cheryan 1998; Porter 1990[a]). Fig. 2.11 shows the principle of batch operation.

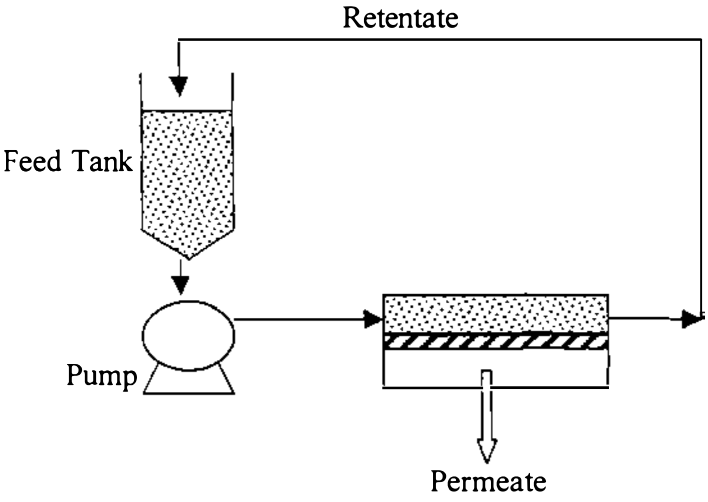


Fig. 2.11 Batch UF with full recycle of retentate (Cheryan 1998)

Batch operation is applicable when permeate is the desired product. Fruit juice clarification and effluent treatment are two examples where UF is operated in a batch mode (Cheryan 1998).

Single-pass operation

In single-pass operation, the feed is pumped to flow over the membrane, but the retentate is not recycled to the feed tank (Fig. 2.12). Hence, the permeate volume is usually small. It is suitable for systems having low concentration polarisation effects and where a higher flux is not desirable. It may be used for hollow fibre bioreactors, water treatment and pyrogen removal. A number of single stages can be used in parallel or in series (Cheryan 1998; Porter 1990[a]).

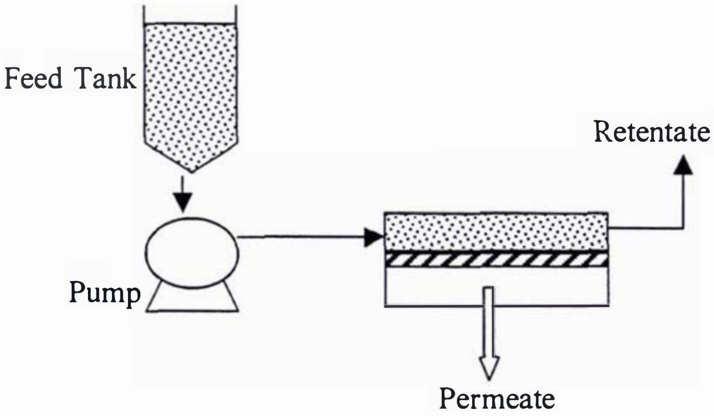


Fig. 2.12 Single-pass continuous filtration (Cheryan 1998)

Feed-and-bleed operation

The feed-and-bleed operation gives continuous filtration where the feed stream is pumped into a recirculating loop. This operation uses two pumps: a feed pump and a recirculation pump (Fig. 2.13). The recirculation pump starts after the feed pump fills the recirculating loop (Cheryan 1998; Porter 1990[a]).

A portion of the retentate is removed and the rest is fed into the recirculating loop, but the ratio of these two portions of the retentate is such that the permeate and retentate mass flows are equal to the feed mass flow. The flux decreases with an increase in concentration of the retained species. The run continues until the desired volume is processed. Sometimes, the run needs to be ended due to cleaning needs of the membrane (Cheryan 1998; Porter 1990^a).

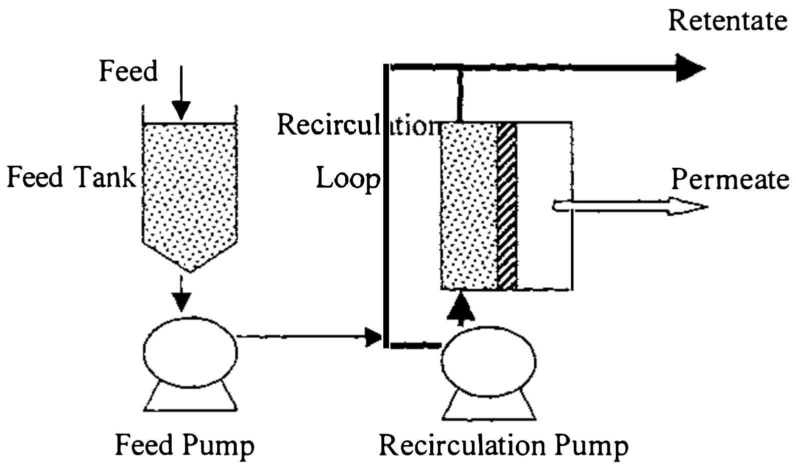


Fig. 2.13 Feed-and-bleed operation (Cheryan 1998)

The feed-and-bleed system discussed above is a single-stage operation where the flux is lower than the average flux in a batch mode. It also needs a large membrane area and is usually used for continuous full-scale operations (Cheryan 1998).

For large-scale operations, one-stage operation is not enough because the flux is low and the membrane is always exposed to the highest solute concentration. In these cases, a multistage system is used where two or more single stages are connected in a series. In a multistage system, the bleed (discarded retentate) from the first stage becomes the feed in the second stage and so on. Each stage needs an additional recirculation pump and operates at a higher feed concentration. The flux is high in the initial stages, but significantly lower in the final stage. Only the membrane in the final stage faces the highest solute concentration. Thus, a multistage system needs a lower membrane area than a single-stage one (Cheryan 1998; Porter 1990^a).

These continuous systems can handle large volumes of feed as the feed has a lower residence time in the system than in the batch operation (Porter 1990[a]).

Diafiltration

Diafiltration is the addition of fresh solvent (water) to the ultrafiltration retentate. By this process, residual low molecular weight and membrane-permeating solutes are continuously diluted and washed out of the retentate solution along with the solvent (Brock 1983; Cheryan 1998).

Diafiltration is accomplished in two ways: discontinuous diafiltration and continuous diafiltration (Fig. 2.14).

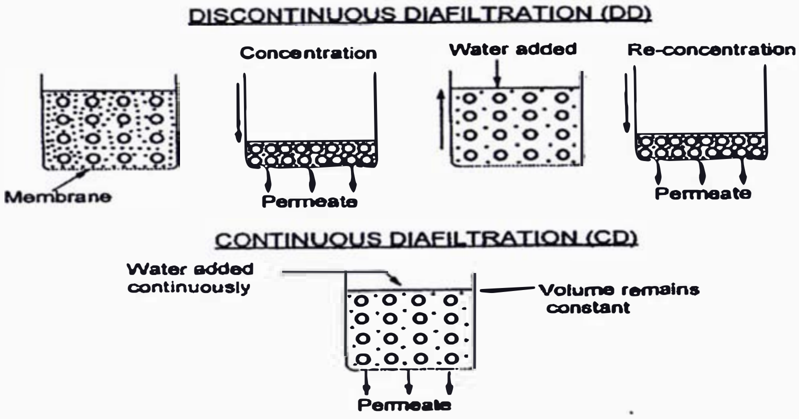


Fig. 2.14 Discontinuous (top) and continuous (bottom) diafiltration (Cheryan 1998)

Discontinuous diafiltration

In discontinuous diafiltration, membrane-permeating solutes are eliminated or exchanged from the retentate by simple volume reduction using repeated redilution and reultrafiltration. That means, a certain volume of water is added to the retentate and reultrafiltered to a desired volume of the retentate. This process is repeated several times until the salts are almost entirely removed from the retentate (Blatt 1976; Cheryan 1998).

If the volume reduction is the same in each stage, the solute concentration in the final retentate (C_r) is given by:

$$C_r = C_0 (V_0/V_r)^{1+(R-1)n} \qquad (2.1)$$

where C_r = solute concentration in the final retentate, mg/L

C_0 = solute concentration in the feed at the start of diafiltration,mg/L

V_0 = initial feed volume, L

V_r = retentate volume, L

n = number of repeats or stages,

and the solute rejection coefficient, $R = 1 - C_p/C_r$ where C_p and C_r are solute concentrations (in mg/L) in the permeate and the retentate respectively (Cheryan 1998).

If the volume reduction is different in each stage, the solute concentration in the final retentate (C_r) is given by:

$$C_r = C_0 (V_{01}/V_{r1})^R (V_{02}/V_{r2})^{R-1} \qquad (2.2)$$

where V_{01}/V_{r1} and V_{02}/V_{r2} are volume concentration ratios in the first and second diafiltrations respectively (Cheryan 1998).

Continuous diafiltration

Continuous diafiltration is a constant-volume ultrafiltration for an ultrafiltration retentate where fresh solvent is continually added to the retentate solution to replace the permeate or filtrate (Brock 1983). Hence, the rate of water addition is equal to the permeate flux (Cheryan 1998).

The solute concentration in the final retentate (C_r, in mg/L) can be calculated from the equation:

$$\ln(C_0/C_r) = (1 - R)(V_p/V_0) \tag{2.3}$$

where V_p is the volume of liquid permeated (in L), and other notations are the same as in the discontinuous diafiltration equations (Cheryan 1998).

2.3.6 Ultrafiltration Flux

The flux is defined as the rate of fluid flow through the membrane per unit area of the membrane. It is an important process variable for UF. For any UF, one of the primary requirements is that a reasonably high flux is to be maintained (Cheryan 1986).

The flux through an ultrafiltration membrane (J_t, in L/m^2/h) can be expressed by Darcy's law for flow through porous media:

$$J_t = K.P_T \tag{2.4}$$

where P_T is the applied transmembrane pressure (in kPa), and K is the permeability constant that depends mainly on porosity and pore size distribution of the membrane and the viscosity of the permeate (Cheryan 1998).

All the membrane properties produce some resistance to flow. The pure water flux (J_w, in L/m^2/h) through the membrane is:

$$J_w = P_T/(\mu R_M) \tag{2.5}$$

where P_T is the applied transmembrane pressure (in kPa), μ is the viscosity of the permeate (in cP) and R_M is the resistance (in kPa/LMH) of the membrane (Cheryan 1998).

When any solution consisting of a solvent and one or more solutes flows through an ultrafiltration membrane, there will be other resistances in addition to the membrane resistance. The permeate flux (J_t) in such a case can be given by:

$$J_t = P_T/\mu\ (R_M + R_F + R_G) \qquad (2.6)$$

where P_T is the applied transmembrane pressure (in kPa), μ is the viscosity of the permeate (in cP), R_M is the intrinsic membrane resistance (in kPa/LMH), R_G is the resistance due to concentration polarisation (in kPa/LMH) and R_F is the resistance due to fouling (in kPa/LMH) (Cheryan 1998).

Factors affecting the flux

The flux through an UF membrane is affected mainly by the following factors.

Pressure

When the applied pressure is low, the flux increases with increasing transmembrane pressure. However, the flux does not increase with increasing pressure after it reaches a critical value called the 'limiting flux', which increases with increasing mass transfer coefficient, but decreases with increasing solute concentration (Cheryan 1986; Mulder 1991).

Feed concentration

The flux decreases with increasing feed concentration. This decrease in flux is not linear, but exponential. Viscosity, density and diffusivity of the feed solution also increase with increasing feed concentration (Cheryan 1986).

Temperature

In general, the flux increases with a temperature increase, provided there are no unusual effects at the same time, such as fouling. Higher temperatures reduce the density and the viscosity of the feed solution by increasing the solubility of solutes. Higher temperatures also increase the diffusivity of solutes. For example, the protein diffusivity increases by 3-3.5% with each centigrade degree (^{0}C) rise in temperature (Cheryan 1986).

Flow rate and turbulence

Increasing flow rate and turbulence sweep away the accumulated solutes from the membrane surface. They reduce the hydraulic resistance and thereby, the thickness of the boundary layer that produces high shear forces. These result in an increase in flux (Cheryan 1986).

2.3.7 Solute rejection and mass transfer coefficient

2.3.7.1 Solute rejection

When any feed solution consisting of a solvent and one or more solutes is allowed to flow through an ultrafiltration membrane, the solvent and some smaller solutes pass through. The larger solute particles or macromolecules are rejected or retained by the membrane. The coefficient of rejection (or retention) can be expressed in several ways.
A permeate-based rejection (or solute retention) is defined as (Hong *et al.* 1998; Uludag *et al.* 1997):

$$R = 1 - C_p/C_f \tag{2.7}$$

where C_p and C_f are the solute concentrations (in mg/L) in the permeate and the feed respectively.

At any point in the process, the rejection coefficient (R) is given by:

$$R = 1 - C_p/C_r \quad (2.8)$$

where C_p and C_r are the solute concentrations (in mg/L) in the permeate and the retentate respectively. This formula is used as a retentate-based rejection (Fillipi *et al.* 1997).

Providing the retentate is completely mixed, the average rejection by a membrane is given by (Amicon 1998):

$$R = \ln(C_r/C_0)/\ln(V_0/V_r) \quad (2.9)$$

where C_r is the final solute concentration in the retentate, mg/L
C_0 is the initial solute concentration in the sample, mg/L
V_0 is the initial feed volume, L
V_r is the final retentate volume, L

Factors affecting the solute rejection

The major factors affecting the solute rejection by a membrane are discussed below.

Size and shape of solutes

If the average size of solute particles is less than the average pore size of the membrane surface facing the feed solution, the solute rejection is lower because smaller solutes easily pass through the membrane. The shape of the solute is also important since solutes having the same molecular weight can have different shapes. Rod-like particles will more easily pass through than the spherical ones and so the rejection will be different. The shape and conformation of the solutes can be affected by ionic strength or pH of the solution (Cheryan 1998).

Membrane material

The chemical nature of the membrane such as hydrophobicity, charge and surface roughness can affect the solute-membrane interactions. Thus, the membranes made of hydrophobic materials show higher solute rejections than those of hydrophilic materials (Cheryan 1998).

Operating parameters

Operating parameters such as transmembrane pressure, flow velocity and turbulence near the membrane surface (provided by stirring in a stirred cell), temperature, and solute concentration have a significant influence on the solute rejection. Increasing pressure may accelerate concentration polarisation effects resulting in an increased solute buildup as well as rejection. The effect of pressure can be seen from the rejection of polyethylene glycol (PEG) by a PM30 membrane (shown in Fig. 2.15). The effect of temperature on the solute rejection is rare in the literature. Higher temperatures reduce the viscosity of the feed solution and increase the diffusivity. Hence, the solute rejection may decrease at a higher temperature, but usually the flux increases. Increased flow rate and turbulence reduce the solute-membrane interactions that may reduce the rejection. The density, viscosity and diffusivity of a feed solution increase with increasing solute concentration, which also affect the solute rejection (Cheryan 1998).

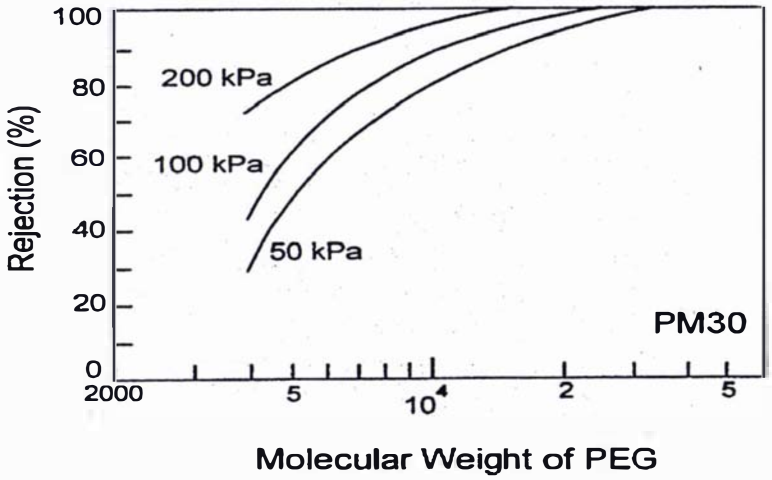


Fig. 2.15 Effect of transmembrane pressure on polyethylene glycol (PEG) rejection by a PM30 membrane (Cheryan 1998).

Concentration polarisation

Concentration polarisation decreases the rejection of lower molecular weight solutes due to an increased solute concentration at the membrane surface, but the rejection of lower molecular weight solutes can increase when higher molecular weight solutes form a layer that acts as a secondary membrane (Mulder 1991).

2.3.7.2 Mass transfer coefficient

The mass transfer coefficient, k, is calculated by the following equation (Cheryan 1998; Mulder 1991):

$$Sh = kd_h/D = a(Re)^b(Sc)^c \tag{2.10}$$

where Sh is the Sherwood number, Re is the Reynolds number, Sc is the Schmidt number, and a,b and c are constants. Re and Sc are defined as:

$$Re = d_h v \rho / \mu$$

$$Sc = \mu / \rho D$$

where d_h = hydraulic diameter = 4*cross-sectional area/wetted perimeter, m

v = flow velocity, m/sec

D = diffusion coefficient, m^2/sec

ρ = solute density, kg/m^3

μ = viscosity, cP

The mass transfer coefficient is a function of feed flow velocity (v), diffusion coefficient (D), viscosity and density of solutes, and the module shape and dimensions. However, the key parameters are v and D (Mulder 1991).

2.3.8 Operational problems with ultrafiltration

The two major problems in the operation of UF are concentration polarisation and fouling.

2.3.8.1 Concentration polarisation

When a feed solution consisting of a solvent and a solute contacts an ultrafiltration membrane with some pressure as a driving force on the feed side, the solute is partly retained by the membrane, but the solvent flows through the membrane. The solute concentration in the permeate becomes less than that of the bulk feed solution. The membrane-rejected solutes accumulate and result in a localised increase in solute concentration close to or on the membrane surface. Thus, there exists a concentration gradient on the feed side of the membrane where the maximum concentration is at the membrane surface and it gradually decreases to a value equal to the bulk feed concentration at some distance from the membrane. However, there is back-diffusion of solutes into the bulk region due to this concentration gradient. After a given period of time, a state of equilibrium will be established at the interface when the solute transport to the membrane will be balanced by the combined effects of back diffusion of solutes and permeation of solutes through the membrane. The rejected solutes, if of high molecular weight, may form a viscous and gelatinous layer on the membrane that resists the flow and lowers the flux. This phenomenon is known as concentration polarisation (Cheryan 1998; Mulder 1991).

There are several models to describe the flux behaviour during concentration polarisation. According to the *mass transfer model,* the solute concentration in the gel layer is constant and the flux is independent of pressure. The permeate flux (J_t , $L/m^2/h$) at any time t is given by:

$$J_t = (D/\delta)\ln(C_G/C_B) \tag{2.11}$$

where D is the diffusion coefficient (in m^2/sec), δ is the thickness of the boundary layer (in m), C_G is the solute concentration in the gel layer (in mg/L) and C_B is the solute concentration in the feed (in mg/L). D/δ is known as the mass transfer coefficient and denoted by k (Cheryan 1998).

The *resistance model* considers that the concentration polarisation layer will impose an additional resistance along with the membrane resistance. In the absence of fouling effects, the model is given by (Cheryan 1998):

$$J_t = P_T/\mu(R_M + R_G) \qquad (2.12)$$

where P_T is the applied transmembrane pressure (in kPa), μ is the viscosity of the permeate (in cP), R_M is the intrinsic membrane resistance (in kPa/LMH), and R_G is the membrane resistance due to concentration polarisation and boundary layer (in kPa/LMH) that is a function of operating parameters and physical properties.

The *osmotic pressure model* hypothesises that the osmotic pressures on both sides of the membrane are different when there is a high solute concentration adjacent to the membrane. Then the decrease in permeate flux (J_t) is due to the difference in osmotic pressures at the membrane surfaces ($\Delta\pi$, in kPa). The model is (Cheryan 1998):

$$J_t = (P_T - \Delta\pi)/\mu R_M \qquad (2.13)$$

Effects of concentration polarisation

Concentration polarisation can be very severe in ultrafiltration (and microfiltration) due to high flux and low mass transfer coefficient resulting from the low diffusion coefficients of macromolecules, small particles, colloids and emulsions (Lonsdale 1972; Mulder 1991). It can produce some negative effects as follows (Lonsdale 1972; Mulder 1991):

- Due to an increased solute concentration at the membrane surface, more amounts of solutes can flow through the membrane. Hence, the solute rejection will be lower than the true or intrinsic rejection. It is usually the case for low molecular weight solutes such as inorganic salts.
- Any one of the solution components reaching its saturation point due to the increased localised concentration can precipitate or form a gel on the membrane surface. Precipitate can reduce the effective membrane area and the gel-layer can act as a second membrane. The result of both processes is a decrease in flux, but the solute rejection is higher for the second case. The flux may also decrease due to an increase in interfacial osmotic pressure.

Minimisation of concentration polarisation

Concentration polarisation effects are reversible. The purpose of minimising concentration polarisation is to increase the permeate flux and also the mass transfer. It can be achieved in several ways (Cheryan 1986; Mulder 1991):

- increasing the feed temperature to reduce the viscosity and increase the diffusion coefficient of retained solutes
- increasing the mass transfer coefficient k by increasing the feed velocity along the membrane and by changing the module shape and dimensions (decreasing the module length or increasing the hydraulic diameter)
- decreasing the transmembrane pressure
- reducing the feed concentration.

2.3.8.2 Fouling

When the membrane interacts with various solutes in the feed or the solvent in some manner and as a result the flux is abruptly decreased, the phenomenon is known as 'fouling' (Cheryan 1986).

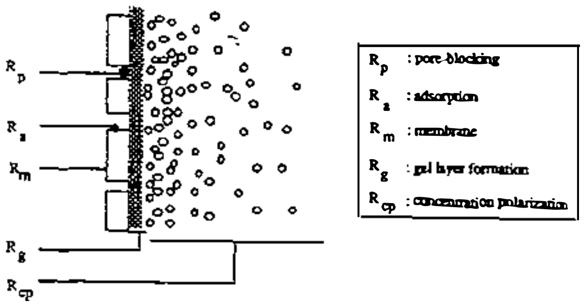


Fig. 2.16 Various types of resistance to the flow through an UF membrane (Mulder 1991).

Fouling usually occurs due to a number of reasons as shown in Fig. 2.16 (Mulder 1991):

- Retained particles, colloids, emulsions, suspensions, macromolecules and salts can be deposited on the membrane, and can block the pores.
- Smaller solutes can be adsorbed inside the membrane pores.
- A gel layer may be formed on the membrane surface due to concentration polarisation.

Fouling is an irreversible process. It is time dependent and partly concentration dependent. There are several empirical models to describe fouling (Cheryan 1998).

One model demonstrates that particles block a fraction of the pores in proportion to the permeate flow. The model is (Cheryan 1998):

$$J_t = J_0 \exp(-J_0 bt) \qquad (2.14)$$

Another model describes the entire surface as being covered continuously by a foulant layer and the cake resistance being proportional to the cumulative permeate volume. The model has the form (Cheryan 1998):

$$J_t = J_0 (1 + 2AJ_0 bt/R_M)^{-0.5} \qquad (2.15)$$

The model that describes the membrane pores being plugged due to deposition or adsorption of microsolutes is (Cheryan 1998):

$$J_t = J_0 (1 + J_0 bt/\varepsilon\eta\ R_M)^{-2} \tag{2.16}$$

Another model that relates the resistances to flow in series is (Cheryan 1998):

$$J_t = P_T/(R_M + R_F + R_G) \tag{2.17}$$

The notations used in the equations are:

J_t = permeate flux at any time t, L/m^2/h (or LMH)

J_0 = permeate flux at start (t = 0), L/m^2/h (or LMH)

t = any time, h

b = characteristic constant for fouling

A = membrane area, m^2

ε = membrane porosity

η = membrane thickness, m

P_T = applied transmembrane pressure, kPa

R_M = intrinsic membrane resistance, kPa/LMH

R_F = membrane resistance due to fouling, kPa/LMH

R_G = membrane resistance due to concentration polarisation and boundary layer (in kPa/LMH), and is a function of operating parameters and physical properties.

Effects of fouling

Fouling results in a decline in permeate flux, which is usually irreversible. The flux decline is rapid in the first few minutes and gradual afterwards. To restore the flux as well as the performance, the membrane must be cleaned, which may require high costs. If the fouling is serious, powerful cleansing chemicals need to be used, which may damage the membrane and shorten its operating lifetime (Cheryan 1986).

Factors influencing fouling

A large number of factors can affect the fouling process. They are categorised into three major groups: membrane properties, solute properties and process parameters.

Membrane properties

Hydrophilicity

In general, hydrophobic membranes adsorb hydrophobic or amphoteric materials and as a result fouling occurs. Hydrophilic membranes have no or low fouling (Cheryan 1998).

Surface topography

Membranes having protuberances on their surfaces are subjected to greater fouling since the protuberances trap suspended materials from the feed. Heterogeneous membranes have considerable solute deposits on their surfaces. Membranes with smooth and uniform surfaces do not face the above problems and so they have very low fouling. For example, cellulose acetate membranes have smooth and uniform surfaces, and polyamide-based membranes have protuberances on their surfaces (Cheryan 1998).

Charge on the membrane

Generally negative charges on most membranes can attract opposite charged particles and enhance fouling (Cheryan 1998).

Pore size

If the average size of the particles to be separated is nearer to the average pore size of the membrane, some smaller particles can partially enter into and block the pores (Cheryan 1998).

Solute properties

Every solute in the feed tends to foul the membranes to some extent. Hence, it is necessary to know the characterstics of all solutes, paricularly their type (e.g., protein, salt, antifoam or humic substance), nature (hydrophobic or hydrophilic) and size and shape (spherical or rod-like) to identify the potential for fouling (Cheryan 1998). Martens *et al.* (1996) reported that UF membranes were fouled rapidly by proteins and lipids during the treatment of biological wastewaters. Defrance *et al.* (1996) worked with activated sludge and found that suspended solids and colloids are mainly responsible for membrane fouling.

Process parameters

Membrane fouling is greatly influenced by process parameters such as temperature, pressure, pH, flow rate and feed concentration.

Temperature

The effect of temperature on fouling is unclear. Usually, increasing temperature increases the flux, but sometimes the flux can decrease; for example, the cheese whey flux decreases with increasing temperature and becomes almost a minimum at 30^0C, after which the flux increases again with increasing temperature. In biological systems, a high temperature can decrease the flux due to protein denaturation and other heat damage (Cheryan 1998).

Pressure

In the pre-gel region, increasing transmembrane pressure increases the flux. A further increase in pressure takes the concentration polarisation layer to a limiting concentration above which pressure has no influence on flux. Fouling layers, when formed, start getting compressed under the high pressure. When the pressure exceeds the 'critical pressure', the fouling layers become more compacted and result in a decrease in flux. At low flow velocities, the gel layer builds up rapidly and the effect of pressure becomes insignificant. For high flow velocities, the flux increases with increasing pressure, but decreases again after a limiting pressure (Cheryan 1998).

pH

The solubility and conformation of feed components, and solute-membrane interaction change with pH. The solubility and the flux are the lowest at the isoelectric point and both increase as the pH is taken away from this point (Cheryan 1998).

Flow rate

At high cross-flow rates, high shear forces develop that reduce the hydraulic resistance of the fouling layer and lower the fouling effects. At very low flow rates, foulants can be deposited due to low shear forces resulting in a severe decrease in flux (Cheryan 1998).

Feed concentration

The viscosity and density of a feed solution increase when its solid content increases. This change decreases the flux and leads to the occurrence of fouling (Cheryan 1998).

Minimisation of fouling

Effective fouling minimisation depends on the nature of the fouling process. Pretreatment of the feed can minimise solute-membrane interactions and thus, fouling. Properly adjusted temperature, feed velocity and pressure can minimise fouling due to concentration polarisation. The feed should be prefiltered to the appropriate particle size. The use of hydrophilic membranes rather than hydrophobic ones and many kinds of turbulence promoters also helps to reduce fouling. The last resort is to shut down the system and clean the membrane by chemical means (Cheryan 1998; Mulder 1991; Porter 1990[a]).

Cleaning of fouled membranes

Fouled membranes can be cleaned by two major methods: hydraulic cleaning and chemical cleaning.

Hydraulic cleaning

The most commonly used hydraulic method is backflushing. After a certain time period, the feed pressure is released. Then the permeate is pumped back into the feed channel. The reversed flow of permeate loosens the deposited foulants off the membrane. The backflushing pressure should be greater than the operating ultrafiltration pressure. However, backflushing is not very effective for sticky gelatinous foulants (Cheryan 1998; Mulder 1991).

Chemical cleaning

Chemical cleaning is the most widely used cleaning method for fouled membranes. A large number of cleaning chemicals either in liquid or powdered form is used to solubilise or disperse the foulants. The selection of a cleaning chemical depends largely on the type, nature and extent of the fouling layers. Sometimes one cleaning chemical alone may not be sufficient, and in that case, two or more chemicals should be used simultaneously or in a sequence (Cheryan 1998; Mulder 1991).

Some important cleaning chemicals are acids, alkalis, enzymes, ammonia, chlorine and complexing agents (e.g., EDTA). Chlorine is very effective for pore fouling, but the chlorine solution should be alkaline to reduce corrosion. Acids are suitable for mineral and inorganic salt foulants, whereas caustic solutions (e.g., NaOH) are effective for protein foulants (Cheryan 1998; Mulder 1991).

Enzymes can effectively be used to remove protein-fouling problems. As enzymes are themselves proteins and foul the membrane again if left on the membrane, the membrane should be cleaned again by another chemical. Organic solvents such as ethanol, can remove hydrophobic materials such as fats, oils and grease (Cheryan 1998), provided the membrane chemistry is comparable with such solvents.

Different researchers used different CIP procedures for cleaning the membrane after ultrafiltration operation. One such procedure used by Huang *et al.* (1994) is as follows:

- After taking the retentate out, the whole system is flushed with water.
- A 8 g/L Terg-A-Zyme solution is stirred in the cell for at least 5 minutes and ultrafiltered to collect some of the solution as permeate.
- The whole system is rinsed with water and a 0.8 g/L D-Acid-HD$^{(TM)}$ solution is ultrafiltered for 5 minutes.
- The whole system is then rinsed with water 3 to 4 times to remove the cleaning solution.
- If the water flux is similar to the water flux measured before the ultrafiltration, the membrane is thought to be clean.

2.3.9 Applications of ultrafiltration

UF applications are expanding rapidly. It can be successfully used to concentrate or purify the retained species where the unwanted contaminants are allowed to pass through the membrane and the retentate is collected as the product. Where the unwanted contaminants are large enough and can be retained by the membrane, the permeate is collected as the product. Both the retentate and permeate are also important in cases where the individual valuable items are to be separated from a mixture. Some of the major UF applications are (Caetano 1995; Cheryan 1998; Gutman 1987; Mulder 1991; Porter 1990^{a}):

- production of potable water for drinking and residential use, and ultra-pure water for industrial use (i.e. semiconductor, electronics and pharmaceutical industries) by successfully removing microorganisms and turbidity without the need of any chemicals, which replace a number of operations within the water treatment plants
- recovery of cheese whey protein; concentration of milk prior to cheese manufacture, particularly in fresh, soft or semi-hard cheesemaking; increasing taste and maximizing the desired protein and calcium concentrations of milk; making better yoghurt with ultrafiltered milk that has better viscosity and firmness
- recovery of drag-out paint; provision of required control in paint bath; keeping of chemical balance in the feed tank and production of required quality of effluent (permeate) for disposal in the automotive industry
- recovery and reuse of polyvinyl alcohol, polyacrylate and carboxymethyl cellulose that are used as sizing agents in the textile industry to improve the strength and surface characteristics of warp yarns; recovery of costly polymeric dyes and indigo; and effectively and successfully treating wool scouring effluent containing particulates, oil and grease, salts, and detergent with a BOD of 20,000-150,000 mg/L in the textile industry
- removal of colour bodies (>90%) from Kraft mill bleaching effluents; concentration of dilute spent sulphite liquor from the sulphite process; recovery of lignin from Kraft black liquor; recovery of paper coatings containing pigments, binders and additives; and treatment of effluent having high pH and highly coloured and nonbiodegradable compounds in the pulp and paper industry
- retention of cloud-stabilizing polysaccharides and bacteria for apple juice clarification producing clear apple juice that has a long shelf-life and production of colloid-free clear filtrate of raw sugar juice
- separation and harvesting of microbial cells; concentration, purification and recovery of enzymes; processing of blood plasma
- removal of excess water as well as undesirable glucose and inorganic salts from egg white for use in baking, confectionery and candy industries; refining of sugar; concentration and clarification of gelatin in the food industry

- effective and efficient treatment of secondary effluent from municipal, industrial and industrial-like wastewater; recovery of valuable by-products from wastewater; separation of oils producing disposable or reusable effluent water from stable oil-water emulsions from metal working, food processing, textile and other industries
- removal of low molecular weight solutes such as heavy metal ions, that are permeable to UF membranes, by making them attached to or complexed to larger aggregated particles (usually called micelles) that can be retained by compatible membranes. This application is very promising, but it is still in the development stage. This phenomenon is discussed in more detail in the section "Micellar-enhanced ultrafiltration".

2.4 Microfiltration

2.4.1 General

Microfiltration is one of the pressure-driven membrane filtration techniques that separates colloidal and suspended particles based primarily on size. The pore size of MF membranes ranges from 0.05 μm to 10 μm. It is essentially a quick conventional coarse filtration based on the sieving mechanism (Mulder 1991).

2.4.2 Membranes for microfiltration

Porous MF membranes can be symmetric or asymmetric, depending on the pore structure. Symmetric membranes offer a uniform pore size distribution throughout the pore channel whereas asymmetric membranes have a thin surface layer with rated pore size supported by a thick layer of larger pore size (Mulder 1991).

MF membranes can be prepared from either organic materials (e.g., polymers) or inorganic materials (e.g., ceramics, metals, glasses). The techniques used for preparing polymeric membranes are usually sintering, stretching, track-etching and phase inversion.

Sintering, sol/gel process and anodic oxidation are some of the techniques used for preparing ceramic membranes (Mulder 1991). Synthetic polymeric membranes can be hydrophobic or hydrophilic. Various materials used for MF membranes are listed in Table 2.6.

Table 2.6

Different MF membranes and their materials (Mulder 1991).

Membranes	*Materials*
Hydrophobic polymeric Membranes	Polytetrafluoroethylene (PTFE, teflon) Poly(vinylidene fluoride) (PVDF) Polypropylene (PP)
Hydrophilic polymeric Membranes	Cellulose esters Polycarbonate (PC) Polysulphone/polyethersulphone) (PS/PES) Polyimide/poly(ether imide) (PI/PEI) (aliphatic) polyamide (PA)
Ceramic membranes	Alumina (Al_2O_3) Zirconia (ZrO_2)
Glass membranes	Glass (SiO_2)
Metal membranes	Palladium, tungsten, silver

Inorganic membranes, especially ceramic membranes, are more commonly used for their improved thermal and chemical stability. They can be operated with a high pressure, are inert to many chemicals including corrosive ones and possess a significantly longer lifetime. Their pore size distribution is usually very narrow since it can be controlled well. Their main disadvantages are that they are costly and brittle (Cheryan 1998; Mulder 1991).

The modules used for MF membranes are hollow fibre, tubular, plate and frame, spiral wound, and pleated sheet (Mulder 1991). MF membranes can be operated in both dead-end and cross-flow modes (Porter 1990^b).

2.4.3 Major problems with microfiltration

Like RO and UF, concentration polarisation and fouling also affect microfiltration operations.

Concentration polarisation

Concentration polarisation results from the retention of solutes by the membrane, particularly when the concentration of rejected solutes increases in the vicinity of the membrane. This high concentration layer exerts a hydrodynamic resistance to the flow through the membrane. However, concentration polarisation is a reversible process and does not need cleaning (Mulder 1991; Vyas 1999).

Fouling

Fouling occurs due to the interaction of the process fluid with the membrane. This interaction can be due to gel layer formation, concentration polarisation, pore-blocking, adsorption of solute particles onto the membrane surface and so on. Fouling decreases the rate of permeation. Solutes in the feed, which are larger than the membrane pores foul the membrane externally and form a cake layer on the membrane surface. The solutes smaller than the pores penetrate the membrane and usually foul the membrane internally by blocking the pores. Smaller solutes can also be retained on the membrane by the cake layer (Mulder 1991; Vyas 1999).

Fouling is usually irreversible and the fouled membrane needs cleaning in order to restore its performance. The fouled membrane can be cleaned by three ways: mechanically, electrically and chemically. Mechanical cleaning is done by introducing a high shear rate at the membrane surface, by periodic backflushing or by using foam balls to remove deposits from tubular membranes. Electrical cleaning is accomplished by using the surface electrical charge acquired either by the membrane (electro-osmotic dewatering) or by the dispersed materials (electrofiltration), when brought in contact with a polar medium. Chemical cleaning involves MF operation with such chemical solutions that loosen and dissolve the foulants. Mechanical or electrical cleaning is effective for external fouling, but chemical cleaning is effective for both external and internal fouling (Vyas 1999).

2.4.4 Applications of microfiltration

The major applications of MF in different fields are listed below (Caetano 1995; Cheryan 1998; Gutman 1987; Mulder 1991; Porter 1990^{b}):

- production of ultrapure water by removing particles in the semiconductor industry
- clarification of whey, alcoholic beverages and fruit juices
- sterilisation, and removal of particles in the pharmaceutical industry
- removal of bacteria for cell recovery in cell culture or for sterilization of liquids by filtering out any bacteria, yeasts and moulds
- recovery of heavy metals from wastewater by precipitating them as particles of filterable size
- treatment of domestic and industrial wastewaters by removing metals, nutrients, radioactive elements and other solids
- separation of fat, removal of bacteria and concentration of caseinate in milk processing
- separation of plasma from whole blood
- concentration of pigment slurry, crude oil (in product water), fermentation broth, crystals (during crystallisation)
- polishing filtration of electronic grade chemicals
- removal of water from latex or solvent water emulsion

- cell harvesting/washing and continuous cell culture.

2.5 Micellar-enhanced ultrafiltration

2.5.1 General

Removal of heavy metals by UF is potentially a very effective and successful technology. In UF, the membranes can retain pollutants having a molecular weight ranging from 300 to 300,000. Smaller pollutants such as heavy metals can be removed if they are attached to larger surfactant macromolecules to increase their size. At a concentration above the critical micelle concentration, 10-200 surfactant molecules attach to each other, and form macromolecules or micelles. A compatible membrane can retain these micelles (Huang *et al.* 1994; Jones and Chapman 1995). This is the basic principle of micellar-enhanced ultrafiltration (MEUF).

2.5.2 Surfactant properties

Surfactants are amphiphilic substances having two well-separated parts, a non-polar or hydrophobic tail and a polar or hydrophilic head. The hydrophobic tail is usually a linear or branched hydrocarbon portion. The balance between the hydrophobic and hydrophilic parts gives the special properties of the surfactant (Hinze 1979; Ottewill 1984; Tsujii 1998).

The important properties of surfactants are as follows (Hinze 1979; Ottewill 1984; Rosen 1978; Tsujii 1998):

- They form aggregates or micelles in aqueous solutions.
- They show a tendency to interact with both water and oil.

- The surfactant and micellar system can solubilise a wide variety of solutes or species, which are insoluble or very slightly soluble in the bulk solvent alone. Solubilisation itself depends on temperature, nature of solute, surfactant concentration, type of micellar system used and so on.
- The solubility of a surfactant increases with increasing temperature, but there is a certain value of temperature at or beyond which there is a sudden increase in solubility, i.e. the material becomes highly soluble. This temperature is known as the Krafft temperature or Krafft point, and at this temperature the solubility becomes equal to the critical micelle concentration of the surfactant.
- The micellar system of a surfactant usually acts as a novel reaction medium and can decrease or accelerate the rates of chemical reactions, alter the position of an equilibrium reaction and affect the products.
- Their surface tension decreases with increasing concentrations and remains constant after the break point.
- At low concentration, the surfactant can be adsorbed onto the surface or interface of the system and can alter its free energy.

2.5.3 Types of surfactants

The hydrophobic group of most surfactants is composed of linear hydrocarbon chains and hence, is biodegradable (Porter 1994). Based on the nature of the polar or hydrophilic head group, surfactants are classified as anionic, cationic, nonionic or zwitterionic.

Anionic surfactants

Anionic surfactants have negatively charged headgroups. Usually, they are electrolytes and produce active anions after dissociation in water. They give an anionic charge to the substrates adsorbed on them. Hence, they are strong detergents with high foaming power (Porter 1994; Tsujii 1998).

The use and manufacture of anionic surfactants is greater than other surfactants. Their manufacture is easy and cheap. Their main application is in every type of detergent. The detergency is optimum when the hydrophobic group is a linear paraffin chain in the range of C12-C16, and the polar headgroup at one end of the chain. The most common hydrophilic groups are carboxylate (-COO-), sulphonate ($-SO_3-$), sulphate ($-OSO_3-$) and phosphate (-OPO(OH)O-) (Porter 1994). The sulphonates and sulphates can tolerate divalent metal ions in hard water more than the carboxylates (Clint 1992). The counterion/cation is usually Na^+. Other common cations are potassium, ammonium, calcium and various amines, mainly isopropylamine, monoethanolamine, diethanolamine and triethanolamine (Porter 1994). Sodium dodecyl sulphate (SDS) and deoxycholic acid (DCA) are two examples of anionic surfactant (Clint 1992; Jones and Chapman 1995).

Cationic surfactants

Cationic surfactants have positively charged headgroups. They are also electrolytes and produce active cations after dissociation in water. They give a cationic charge to the substrates adsorbed on them (Tsujii 1998). The counterion is usually Br^- or Cl^-. Cetyltrimethyl ammonium bromide (CTAB) is an example of cationic surfactant (Clint 1992; Jones and Chapman 1995).

Most commercial cationic surfactants are based on the nitrogen atom with the positive charge. Other products are based on phosphorus and sulphur, but most of them are not commercially available. They are usually quaternary ammonium or alkyl pyridinium compounds (Clint 1992; Porter 1994).

Non-quaternary cations are sensitive to high electrolyte concentrations, high pH and polyvalent ions whereas quaternary cations are not. Because of their positively charged headgroups, cationic surfactants have higher substantivity on negatively charged surfaces such as fibres, cellulosics, plastics, polyvinyl chloride, polyvinyl acetate, silicates, metals and pigments. Hence, they are used as softeners and antistats for textiles, anticaking agents in fertilisers, emulsifiers for bitumen, corrosion inhibitors in oilfields, dispersing agents for pigments, and floatation agents in mineral processing. Their disadvantages are that they are costlier than anionic and nonionic surfactants, have poor detergency and poor suspending power for carbon (Clint 1992; Porter 1994; Rosen 1978).

Nonionic surfactants

Nonionic surfactants have uncharged but polar headgroups. They are not electrolytes since they are not ionised in aqueous solutions, but can tolerate added salts or hardness. Thus, they are stable in varying pH. A typical example of nonionic surfactant is dodecylhexaoxyethylene glycol monoether (Ottewill 1984; Porter 1994; Tsujii 1998).

Nonionic surfactants include mainly polyoxyethylene and polyoxypropylene derivatives. Other surfactants such as anhydrohexitol derivatives, sugar esters, fatty alkanolamides, and fatty amine oxides also fall under this group (Schick 1966).

Nonionic surfactants act as intermediates for the synthesis of ionic surfactants. The critical micelle concentration (cmc) for nonionic surfactants is much lower than that for ionic surfactants of similar surface activity (Bumette 1966). They are mostly used as emulsifiers, solubilisers and low-temperature detergents (Clint 1992; Dennis *et al.* 1979). However, they are disadvantageous because of poor foaming power with very low or no electrical effects and because they are rarely nontacky solids (Rosen 1978).

Zwitterionic surfactants

Zwitterionic surfactants have a headgroup carrying a positive and a negative charge. They have less corrosive effects on the skin and eyes than the anionic surfactants. Hence, they are suitable for use in toiletries and baby shampoos. Their main disadvantage is that they are usually not soluble in most organic solvents, even in ethanol. Lecithin, a naturally occurring surfactant, is a zwitterionic surfactant (Clint 1992; Ottewill 1984; Rosen 1978).

According to their sources, major types of surfactants in use are synthetic and natural.

Synthetic surfactants:

Synthetic surfactants are prepared from petroleum-derived feedstocks (e.g., alcohols) or natural raw materials (e.g., carbohydrates). They are widely used in the study of biological membranes for composition analysis or to get them in a suitable form for manipulation. Usual synthetic surfactants have a single alkyl chain. Sodium dodecyl sulphate and cetyltrimethyl ammonium bromide are two examples of synthetic surfactant (Clint 1992; Jones and Chapman 1995).

Natural surfactants

Natural surfactants are derived from cholesterol, specifically bile salts and saponins. They have a wide number of applications. For membrane solubilisation, sodium salts of cholic and deoxycholic acids are usually used. These salts can form mixed micelles with membrane phospholipids and solubilise proteins without denaturation (Jones and Chapman 1995). Deoxycholic acid and lecithin are two examples of natural surfactants.

Synthetic versus natural surfactants

Synthetic surfactants introduce secondary pollutants into the treated effluent when they are applied in the effluent treatment systems. In contrast, natural surfactants are nontoxic, biodegradable, abundant and usually less expensive. Moreover, natural surfactants have high molecular weight, form large-size micelles and have small critical micelle concentration that minimises surfactant monomers in the permeate. Concentration polarisation and fouling effects are also not significant with natural surfactants in most cases (Huang *et al.* 1994). Natural surfactants, especially DCA, can be precipitated from the solution by acidification (to pH <4) and hence, can be recovered.

2.5.4 The micellar state

2.5.4.1 Formation of micelles

In aqueous solution, each surfactant has a certain concentration above which the surfactant monomers aggregate together and form larger molecules called micelles. This concentration of the surfactant is called the 'critical micelle concentration' (cmc). When the surfactant concentration is below its cmc, most of it remains as monomers. However, above the cmc, a dynamic equilibrium is established between the monomers and the micelles. Roughly spherical or ellipsoidal shaped micelles are formed at the surfactant concentration near the cmc. The solution of each surfactant below the cmc has certain properties such as surface tension, conductivity and turbidity. There is an abrupt change in these properties when the surfactant solution reaches its cmc (Jones and Chapman 1995; Hinze 1979).

The cmc of a surfactant solution can be determined experimentally. Surface tension, turbidity, conductivity, osmotic pressure, solubilisation, self-diffusion and magnetic resonance of the surfactant solution can be plotted as a function of surfactant concentration (Fig. 2.17). If the curves are plotted from low concentrations to high concentrations, a dramatic change in the shapes of these curves is observed. The points of shape change of all curves correspond to a single vertical line, which is the cmc line (Jones and Chapman 1995; Lindman and Wennerstrom 1980).

The cmc of a surfactant is not constant, but varies with its chemical structures. The cmc is also influenced by temperature, pressure or addition of electrolytes/salts (Lindman and Wennerstrom 1980). The micellisation process can affect the solution properties of surfactants. In dilute solutions and below the cmc, ionic surfactants act as strong electrolytes. Above the cmc, the solution behaves nonideally because of micelle formation (Jones and Chapman 1995; Hinze 1979).

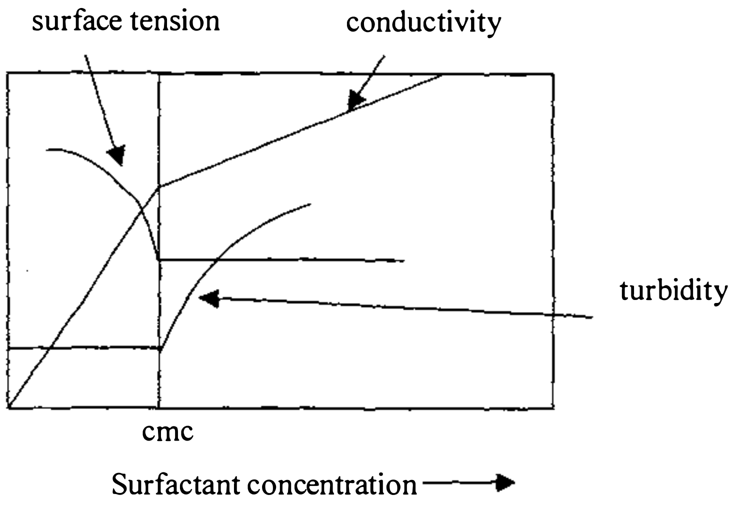


Fig. 2.17 Schematic diagram of surface tension, conductivity and turbidity as a function of surfactant concentration (Jones and Chapman 1995).

Each micelle is formed by aggregating a certain number of surfactant molecules or monomers. This number is called the aggregation number that usually controls the general properties of the particular micellar system (Hinze 1979). The aggregation number varies usually from 10 to 200. The tendency of micelle formation can be increased by increasing the hydrophobicity of the surfactant molecules and decreased by increasing the hydrophilicity (Couper 1984; Jones and Chapman 1995).

The micelles formed in an aqueous system are called 'normal micelles'. For a spherical ionic micelle, the polar heads remain in contact and aligned towards the aqueous solution. Micelles can also be formed in various nonpolar solvents and these micelles are called 'reversed or inverted micelles'. For a spherical reversed micelle, the polar heads are directed towards the interior of the aggregates. The central core becomes hydrophilic and the hydrophobic tails form a spherical nonpolar surface that remains in contact with the bulk nonpolar solvent (Hinze 1979).

Depending on the nature of the hydrophilic headgroups, micellar systems can also be ionic (anionic or cationic), zwitterionic, or nonionic (Hinze 1979).

When micelles are first formed, they are nearly spherical in shape. If the surfactant concentration in the solution is high, the micelles formed are larger and are usually laminar or rod-shaped (Couper 1984; Lindman and Wennerstrom 1980).

2.5.4.2 Structures of micelles

In a surfactant solution, the polar headgroups repel one another and the hydrocarbon groups attract one another. When they tend to form micelles, the relative size of the headgroup and the hydrophobic group will determine their shapes and sizes. The usual micellar shapes are spherical, nonspherical, bilayer or vesicle, and inverted (Fig. 2.18) (Clint 1992; Israelachvili 1985; Porter 1994).

For an ionic group, the effective size is the actual size plus electrostatic forces. For a nonionic group, the effective headgroup size is the actual size plus bound water. The area of the hydrophilic group is defined by a_0 (in Å^2) and of the hydrophobic group by v/l_c, where v and l_c are alkyl chain volume (in Å^3) and maximum chain length (in Å) respectively as in Fig. 2.19 (Clint 1992; Israelachvili 1985; Porter 1994).

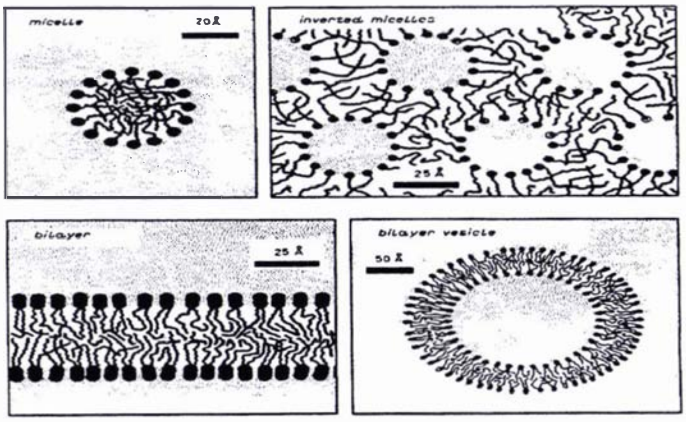


Fig. 2.18 Various shapes of micelles (Israelachvili 1985)

Spherical micelles

Spherical micelles are formed when $v/(a_0 l_c) < 1/3$. Anionic surfactants usually form spherical micelles. Because of the electrostatic repulsive force between adjacent headgroups, their hydrophilic headgroup area (a_0) is sufficiently large. Their alkyl chain volume (**v**) is sufficiently small so that the radius of the micelle does not exceed the maximum chain length (l_c). Hence, spherical micelles are extremely small (Clint 1992; Israelachvili 1985; Porter 1994).

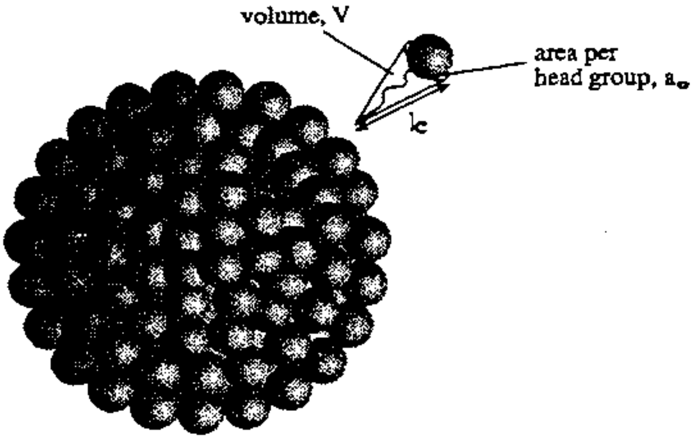


Fig. 2.19 Optimum headgroup area (a_0), alkyl chain volume (v) and maximum chain length (l_c) (Hamley 1985)

Nonspherical micelles

Nonspherical micelles will be formed when $1/3 < v/(a_0 l_c) < 1/2$. A number of shapes fall under this category, but the cylindrical shape is the most common. The cross-section of a cylindrical micelle is similar to that of a spherical micelle, but the ends are rounded like a hemisphere. Any change in the system that will decrease the effective headgroup area will increase the micellar size. This change can be made by the addition of an electrolyte (e.g., NaCl), addition of a cosurfactant with a very compact headgroup, changing the counterion, changing the anion for cationic surfactants, changing the hydrophilic nature of the nonionic headgroup by electrolyte addition or temperature change and changing the pH of zwitterionic surfactants. This change will screen the electrostatic headgroup repulsion and thereby, reduce the hydrophilic headgroup area. These smaller headgroup areas cannot pack into spherical micelles, but can form cylindrical (rodlike) structures. Cylindrical micelles show very unusual properties such as they are large and polydisperse, and more viscous (Clint 1992; Israelachvili 1985; Porter 1994).

Bilayers

Bilayers are formed when $1/2<(v/a_0l_c)<1$. Sometimes surfactant molecules cannot be packed into small structures due to their small headgroup area or because their hydrocarbon chains are so bulky that they cannot be fitted into small aggregates with maintaining the optimum surface area. Bilayers are formed in such situations. For example, lipids with two chains form bilayers. Bilayers can be of infinite length. Sometimes closed spherical bilayers known as 'vesicles' are formed (Israelachvili 1985).

Inverted micelles

Surfactant molecules having $v/(a_0l_c)>1$ cannot even form bilayers because of their too small headgroup area. In this case, they pack into inverted micelles or precipitate out of the solution (e.g., cholesterol) (Israelachvili 1985).

2.5.4.3 Solubilisation in micelles

Solubilisation, a dynamic equilibrium process, is the most important property of a micellar system. It is affected by temperature, surfactant concentration, nature and type of solute and the micellar system. Above the cmc, the amount of solute solubilised is usually directly proportional to the surfactant concentration (Hinze 1979).

Each micellar system has a number of solubilisation sites. The nature of the solute and the micelle determines the site where a solute will be attracted. Usually a nonionic solute is attracted near the centre of the hydrophobic core. An amphipathic solute can be radially aligned and adsorbed in the micelle. The ionic solutes are adsorbed on the polar micellar surface. In cases of reversed micelles, ionic solutes are oriented in the cores of the micelles and the polar heads of the amphipathic solutes are directed near to or in contact with polar micellar cores (Hinze 1979).

At a given concentration for many ionic surfactants, the solubility of a solute increases with the addition of an electrolyte and in some cases the solubilisation capacity remains constant (Hinze 1979).

2.5.4.4 Factors affecting the critical micelle concentration

As previously mentioned, a number of factors can affect the critical micelle concentration of a surfactant. They are discussed in details.

Effect of the hydrophilic group

When the effective size of the polar hydrophilic group becomes larger, the electrostatic repulsion between the polar headgroups goes higher and as a result, the cmc increases. Thus, the cmc of a highly ionised group such as sulphates is higher than that of a less ionised group (Porter 1994). The cmc of a surfactant having more than one hydrophilic group is even higher than that of a surfactant having one hydrophilic group with the equivalent hydrophobic group (Rosen 1978).

For zwitterionic surfactants, the cmc increases if the two charges of the molecule are separated and farther apart (Porter 1994).

Effect of the hydrophobic group

Generally in aqueous surfactant solutions, the electrostatic attraction force for bonding is proportional to the hydrophobic chain length. Hence, the cmc decreases with an increase in the number of carbon atoms or methylene groups in the hydrophobic group (Porter 1994; Rosen 1978).

The carbon atoms on the branches of a branched hydrophobic group have about one-half the effect of carbon atoms on a straight chain. For unsaturated carbon bonds in the hydrophobic chain, the cmc is higher than that of saturated bonds (Rosen 1978).
When a straight-chain hydrophobic group consists of more than 16 carbon atoms, the cmc decreases slowly with increasing carbon atoms. However, when a straight-chain hydrophobic group consists of more than 18 carbon atoms, the cmc does not change with increasing carbon atoms because the long chains may be coiled in water (Rosen 1978).

If a polar group like -O- or -OH can be added to the hydrophobic chain in the aqueous solution, the cmc increases significantly (Rosen 1978).

If a hydrocarbon-based hydrophobic group is replaced by a fluorocarbon-based hydrophobic group without altering the number of carbon atoms, the cmc usually decreases. When a terminal methyl group of a hydrocarbon-based hydrophobic group is replaced by a trifluoromethyl group, the cmc increases (Rosen 1978).

Effect of counterions

The presence of counterions in aqueous surfactant solutions will reduce the charge density on the polar groups because of the increased binding between the two groups. As a result, the electrostatic repulsion between the polar groups will be reduced and the cmc will be decreased. For example, the cmc of a calcium salt of sulphonates is lower than that of a sodium salt (Porter 1994; Rosen 1978).

Effect of temperature

For nonionic surfactants based on polyethylene oxide (PEO), increasing temperature reduces the bonds between the PEO groups and water resulting in a decrease in the cmc (Clint 1992; Porter 1994).

For ionic surfactants, the temperature effect on the cmc is complex with a decrease at first to a minimum and then an increase as the temperature increases. The increase or decrease in cmc with increasing temperature will depend on the resultant of two opposing effects: (i) the partial dehydration of nonionic polar groups increases and the hydrophobic bonding becomes more stable, which favour micellisation, and (ii) the repulsive forces between the anionic polar heads increase resulting in an enhanced molecular motion, which acts against micellisation with structure breaking effects. Usually hydrophobic forces are balanced by the ionic repulsion in the temperature range of 10-40^{0}C and the cmc does not vary a lot. The cmc-temperature curve is usually parabolic with respect to the vertical axis. The minimum point on this curve is usually around 25^{0}C (Clint 1992; Rosen 1978; Small 1971).

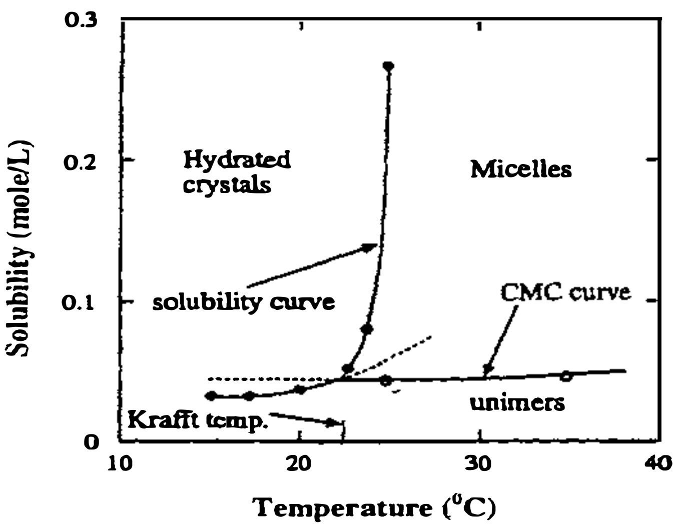


Fig. 2.20 Krafft temperature of sodium decyl sulphonate (Hamley 2000)

The solubility of ionic surfactants depends on the temperature. The intersection of the solubility curve and the cmc curve (Fig. 2.20) is the Krafft point, which defines the Krafft temperature. With increasing temperatures, the solubility of the surfactant increases dramatically above the Krafft temperature and this is due to the fact that both the solubility and the cmc of the surfactant molecules depend on the temperature. The solubility of the surfactant is low below the cmc, but increases dramatically with increasing temperature above the cmc since the surfactant molecules form soluble micelles (Hamley 2000).

The Krafft point depends on the crystal structure of amphiphilic (surfactant) molecules and it increases as the alkyl chain length increases because the cmc of a surfactant depends on the alkyl chain length (Hamley 2000). According to Sadaoui *et al.* (1998), micelles will not appear in a solution if its temperature is below the Krafft temperature.

Effect of pressure

There is only limited information in the literature on the pressure dependence of cmc. The pressure has a slight effect on the cmc. For ionic surfactants, the cmc increases to a maximum and then decreases as the pressure increases (La Mesa 1990).

Effect of pH

The dissociation of the hydrophilic group of surfactants containing ionisable groups such as –NH2 and -COOH depends on pH. At the pH value at which the group is charged, the cmc will be high, but low when uncharged. For example, -NH2 is charged at low pH and –COOH at high pH (Clint 1992).

At low pH, some zwitterionic surfactants can become cationic and then the cmc increases (Clint 1992).

Effects of added electrolytes/inorganic salts

The addition of an electrolyte to an ionic surfactant solution increases its ionic strength since it decreases the absolute magnitude of electrical potential at the micellar surface. Then the electrostatic repulsive force between the polar hydrophilic headgroups is decreased and the micelles can form at lower surfactant concentrations. Hence, the cmc of an ionic surfactant solution will decrease with the addition of an electrolyte. Nevertheless, added electrolytes have insignificant effects on nonionic and zwitterionic surfactant solutions (Clint 1992; Lindman and Wennerstrom 1980; Porter 1994; Scamehorn *et al.* 1989; Tounissou *et al.* 1996).

2.5.5 Micellar-enhanced ultrafiltration of heavy metals

Mechanism/mode of metal ions binding to micelles and MEUF with anionic surfactants

Heavy metal salts are usually present as ions in aqueous systems. A surfactant of opposite charge to that of the target metal ions is added to such systems for their removal or separation (Scamehorn *et al.* 1989). The surfactant molecules will aggregate into micelles at a concentration above the cmc with the hydrophobic tail groups intertwined together in the 'core', while the hydrophilic and anionic headgroups are packed on the surface toward the aqueous solution. Thus, the micellar surface possesses a high charge density and a high absolute electrical potential. The multivalent metal cations become electrostatically adsorbed or bound onto the charged micellar surface (Huang *et al.* 1994; Scamehorn *et al.* 1994).

The aqueous stream containing the metal ions and micelles is treated by UF where a compatible membrane retains the micelles (Huang *et al.* 1994; Scamehorn *et al.* 1994). The concentrations of metal ions and the surfactant will be very low in the resulting permeate stream, but very high in the retentate stream mostly in the form of micelles (Scamehorn *et al.* 1994). In some cases the micelles, after separated from the retentate, can be treated further by monovalent or multivalent counterions to precipitate the surfactant (e.g., in the case of DCA). In such cases, the surfactant and the metals can be recovered and reused (Brant *et al.* 1989; Huang *et al.* 1994).

A number of works are available in the literature on the MEUF removal of metal ions from aqueous solutions. Huang *et al.* (1994) utilised MEUF successfully to remove five heavy metals (cadmium, lead, copper, nickel and zinc), present individually or together, from simulated waste streams by using sodium salt of deoxycholic acid and sodium dodecyl sulphate as the surfactants. Two other surfactants namely lecithin and soybean protein were also used in this study. The experiments were carried out at 30^0C with 276 kPa pressure drop across the membrane, and using a RGO3 membrane made of anisotropic acrylanitryl with MWCO of 2000 daltons. The surfactant to metal (S/M) ratio, surfactant type and concentrations, and metal type and concentrations were found to have substantial influence on the metal rejection. The metal rejection increased with increasing feed surfactant concentrations relative to metal concentrations because of the increasing surfactant fractionation in the micellar form. An increase in the operating pressure increased the permeate flux, but not the metal rejection. The optimal S/M ratio was 2.5 for DCA for above 99.9% rejection of metals and 5.0 for SDS for above 98% rejection of metals. The performance of DCA was better than that of SDS, lecithin or protein.

Scamehorn *et al.* (1994) successfully removed four individual metals (cadmium, zinc, copper and calcium) and their mixtures by using sodium dodecyl sulphate. The experiment was carried out at 30^0C with a transmembrane pressure of 414 kPa and using anisotropic cellulose acetate membranes with MWCO of 1,000 and 5,000 daltons. The metal rejection was 99% or greater.

Paulenova *et al.* (1996) effectively removed and recovered cadmium (95-98% recovery) by using sodium dodecyl sulphate (SDS) as a surfactant, n-butanol as a co-surfactant and 8-hydroxyquinoline (8-HQ) as an extractant. The experiments were carried out using cellulose acetate membranes at a constant pressure of 400 kPa. The cadmium recovery increased with increasing pH and was quantitative at a pH of 4 or greater. The cadmium recovery also increased with increasing concentrations of surfactant and chelating agent. The recovery was 98% at 4.8 mM SDS and 1.99 mM 8-HQ for 0 .1175 mM initial Cd.

Hong *et al.* (1998) removed four metals (cadmium, zinc, copper and nickel), present individually or together, from aqueous streams by using a polycarboxylic acid type biosurfactant namely sodium salt of 2-(2-carboxyethyl)-3-decyl maleic anhydride (DCMA-3Na) derived from spiculisporic acid. The experiment was carried at a transmembrane pressure of 400 kPa with cellulose acetate membranes having MWCO of 1,000-3000 daltons. The metal rejection was the maximum (>98%) at a S/M ratio of 1.

MEUF with cationic surfactants

Practically, all heavy metals do not always present as cations. A number of metals (e.g., chromium, iron and cadmium) may exist in divalent or trivalent anionic forms such as complexes with halide or cyanide ions, or as oxy-acid ions. In such cases, cationic surfactants are to be used to bind the anionic forms of metals (Christian *et al.* 1988).

Christian *et al.* (1988) removed chromate ions (CrO_4^{2-}) from aqueous streams by MEUF using a cationic surfactant hexadecylpyridinium chloride. The experiment was carried out at 30^0C with anisotropic cellulose acetate membranes having MWCO of 5000 daltons and using a pressure of 414 kPa across the membrane. The removal of chromate ions was greater than 98%.

Selective removal/separation of metal ions

In a mixture of metal ions, when the quantity of a surfactant is limiting, competitive binding occurs between them for the surfactant because of their differential affinity for the surfactant (Hong *et al.* 1998; Huang *et al.* 1994). Huang *et al.* (1994) reported that the affinity of Cu, Ni, Zn, Pb and Cd ions is in the order of Pb>Cu>Cd>Zn>Ni for DCA and Pb>Cu>Ni>Zn>Cd for SDS. Scamehorn *et al.* (1994) found that the affinity of Cu, Zn, Cd and Ca ions for SDS is in the order of Ca>Cu>Zn>Cd. Hong *et al.* (1998) also reported that the affinity of four metals is in the order of Cd>Cu~Zn>Ni for sodium salt of 2-(2-carboxyethyl)-3-decyl maleic anhydride. Therefore, from a mixture, metal ions can selectively be separated in principle by using an appropriate amount of a surfactant (Huang *et al.* 1994).

Practically, MEUF faces lack of selectivity to remove or separate a target metal species from a mixture of metals in aqueous streams, because the selectivity is based only on charge (Fillipi *et al.* 1997). Since the electrostatic attraction is the main binding force between the metal ions and the surfactant, selective removal of metal ions with the same electric charge cannot be done (Akita *et al.* 1999). Therefore, the binding capacity and separation efficiency of a target metal cation may be reduced because of the presence of other cations that may also bind to the same anionic surfactant to the same extent. A potential solution of this problem is the addition of a complexing agent or ligand to the MEUF system that has an affinity to the target metal ion within the surfactant micelles, and this process is named as ligand-modified micellar enhanced ultrafiltration (LM-MEUF). In LM-MEUF, an anionic surfactant and a ligand (which is highly insoluble in water in the absence of the surfactant) are added to an aqueous solution containing ions of like charge, one of which is to be selectively removed. The ligand having a hydrophilic moiety forms a complex with the target ion of interest and solubilises or dissolves inside the organic interior of the micelles. Hence, the formation constant of the metal-ligand complex should be large enough to overcome the charge repulsion between the positively charged target metal ion and the positively charged micelles (Akita *et al.* 1999; Fillipi *et al.* 1997).

Fillipi *et al.* (1997) utilised a cationic surfactant cetyltrimethylammonium bromide (CTAB) and a beta-diketone ligand (1-phenyl-3-isoheptyl-1,3-propane dione) to separate copper ions from a mixture of copper and calcium ions. The micelles and their associated copper-ligand complexes were retained by the membrane, while calcium ions remained unbound and passed with the permeate. The experiment was carried out with regenerated cellulose membranes (MWCO of 6000 daltons) under selected operating conditions (a temperature of 30^0C and a pH of 3.5-5.5). The feed ligand concentration and the pH influenced the copper rejection. A pH of 5.5 was better than 3.5. The copper rejection increased with increasing feed ligand concentrations and a rejection of greater than 99% was achieved at the pH of 5.5. However, for any feed surfactant concentration, the feed ligand and copper concentrations should be below the ligand-copper complex solubility limit to avoid precipitation of the complex.

Akita *et al.* (1999) reported the selective separation of cobalt from a mixture of cobalt and nickel by using a micelle-solubilised hydrophobic ligand 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHPNA) with a nonionic surfactant polyoxyethylene nonyl phenyl ether with 10 ethylene oxide units (PONPE10). The separation of the two metals was not as high as was found in the solvent extraction and was affected by a pH change and feed ligand concentrations. Starting with a low pH value, the maximum separation (a separation factor of 13.7) was obtained at the pH of 5.5. Akita*et al.* (1999) defined the separation factor (α) as follows:

$$\alpha = \frac{[C_r/C_p]_{\text{higher rejected metal}}}{[C_r/C_p]_{\text{lower rejected metal}}} = \frac{[(V_r+V_r.R)/(V_r-V_p.R)]_{\text{higher rejected metal}}}{[(V_r+V_r.R)/(V_r-V_p.R)]_{\text{lower rejected metal}}} \qquad (2.18)$$

where C_r, C_p, V_r, V_p and R denote the retentate metal concentration (in mg/L), permeate metal concentration (in mg/L), retentate volume (in L), permeate volume (in L) and rejection ratio respectively. These authors defined the rejection ratio (R) by $R=1-C_p/C_f$, where C_f is the feed metal concentration (in mg/L). They ultrafiltered 100 ml feed solution until 50 ml permeate was collected.

Comparison of MEUF with solvent extraction

MEUF is a simple one-stage process, whereas solvent extraction needs a number of stages for each of extraction and stripping operations. Thus, solvent extraction needs more frequent attention and skilled operation than MEUF. The aqueous phase in solvent extraction is usually contaminated by the organic solvent because of the solvent's (finite, even if low) water-solubilty. Moreover, solvent extraction is better suited for operations at high metal concentrations and may be expensive at low metal concentrations because the same quanity of power is consumed for its operation though the metal recovery is low. In contrast, MEUF may not be suitable at high concentrations because of possible membrane fouling that may severely reduce the flux or damage the membrane. Overall, MEUF is usually less energy intensive and environmentally safer than solvent extraction (Alguacil and Cobo 1999; Fillipi *et al.* 1998; Hebrant *et al.* 1998).

Hebrant *et al.* (1998) compared the performance of MEUF and solvent extraction in removing copper ions from aqueous solutions. They carried out the first series of experiments using 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline (C_{11}-HQ) as the extractant in both solvent extraction and MEUF. The MEUF experiments were carried out using cetyltrimethylammonium bromide (CTAB) or hexaethylene glycol n-dodecyl ether ($C_{12}EO_6$) as the surfactant to solubilise the C_{11}-HQ-copper micelles in the aqueous phase. In the second series of experiments, they used 6-[(alkylamino) methyl]-2-(hydroxymethyl) pyridine as the extractant and $C_{12}EO_6$ or CTAB as the solubilising surfactant. The UF experiments were performed in a stirred cell using cellulosic membranes with MWCO of 10,000 daltons. Based on the experimental results, they concluded that solvent extraction and MEUF using a non-ionic surfactant have similar efficiencies when the phase volume ratios (organic/aqueous and micellar pseudophase/aqueous pseudophase) are the same in both processes, and MEUF is more efficient than solvent extraction with a 1/1 volume ratio. Solvent extraction takes place at a less acidic pH than the micellar extraction. For a fixed pH, the yield of copper extraction was larger in micellar extraction than in biphasic extraction. At the fixed pH of 3.0, the biphasic extraction of copper with a volume ratio of 1/1 was less than 80% at an extractant-to-metal ratio of 6, and the yield was nearly 100% for micellar extraction at an extractant-to-metal ratio of 3 or greater.

Fillipi *et al.* (1998) reported a comparative economic analysis in removing copper ions from water by ligand-modified micellar-enhanced ultrafiltration (LM-MEUF) and solvent extraction. They used a commercially available ligand (1-phenyl-3-isoheptyl-1,3-propanedione, LIX 54) and a cationic surfactant (CTAB) where the ligand complexed with the target metal (i.e. copper) and the ligand-metal complexes were associated with the micelles through solubilisation. In continuous operations (both solvent extraction and LM-MEUF) for a feed stream rate of $15.8\text{x}10^3$ L/h, the incoming copper concentration of 190 mg/L was lowered to 4 mg/L. The authors found that the LM-MEUF process required a 17% higher capital and 43% higher operating costs than the solvent extraction. The higher operating cost of LM-MEUF arose from its higher reagent and electrical costs.

Choice of an ideal surfactant

In aqueous solutions, the majority of heavy metals exist as cations, which require anionic surfactants for their removal by MEUF. The anionic surfactants used so far are of two kinds – natural and synthetic. The reports of Huang *et al.* (1994) and Hong *et al.* (1998) suggest that natural surfactants have a number of potential advantages over synthetic surfactants.

Huang *et al.* (1994) worked with the natural surfactants DCA and lecithin, and the synthetic surfactant SDS. They observed that DCA offered less membrane fouling, higher permeate flux and high metal rejections compared to lecithin whereas lecithin showed weaker binding forces to metal cations compared to DCA. Thus, the performance of DCA was found to be better than that of lecithin. When compared to SDS, DCA required a S/M of 2.5 compared to 5 for SDS and DCA was equally effective for each metal. Moreover, DCA could be recovered and reused, which was not possible in the case of SDS or lecithin. Hence, selecting DCA over lecithin or SDS would be more efficient and economical.

According to Ahmadi *et al.* (1995), an ideal surfactant generally should have a low cmc to minimise the concentration of surfactant molecules in the permeate, high molecular weight to form larger micelles and biodegradability. They worked with three surfactants:

deoxycholic acid, taurocholic acid (TCA) and sodium dodecyl sulphate and suggested that DCA was better for MEUF than TCA and SDS.

The above considerations indicate that DCA is the most appropriate anionic surfactant in removing heavy metals from aqueous streams.

2.6 Scope of this work

MEUF has been a promising technique for removing toxic metals from aqueous streams, but its applications are still in the development stage and yet to be applied in a large scale for real wastewater. Since the surfactant is the principal requirement for MEUF, the selection of a suitable surfactant is important. The principal natural surfactants selected for this study are the derivatives of cholesterol, i.e. bile acids. The sodium salts of a number of bile acids such as deoxycholic acid, taurocholic acid and taurodeoxycholic acid (TDCA) have potential to be used as surfactants.

The reported studies with DCA (Huang *et al.* (1994) in the laboratory scale suggest that bile acids can be used for heavy metals removal. However, the key process parameters such as temperature, pH and membrane type/material have not been investigated.

Huang *et al.* (1994) reported that the metals bound with DCA micelles can be separated, and the surfactant and the metals can be reused. If metals are present in mixtures, the recovered metals cannot be reused until the individual metals are separated. Previous researchers (Hong *et al.* 1998; Huang *et al.* 1994; Scamehorn *et al.* 1994) have indicated that metal ions have differential affinity for the surfactant and hence, the individual metals can be separated from their mixtures. Only a few studies are available in the literature on the separation of two metals, but in all cases an extractant was used in addition to the surfactant and hence, the selectivity of a surfactant alone was not known. Though Huang *et al.* (1994) mentioned the selectivity of DCA in separating individual metals from a mixture, there was no data to verify the efficiency of separation. There is, thus, scope for work with DCA regarding the mechanism of metal removals, complexation equilibria and effects of process parameters, and separation of individual metals from their mixtures.

This research investigates:

(1) the separation of copper, nickel and zinc from aqueous solutions using sodium salt of DCA as the surfactant

(2) the feasibility of separation of individual metals from mixtures.

Chapter 3

MATERIALS AND METHODS

3.1 Materials

Deoxycholic acid (DCA) powder was supplied by NZ Pharmaceuticals Limited. DCA has been graded as 99% pure and its heavy metal contents were assumed negligible. DCA structure is given in section 4.1.

Nickel chloride ($NiCl_2.6H_2O$) and copper sulphate ($CuSO_4$, anhydrous) were supplied by Scientific Supplies Ltd, Auckland.

Zinc sulphate ($ZnSO_4.7H_2O$) and ethylenediaminetetra-acetic acid (EDTA) disodium salt were supplied by BDH Chemicals Ltd, England.

Purified water at room temperature, obtained by passing distilled water through a Milli-Q water purification system, was used to prepare all solutions and reagents, to soak and rinse the membrane, and to measure the water flux of the membranes before the experiment and after cleaning the membranes.

3.2 Equipment

3.2.1 Ultrafiltration

An Amicon model 402 stirred cell having a capacity of 400 ml and a maximum pressure tolerance of 75 psi (518 kPa) was used for performing UF operations. The schematic diagram of the experimental set-up for UF is shown in Fig. 3.1.

The stirred cell was placed upon a magnetic stirring plate to provide the required rotational speed (rpm) for the cell. A cylinder of nitrogen gas to apply the required pressure for UF was connected to the cell. A reservoir was placed between the gas cylinder and the cell via a three-way valve for diafiltration or continuous feed if necessary. The membrane was placed at the bottom of the cell. The permeate came out through the permeate collection tube and was collected by using any suitable collection equipment (beaker, conical flask or measuring cylinder).

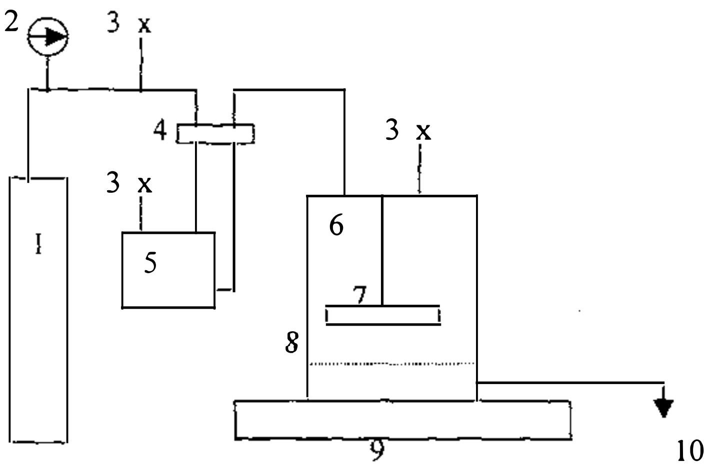


Fig. 3.1 Schematic of experimental set-up for UF, (1) nitrogen gas cylinder, (2) pressure gauge, (3) quick pressure release coupling , (4) three-way valve, (5) reservoir, (6) stirred cell, (7) stirrer bar, (8) membrane, (9) magnetic stirring plate, and (10) permeate

3.2.2 Ultrafiltration membranes

A number of ultrafiltration membranes made of different materials and having different molecular weight cut-off (MWCO) were used. Each membrane had a diameter of 76 mm, but its effective diameter became 70 mm into the stirred cell. The membranes were supplied by Amicon Corporation or its division Millipore Corporation. Their details are shown in Table 3.1. The pure water fluxes (PWFs) of all membranes were measured at the pressure of 345 kPa.

Table 3.1

UF membranes used in this research

Membrane	***MWCO***	***Material***	***Pure water flux (L/h/m^2)***
PBCC5	5,000	Polyethersulphone	370-390
PM10	10,000	Polyethersulphone	120-130
PM30	30,000	Polyethersulphone	420
YM3	3,000	Regenerated cellulose	52
XM100	100,000	Polyacrylonitrile/polyvinyl chloride copolymer	265
UM2	1,000	Polyelectrolyte complex made of vinylbenzyltrimethylammonium chloride and sodium polystyrene sulphonate	33

[pressure is 345 kPa]

The pure water flux of each membrane was measured before each experiment and after cleaning when the UF was finished. The membrane was used again if the flux value after cleaning was close to the value measured before the experiment. The membrane was usually discarded when the flux value fell to one third of the flux before the very first experiment. The measured flux of each membrane before the very first experiment has been shown in Table 3.1 where PBCC5 and YM3 were new, but PM10, PM30, XM100 and UM2 were moderately old membranes. The effect of membrane age was significant on the flux as found from the data in Table 3.1, but would not be significant on the metal rejection.

New membranes were "conditioned" by ultrafiltering pure water until 3-5 litre of permeate to remove protective glycerol layer before use. Between experiments, membranes were stored in pure water at 4^{0}C, but for long time storage, membranes were kept in 10% ethanol solution at 4^{0}C.

3.2.3 Microfiltration apparatus

The schematic diagram of the experimental set up for microfiltration is shown in Fig. 2.2.

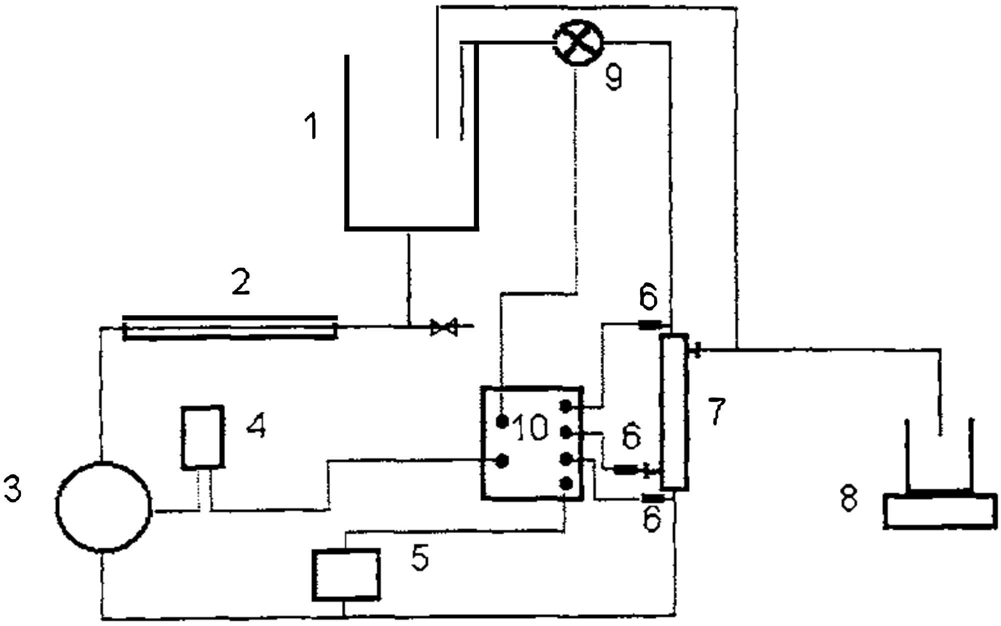


Fig. 3.2 Schematic of experimental set-up for MF, (1) jacketed feed tank, (2) heat exchanger, (3) rotary type positive displacement pump, (4) frequency inverter, (5) magnetic flowmeter, (6) pressure transducers each on inlet side, outlet and permeate side of membrane module, (7) membrane module, (8) permeate collection, (9) electro-pneumatic valve, and (10) control panel

The feed tank was a 60L capacity stainless steel tank with bottom surface sloped towards the central outlet. A tubular heat exchanger was provided in the line. A twin lobe rotary positive displacement pump (model 55S, Flow Pump Ltd., UK) was used to pump the feed. The control panel comprised an automatic loop controller (Toshiba, model EC320, Japan) with two loops- one for controlling feed velocity through a frequency inverter (Zener, model MSC-M3, Australia) and for controlling transmembrane pressure through an electro-pneumatic valve (Keyston, model IP6100, Australia). The frequency inverter was connected between the automatic loop controller and the rotary pump. Diaphragm type pressure transducers (Wika, Alexander Wiegand GmBH & Co., reading range 0-250 kPa, Germany) were placed at the inlet, at the outlet, and on the permeate side of the membrane. A magnetic flowmeter (Yokogawa, model AM202A, Japan) on the feed flow line and three pressure transducers were connected to the controller. The membrane module was vertically placed in the line. The electropneumatic valve was placed on the exit side of the membrane module. Alumina membrane in a tubular module (Ceraflow, Millipore Corporation) was used, which was was 21 cm long multi-channel type with 19 lumen, each having 2.5 mm of inner diameter with the pore size of 0.2 μm.

3.2.4 Atomic Absorption Spectrophotometer

A GBC 933 Atomic Absorption (AA) Spectrophotometer (supplied by GBC Scientific Equipment Pty Ltd, Australia) was used to measure the metal concentrations of the samples. AA used air/acetylene as fuel under a pressure of 150 kPa.

3.3 Methods

3.3.1 Setting operating parameters for UF

The feed solution was placed into the stirred cell and was continuously stirred at 400-500 rpm with a constant pressure of 345 kPa (50 psi) at ambient temperature (room temperature) unless otherwise mentioned. The feed volume was maintained at 400 ml in all experiments. The volume concentration factors (VCFs) for single-metal and two- or three-metal systems were 4 and 8 respectively. The initial permeate flux was measured 2 minutes after the pressure was effective and the final flux was measured at 300 ml of permeate.

3.3.2 Preparation of sodium deoxycholate

Deoxycholic acid is water-insoluble, but its sodium salt (i.e. sodium deoxycholate) is water-soluble. Sodium deoxycholate (NaDC) solution is prepared by mixing commercially available DCA powder with NaOH solution. The reaction is:

$$\underset{\text{(Deoxycholic acid)}}{\text{R-COOH}} + \text{NaOH} \longrightarrow \underset{\text{(sodium deoxycholate)}}{\text{R-COONa}} + H_2O$$

Thus, one mole of DCA (i.e. 392.5 g) reacts with 1 mole of NaOH (i.e. 40 g)to make 1 mole of NaDC (i.e. 414.5 g).

In this research, all NaDC solutions were prepared by the same procedure as follows: Solid NaOH pellets (0.40 g) were dissolved in 50 ml of water. The solution was heated to 80^0C with continuous stirring from a magnetic hot plate. Then 3.925 g of DCA powder was added in three portions to the hot solution and stirred until dissolved. The solution was then cooled to room temperature and diluted to 1 L, which was the 10 mM NaDC solution.

3.3.3 Preparation of metal/NaDC feed solution

A known volume of a metal solution was added to an equal volume of NaDC solution. The strength of each solution before mixing was twice the desired final strength. At a S/M of 2.5, for example, 200 ml of 2 mM Ni solution was added to 200 ml of 5 mM NaDC solution to prepare 400 ml of feed solution with final Ni and NaDC concentrations of 1 mM and 2.5 mM respectively.

3.3.4 Sample analysis

For each metal to be determined, a plot of the absorbance versus the cation concentration was constructed from a series of standard solutions to provide a calibration curve. The absorbance of a sample containing the metal was measured and the concentration from the calibration curve corresponding to the sample's absorbance was the metal concentration of the sample. The AA unit automatically produced the calibration curve from a series of standard solutions for each metal and measured its concentrations in the samples.

3.3.5 Cleaning the membrane

At the end of each run, the membrane was cleaned to remove any deposited particles or foulants so as to re-establish the same initial clean water flux, and also for using the membrane for further operations. The following cleaning procedure was found satisfactory for UF and followed throughout this project.

The stirred cell containing the membrane was flushed with water. Nearly 100 ml of 5% EDTA solution adjusted with ammonia to pH greater than 10 was charged into the stirred cell and ultrafiltered to collect nearly 30 ml of permeate. Then the whole system was rinsed with distilled water 3 or 4 times to remove the cleaning solution. The water flux of the cleaned membrane was checked. When it was close (greater than 90%) to the water flux measured before the ultrafiltration experiment, the membrane was judged to have been sufficiently cleaned.

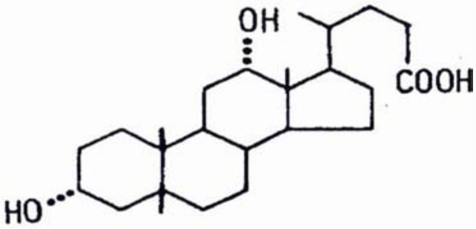
The MF membrane was cleaned by circulating hot RO water (50^0C) for 10 minutes, and then 1% Ultrasil 2500 solution (50^0C) for 20 minutes, followed by RO water at room temperature for 20 minutes. Each circulation was made at 5 m/s cross-flow velocity and without any applied pressure.

Chapter 4

REMOVAL OF HEAVY METALS USING SODIUM DEOXYCHOLATE: EFFECT OF OPERATING PARAMETERS

4.1 Introduction

The majority of heavy metal salts are completely soluble and dissociated into ions in aqueous systems of appropriate pH. The heavy metal ions are so small that they cannot be removed by classical filtration or ultrafiltration techniques. However, ultrafiltration (UF) membranes can retain the metal ions along with surfactant micelles when the ions are entrapped onto the micellar surfaces (Hong *et al.* 1998, Scamehorn *et al.* 1994). Deoxycholic acid (DCA), a biological detergent, has been selected as the surfactant for this study because it shows a number of potential advantages over other surfactants (Huang *et al.* 1994). The role of DCA in separating three heavy metal ions (copper, zinc and nickel) is reported in this chapter. The different systems investigated were single-metal systems, two-metal systems (binary) and three-metal systems (ternary) where the sodium salt of deoxycholic acid known as sodium deoxycholate (NaDC) was used. The structure of DCA is (Small 1971):



4.2 Method

4.2.1 Experimental techniques

Ultrafiltration

Ultrafiltration experiments were carried out in a batch system using a dead-end UF mode. The feed mixtures or slurries having low metal concentrations were charged into the stirred cell and continuously stirred prior to and during the entire course of ultrafiltration. The feed volume was maintained at 400 ml in all the experiments. UF runs usually continued until collection of 300 ml of final permeate in the single-metal systems and 350 ml in the two-metal and three-metal systems. The final volume concentration factor (VCF) was thus 400/100 or 4 in the single-metal systems and 400/50 or 8 in the two-metal and three-metal systems. In cases of high copper concentrations, the feed slurries were dense and a thick layer of precipitate was formed over the membrane surface that reduced the rate of permeation to a very low value, probably, through fouling. The slurries in such high metal cases were stirred outside the stirred cell prior to ultrafiltration to obviate the low flux problems and UF of these dense slurries (with stirring) was carried on until collection of a sufficient amount of permeate for analysis since the flux was still very low. The VCF was, therefore, low and variable between runs. The permeate flux was measured at 15-30 minute intervals. The pH of the feed mixture was measured to be in the range of 6.5 to 7.5 in general. The experiments were performed at room temperature (~20^0C) unless otherwise stated.

Vacuum-filtration or/and centrifugation

The purpose of using vacuum-filtration and centrifugation was to observe the ultrafiltration of the liquid phase alone and hence, separate the contributions of precipitation and ultrafiltration on the overall metal removal. The mixtures of metal and NaDC solutions were vacuum-filtered on a Buchner funnel using Whatman No. 1 filter papers after the required equilibration time. Filtration on the same filter paper was repeated once or twice to obtain a clear filtrate. Sometimes, vacuum-filtration was not possible, particularly in cases of high feed metal concentrations because of the extremely low filtration rate or because a large proportion of precipitate passed through the filter paper. In these cases, the feed mixtures were centrifuged (Sorvall RC-5C Automatic Superspeed Refrigerated Centrifuge) for 0.5-2 hours at 15000 rpm (20,500 relative centrifugal force), which produced clear supernatant. The supernatant, when cloudy, was vacuum-filtered to make it clear.

4.2.2 Sample analysis

Copper and zinc concentrations in the permeate and retentate samples from all systems investigated were measured by atomic absorption spectroscopy using a GBC 933 Atomic Absorption Spectrophotometer (AA unit).

In the case of nickel, the colorimetric dimethylglyoxime method, a second method alternative to the AA method was available that used a PU 8625 UV/VIS Spectrophotometer. The procedure (Vogel 1961) was as follows:

A 5 ml aliquot analyte was placed into a 25 ml volumetric flask and then 5 ml of 0.5M HCl was added to it. The mixture was diluted to about 15 ml after which 2 ml of concentrated ammonia solution was added, followed by 1 ml of concentrated bromine water. Then 1 ml of 1% dimethylglyoxime solution was added and the whole mixture was diluted to exactly 25 ml. The absorbances were measured at 445 nm (445×10^{-9} m) 15 minutes after mixing of dimethylglyoxime. The absorbances of a set of standard solutions were also measured to construct a calibration curve from which the nickel concentration of any sample was determined.

Formation of nickel dimethylglyoxime complex is the basis of the colorimetric method that is likely to be affected by the presence of other metals such as copper and zinc, but the method does not clearly describe the situation when nickel is present in a mixture with other metals. Therefore, nickel concentrations in the samples from binary and ternary systems were not measured by the colorimetric method, rather the AA method was used. Thus, the samples from the single metal system of nickel only were suitable for colorimetric analysis.

According to the specifications of the AA unit, all the samples and standard solutions of metals were acidified; nickel and copper with nitric acid to 0.3N final concentration and zinc with hydrochloric acid to 0.2N final concentration. There was an upper limit for each metal that could be measured by the AA unit. Therefore, appropriate dilutions were made with water, where necessary keeping the final acid concentration unchanged.

The duration of stable colour formed by the nickel dimethylglyoxime complex was investigated by measuring the absorbances of a 10 mg/L nickel standard solution at 5 minute intervals during a course of 60 minutes. The absorbances over a period between 5 and 60 minutes remained almost the same. However, the nickel results reported in this research were measured between 10-30 minutes after addition of dimethylglyoxime.

The permeate samples when acidified to the final acid concentrations showed a pH value of below 3. Any DCA present was precipitated at this pH and was filtered out to make the samples free of DCA. The retentate samples contained most of the feed DCA (as the metal-DCA complex) in the particulate form. They were acidified with concentrated nitric or hydrochloric acid to lower the pH below 3 to precipitate the DCA. The DCA was filtered out and washed with distilled water several times to remove the metal ions. The combined filtrate and washings were made to volume and analysed for nickel to represent the retentate nickel concentration.

4.3 Results and Discussion

4.3.1 Single-metal systems

Each metal (nickel, copper or zinc) was studied separately. Three equations (equations 2.7, 2.8 and 2.9) were available to calculate the metal rejection (R):

$\% R = 100(1 - C_p/C_f)$ .... Eq 2.7

$\% R = 100(1 - C_p/C_r)$ .... Eq 2.8

$\% R = 100(\ln C_r/C_f)/(\ln V_f/V_r)$ .... Eq 2.9

where C_p, C_r and C_f are the metal concentrations in the permeate, retentate and feed respectively, V_f is the feed volume and V_r is the retentate volume.

Equation 2.7 is permeate based and used to calculate the total rejection by the membrane process. The feed metal concentration is already known, and the permeate metal concentration can be determined with high accuracy since it does not need large dilutions. The permeate metal concentration does not vary with its volume, so the metal rejection calculated by the equation 2.7 would represent the actual rejection by the membrane system.

Equation 2.8 is retentate based and used to calculate the instantaneous rejection at any point in the process. In the present research, the permeate metal concentration did not vary with its volume, but the retentate metal concentration did since it contained the rejected metal-DCA complexes. The retentate volume varied between different experiments because the permeate volume usually was 300 ml in normal conditions, and was much less than 300 ml in difficult situations. Therefore, the equation 2.8 is not applicable in this research since the final rejection can not be obtained for all experiments.

Equation 2.9 is also retentate based and used to represent the average rejection by a membrane. It is better than the equation 2.8 in the sense that it considers the retentate volume along with the retentate concentration. In the present research, the retentate in the stirred cell contained the precipitate deposited on the membrane and a small volume of the liquid phase. Measuring the metal concentration in the retentate needed a large dilution factor (e.g., 1 in 100 or more) where a small error in measuring the highly concentrated retentate could make a big difference. Therefore, equation 2.9 is applicable if the retentate volume and the retentate metal concentration can be measured accurately.

In this research, efforts have been made to accurately collect and analyse the permeate and the retentate. The retentate was collected after dissolving with ammonia solution, but a small portion might be lost during this process. It was noted that the membranes were quickly fouled before collecting the desired volumes of permeate (300 ml) during MEUF with high feed metal concentrations, and the retentate could not be collected quantitatively. In addition, there was basically no retentate liquid from vacuum-filtration. In these two situations, equations 2.8 or 2.9 could not be used. The equation 2.7 is the only equation that can be used with more confidence in all the situations and it does not include the probable errors that usually occur in collecting and analysing the retentate. Therefore, equation 2.7 was used for calculating the rejection of metals.

4.3.1.1 Nickel: Effect of variables on MEUF of Ni/NaDC system

A number of experiments were carried out with nickel under various conditions. The important variables investigated were equilibration time, surfactant-to-metal (S/M) ratio, feed metal concentration, membrane type/material, temperature and pH. All experiments were carried out in duplicate runs using 1 mM nickel solution (59 mg/L) unless otherwise stated. The MEUF results of Ni/NaDC mixtures are given in Table 4.1 and Table 4.2.

Table 4.1

MEUF of Ni/NaDC system (1 mM Ni)

Expt. No	Membrane	S/M	Equilibration time (h)	Permeate Ni (mg/L)	Initial permeate flux as % of PWF	Rejection (%)
1	PM10	2.5	0	13	4	78.0
2	PM10	2.5	1	12	5	79.7
3	PM10	2.5	2	11	8	81.4
4	PM10	2.5	3	6.3	32	89.3
5	PM10	2.5	4	5.8	35	90.2
6	PM10	2.5	6	4.9	40	91.7
7	PM10	2.5	12	4.7	43	92.0
8	PM10	2.5	24	4.2	52	92.9
9	PM10	2.0	24	14	56	76.3
10	PBCC5	2.5	0	12	14	79.7
11	PBCC5	2.5	3	5.9	40	90.0
12	PBCC5	2.5	6	4.8	50	91.9
13	PBCC5	2.5	12	4.0	45	93.2
14	PBCC5	2.5	24	3.4	50	94.2
15	PBCC5	3.0	24	1.1	41	98.1
16	PBCC5	4.0	24	0.92	30	98.4
17	PBCC5	5.0	24	0.19*	27	99.7
18	PBCC5	2.0	6	14	62	76.3
19	PM30	2.5	24	6.0	48	89.8
20	YM3	2.5	24	17	90	69.5

[*permeates concentrated 10 times prior to colorimetric measurement,
PWF= pure water flux]

Table 4.2

MEUF of Ni/NaDC system (high Ni)

Expt. No	Membrane	S/M	Equilibration time (h)	Feed Ni (mg/L)	Permeate Ni (mg/L)	Initial permeate flux as % of PWF	Rejection (%)
21	PBCC5	2.5	24	600	0.053*	38	99.9+
22	PBCC5	2.5	24	1200	0.28*	28	99.9+
23	PM30	2.5	24	600	0.33*	54	99.9+

[*permeates concentrated 5-10 times prior to colorimetric measurement]

[Details of fluxes and UF times of all experiments are given in Appendix B]

Equilibration time

On mixing the nickel solution with the sodium deoxycholate solution, a precipitate was quickly formed, indicating that the mixture was heterogeneous, but precipitation might not be completed instantly or within a short period after mixing. A series of experiments (expts. 1-8 in Table 4.1) were carried out to investigate the effects of time elapsed before ultrafiltration was commenced. For each experiment, the nickel solution was added to a NaDC solution into the stirred cell and continuously stirred for the stated time period. The time elapsed before ultrafiltration was referred as 'equilibration time'.

The experimental results indicate that the permeate nickel concentration decreases with increasing equilibration time. The possible explanation is that the reaction, which is ionic, is complete instantly after mixing, but the formation of solid precipitate aggregates (i.e. insoluble nickel deoxycholate) is slow and thereby, is not complete. The effects can be seen from the graph of nickel rejection (%) against equilibration time shown in Fig. 4.1. A major proportion of precipitation was completed after 3 hours, resulting in a nickel removal of about 89%. It was observed that the initially green precipitate formed by mixing NaDC with nickel, changed over a period of time to white, regardless of initial nickel concentration. The reason for the colour change was not investigated, but for 1 mM nickel, the colour change was observed to start 2 hours after mixing and took 30-60 minutes for a total change to white.

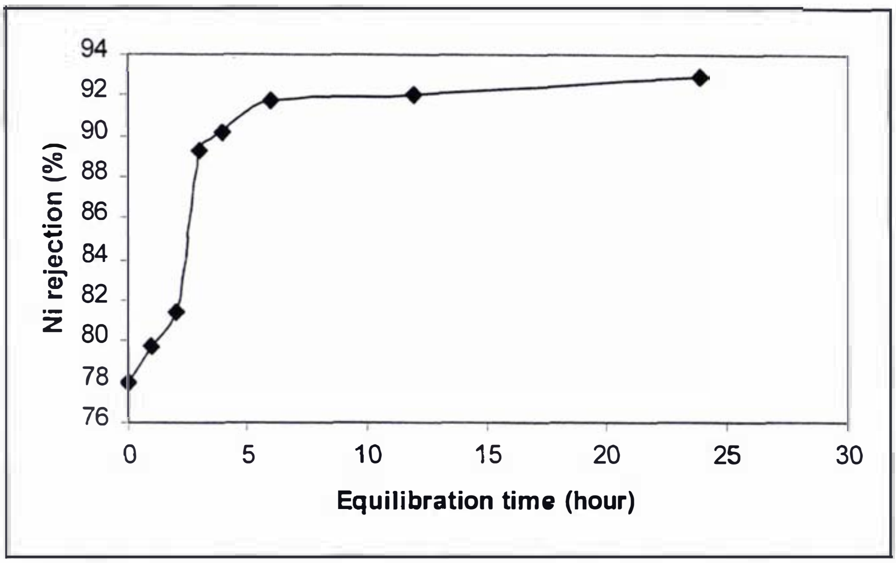


Fig. 4.1 Effect of equilibration time on the MEUF performance of Ni/NaDC mixtures (PM10 membrane)

The experimental results also suggest that allowing more time for stirring, even after 3 hours, gives higher nickel rejections (i.e. lower permeate nickel). The improvement in rejection or permeate quality was slight as the equilibration time neared to 24 hours and so, investigation was not carried out beyond 24-hour equilibration time.

The NaDC concentration in the feed mixture containing 1 mM nickel was 2.5 mM, which was below its critical micelle concentration (cmc) of 5 mM (Small 1971). Huang *et al.* (1994) also reported the removal of heavy metals using NaDC, but did not indicate that the metal deoxycholate would precipitate as was observed in the present research. These authors stated that metal ions were removed by forming metal-surfactant complexes at a surfactant concentration below the cmc, but forming both metal-surfactant complexes and micelles above the cmc. This distinction on the molecular level is a valid one, but on an operational viewpoint, which is concerned with such effects of flux rate and fouling, the distinction is, probably, of minor significance. From the present observations, it can be argued that metal-surfactant complexes and micelles are virtually the same.

Ni/NaDC mixtures with different equilibration times produced different permeate fluxes at the start and end of UF runs. Feed mixtures with equilibration time less than 3 hours started with low fluxes (expts. 1-3 and Fig. 4.2) that increased continuously with time during the entire course of ultrafiltration (total UF time 4.5 to 6 hours). The final fluxes in these cases were 2 to 4 times of their initial values. As an example, the experiment with 1-hour equilibration time (expt. 2) had initial and final permeate fluxes of 6 L/h/m^2 and 24 L/h/m^2 respectively, and the total UF time was 4.5 hours.

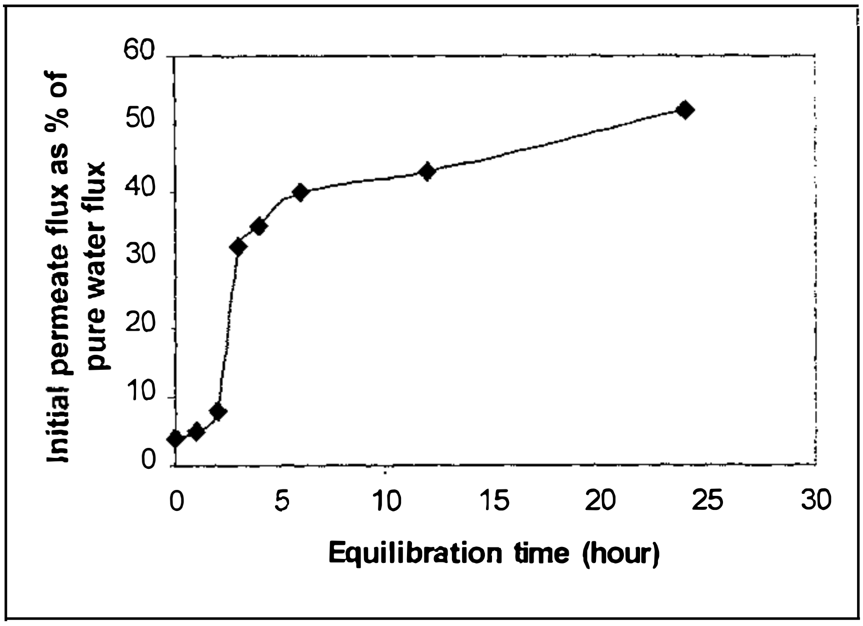


Fig. 4.2 Initial permeate fluxes expressed as percentage of the pure water flux for different equilibration times (PM10 membrane)

The flux of an UF membrane is governed by three resistances: intrinsic membrane resistance, resistance due to fouling and resistance due to concentration polarisation or gel-layer (Cheryan 1998; Markels *et al.* 1995). In the present experiments, there was a residual free NaDC concentration of 0.5 mM (stoichiometrically) after reacting with nickel. The effects of free residual NaDC on the permeate flux were studied by carrying out UF experiments with NaDC solutions. The results are shown graphically in Fig 4.3, which shows that the permeate flux of 0.5 mM NaDC solution was only 77% of the pure water flux. This decline in flux was attributed to concentration polarisation (CP) rather than fouling. This was confirmed by a simple experiment where the UF cell, after decanting the retenate solution of 0.5 mM NaDC experiment, was filled with pure water and ultrafiltered again to check the flux. The initial flux was 91% of the pure water flux and rose over 20 minutes to the pure water value. The graph (Fig. 4.3) also indicates that the concentration polarisation effect (i.e. flux decline) increases with increasing free NaDC concentrations (as expected).

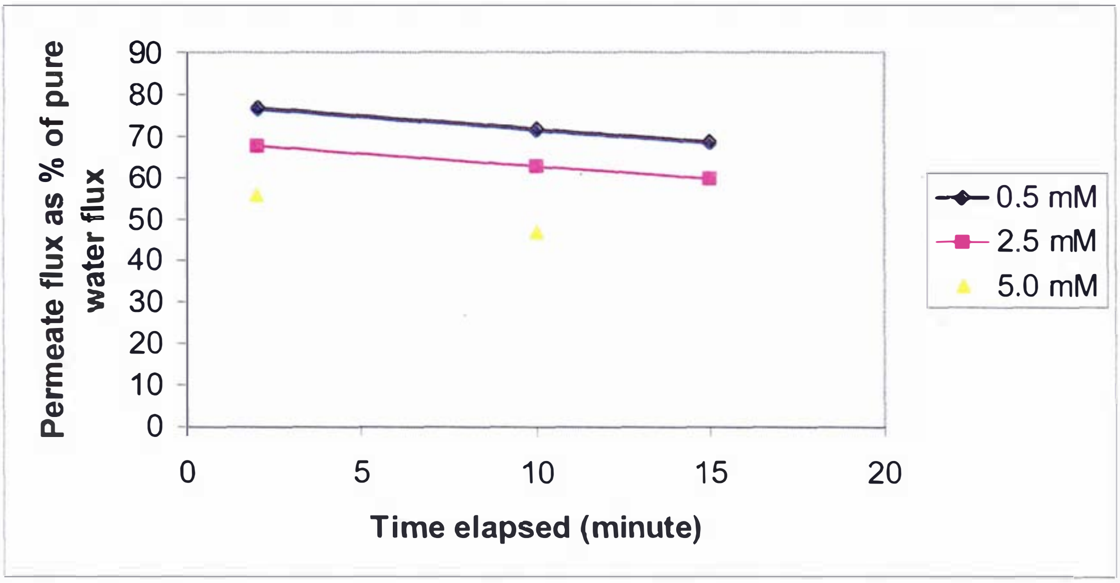


Fig. 4.3 Permeate fluxes of NaDC solutions through the PBCC5 membrane

According to Small (1971) and Coello *et al.* (1996), NaDC forms primary aggregates with aggregation number 2-7 and these primary aggregates can further agglomerate into larger ones. The larger aggregates, thus, can be expected to be retained by the 5, 000 and 10,000 daltons cut-off membranes resulting in concentration polarisation effects. This might cause the observed flux reduction. Since the solubility of NaDC is 334 g/L (Small 1971), it is open to question whether an actual gel layer as such has been reported during UF of proteins (Cheryan 1998), will be formed due to concentration polarisation. However, there will be a non-gel boundary layer (i.e. a CP layer) whose viscosity would be higher than the bulk solution and this layer would provide an additional resistance to flow. Such a non-gel CP layer should aid in increasing retention of aggregates if only because diffusion through such a layer is slow, and there is a back-transport of solids into the bulk solution (Cheryan 1998).

Huang *et al.* (1994) also observed a lower permeate flux at 16 mM free NaDC concentration compared to that at 8 mM free NaDC concentration, but they attributed it to the higher bulk feed viscosity at the higher NaDC concentration. The flux through a microporous membrane is inversely proportional to the viscosity according to the Hagen-Poiseuille law of fluid flow only when there is negligible concentration polarisation and no fouling, and the viscosity of a solution increases with increasing solids concentration (Cheryan 1998). Cussler and Duncan (1972) reported that the viscosity of sodium cholate (NaC) in water at 25^0C was about 5 cP(centripoise), 25 cP and 625 cP at the concentrations of 0.5M, 1M and 2M respectively. This indicates that the increase in viscosity would be very small at the low NaC concentrations used in this study. Assuming the viscosity of NaDC is similar to NaC, an increase in viscosity with concentration will be very low at the NaDC concentrations of 8 mM and 16 mM as mentioned by Huang *et al.* (1994). Zakrzewska *et al.* (1990) also reported that viscosity changes were negligible at lower NaDC concentrations. That the decline in the permeate flux of NaDC solutions is due to increasing bulk viscosity is thus unlikely. The free NaDC does not foul the membrane and hence, concentration polarisation is a more likely reason for the observed flux decline.

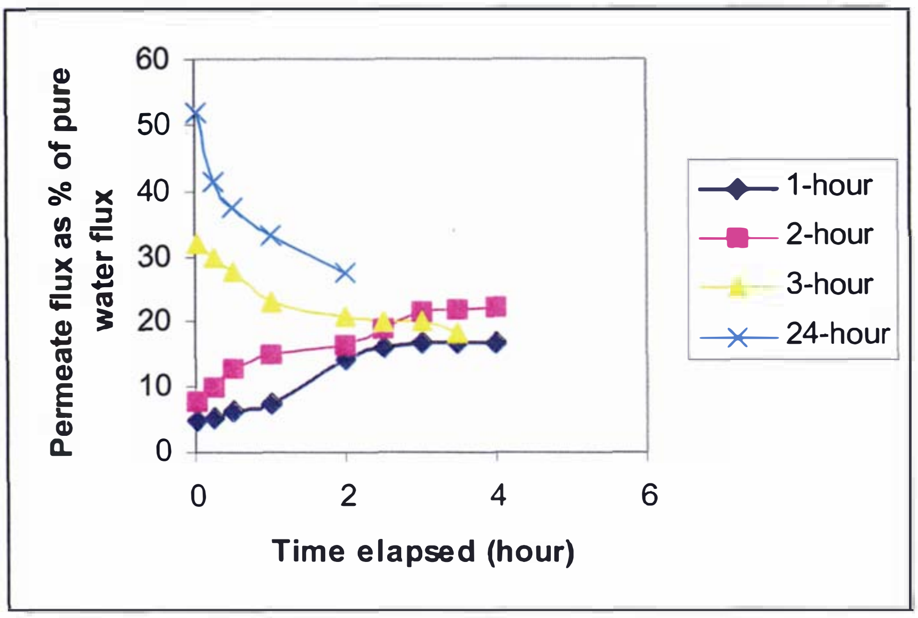


Fig. 4.4 Flux behaviour of Ni/NaDC mixtures with elapsed time for different equilibration times (PM10 membrane)

Scamehorn *et al.* (1989) reported the zinc (1.3 mM) removal by a submicellar SDS concentration (3.3 mM) where a 48.6% zinc rejection was obtained instead of 0% as expected. They postulated that this resulted from a gel layer formed next to the membrane at the low surfactant concentration because of concentration polarisation. They also considered the possibility of rejection of surfactant monomers to some extent in MEUF. The surfactant thus accumulated at the membrane surface can reach or exceed the cmc even when the bulk retentate solution has no micelles.

In the present experiments with 1 mM Ni at a S/M of 2.5, the concentration polarisation effect due to 0.5 mM free residual NaDC is reasonably constant. The resistance due to membrane material is usually a small part of the total resistance in actual operation with a real feed (Cheryan 1998) and is likely to be constant in the present experiments with a polyethersulphone membrane (i.e. PBCC5, PM10 or PM30). Therefore, other factors along with concentration polarisation and membrane resistance are responsible for further increase (expts. 1-3) or decrease (expts. 4-8) in flux with elapsed time (Fig. 4.4). The observed increase in flux may be attributed to a lessening of fouling as follows:

The rate of precipitation of insoluble $Ni(DC)_2$ aggregates is slow at the very low concentration of soluble $Ni(DC)_2$. The insoluble $Ni(DC)_2$ aggregates are small at the initial stages of mixing, and the total surface area of these small particles at the membrane surface is large. Faust and Aly (1983) reported that the interface of the large surface area was associated with a substantial free energy. The small particles on the membrane surface also foul the membrane to a greater extent. Thus, the permeate fluxes are low at the start of UF with feed mixtures having an equilibration time of less than 3 hours. When the small particles fouling the membrane agglomerate, the free energy is reduced. Faust and Aly (1983) maintained that the process of agglomeration was time-dependent and associated with a decrease in free energy. Sonntag and Strenge (1969) also reported that a decrease in free energy spontaneously would increase the particle size. The larger particle size may, in turn, allow for an increase in flux because of packing considerations. Thus, an increase in particle size with time would increase the flux. This could be confirmed by measuring the particle sizes at different equilibration times, but for those experiments the particle sizes could not be measured due to unavailability of a suitable apparatus.

For Ni/NaDC mixtures with an equilibration time of 3 hours or greater, the permeate fluxes were considerably higher (expts. 4-8 and Fig. 4.2) at the initial stage (34 to 58 L/h/m^2) and continuously decreased with elapsed time until the runs finished. The final fluxes were 50-60% of the initial values and the total UF time was 2.0-3.5 hours. For example, the initial permeate flux for the 6-hour equilibration experiment was 51 L/h/m^2 and it decreased to 25 L/h/m^2 after 2.5 hours of total UF time. The higher initial permeate flux also supports the increased (i.e. larger) particle size with increased aging. The decrease in permeate flux with elapsed time (Fig 4.4) is caused, probably, by the formation of a surface-fouling layer the thickness of which increases by the accumulation of aggregates because the solids concentration in the retentate increases. Since the distilled water flux was restored after cleaning the membrane to the value before the experiment, the reduction in flux could not be ascribed to membrane compaction or permanent fouling.

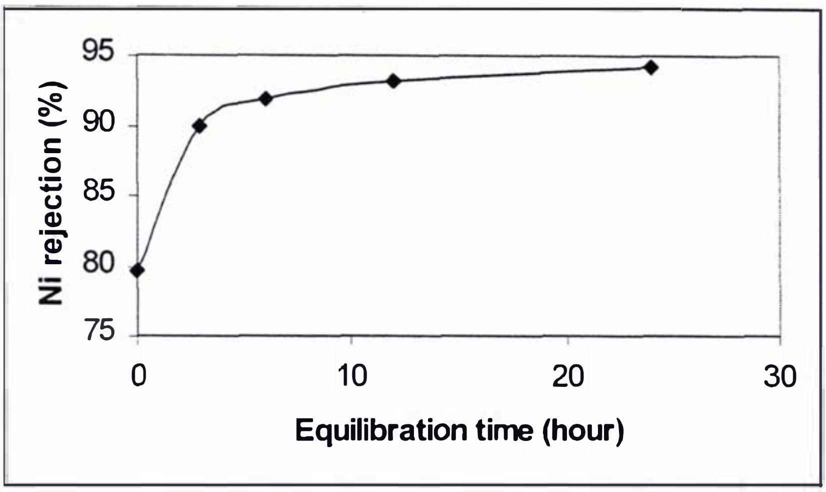


Fig. 4.5 Effect of equilibration time on the MEUF performance of Ni/NaDC mixtures (PBCC5 membrane)

A series of experiments were also performed using PBCC5 membranes. Experiments 10-14 in Table 4.1 and Fig. 4.5 represent these results. Similar trends in results from PM10 and PBCC5 membranes were observed in that the nickel rejection increased with increasing equilibration time. When the equilibration time was less than 3 hours, the nickel rejection and the permeate flux were low, but increased dramatically when the time was greater than 3 hours. The nickel rejection was higher for the PBCC5 membrane as expected because of its lower molecular weight cut-off (MWCO), but the improvement in rejection was relatively small. The reason for the relatively higher permeate flux of the PBCC5 membrane than the PM10 membrane was that the PM10 was an old membrane compared to the new PBCC5 membrane as reflected from the pure water flux of PM10 (130 L/h/m^2), which was almost one third of the pure water flux of a new PBCC5 membrane (390 L/h/m^2, after processing with 4 litres of water collected as permeate). Continuous use of the new PBCC5 membrane resulted in a "steady state" water flux of about 160 L/h/m^2.

The experimental results from PM10 and PBCC5 membranes indicate that the highest Ni rejection (best permeate quality) was obtained after 24-hour equilibration, and the latter was the better of the two membranes. The experimental evidence also indicates that when NaDC is used as the surfactant, not MEUF as was reported by Huang *et al.* (1994) but precipitation of insoluble metal deoxycholate is mainly operative in metal removal.

S/M ratio

The S/M ratio is an important operating parameter that affects the performance of surfactant-based UF (Hong *et al.* 1998). The optimal S/M ratio for effective removal of metal ions is different for different surfactants as found in the literature. The suitable S/M ratio reported by Huang *et al.* (1994) was around 2.5 for NaDC and 5 for SDS for removing over 99.9% of metal ions.

Experiments 8-9 and 14-17 (Table 4.1) refer to the effects of S/M ratios on the nickel rejection by UF using NaDC. At a S/M ratio of 2.5, a PM10 and a PBCC5 membrane removed 92.9% and 94.2% of nickel ions respectively after 24-hour equilibration time, and 78.0% and 79.7% of nickel ions respectively when no equilibration time was allowed. The results of this study were comparable to the result of Huang *et al.* (1994) where about 70% nickel ions were removed by a RGO3 membrane (made of anisotropic acrylanitryl with MWCO of 2000 daltons) at a S/M ratio of 2.5 for NaDC using a 1.2 mM Ni solution.

A S/M ratio smaller than 2.5 was not at all effective for NaDC because the nickel removal/rejection at a S/M ratio of 2.0 was found to be significantly lower (76.3% for both PM10 and PBCC5 membranes) than that from a S/M ratio of 2.5. The experimental results (expts. 14-17) also indicate that when the S/M ratio was increased from 2.5, the Ni removal also increased (Fig. 4.6). The Ni removal was excellent with 99.7% at a S/M ratio of 5.0. Huang *et al.* (1994) reported that a S/M ratio of greater than 8 would be necessary for complete removal of nickel ions at a concentration of 1.2 mM using NaDC. The experimental results (expts. 21-22) also suggest that the S/M ratio of 2.5 was sufficient for almost complete removal of nickel ions (over 99.9%) at higher concentrations (10 mM and 20 mM) using NaDC and the same PBCC5 membrane.

When the S/M ratio was increased, while keeping the feed metal concentration constant, the only change in the feed mixture was the increase in free NaDC. Theoretically 1 mole of metal binds 2 moles of deoxycholate. For 1 mM feed nickel, the S/M ratios of 2.0, 2.5, 3.0, 4.0 and 5 give a free residual NaDC of 0, 0.5, 1.0, 2.0 and 3.0 mM respectively. An increase in free NaDC increases the concentration polarisation effect as evidenced from Fig. 4.3. Hence, the decline in initial permeate flux with the increasing S/M ratio (Fig. 4.6) was mainly due to increased CP resulting from the increased free NaDC.

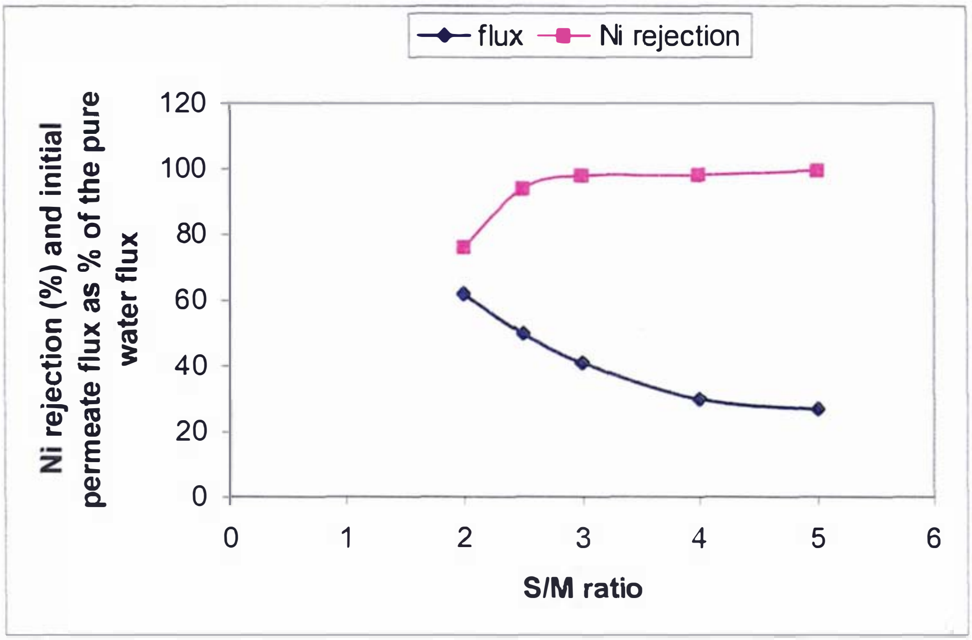


Fig. 4.6 The effect of S/M ratios on the Ni rejection and the initial permeate flux (PBCC5 membrane) (expts. 14-18).

In the S/M ratio of 2 experiment, there was no CP due to NaDC, yet the initial permeate flux was 62% of the pure water flux (expt. 18). This lower value of the initial permeate flux compared to the pure water flux was, probably, due to CP of soluble nickel deoxycholate, which has been discussed in the section ***Membrane type/material/MWCO***.

The decline in permeate flux with elapsed time (e.g., 3-hour and 24-hour curves in Fig. 4.4) was mainly due to the influence of fouling as a result of solids buildup by insoluble nickel deoxycholate. In the S/M of 2 experiment, the membrane fouling was lower because of the smaller amounts of insoluble $Ni(DC)_2$ as evidenced from the higher permeate Ni (14 mg/L). In other experiments when the S/M ratio was greater than 2, the membrane fouling was relatively higher because of relatively larger amounts of insoluble $Ni(DC)_2$ (i.e. lower permeate Ni). For example, the amounts of insoluble $Ni(DC)_2$ in the S/M of 2, 2.5 and 5 experiments (expts. 18, 14 and 17) were 641 mg/L, 793 mg/L and 839 mg/L respectively. As a consequence, the decline in flux with elapsed time of a run was higher at the S/M ratio of 2.5 or greater than that at the S/M of 2.

A decrease in initial permeate flux with the increasing S/M ratio for metal/NaDC systems was also observed by Huang *et al.* (1994). These authors postulated that the flux decline might be due to increasing interaction between the micelles and the membrane surface. Their explanation implies membrane fouling. However, Cheryan (1998) reported that membrane fouling occurred from specific solute-membrane interactions resulting in a physical adsorption of the solute by the membrane. Huang *et al.* (1994), in their study, increased the S/M ratio by increasing the NaDC, while keeping the metal concentration constant. This is similar to the present experiments (Fig. 4.6). The data obtained from experiments 14 and 20 indicate that specific solute membrane interactions were present since the rejection behaviour was different between polyethersulphone (i.e. PBCC5) and regenerated cellulose (i.e. YM3) membranes. However, it may be argued that adsorption sites on the membrane must be limited and must approach saturation at a certain NaDC concentration. The $Ni(DC)_2$ adsorption may be neglected because the nickel deoxycholate is neutral (i.e. free of charge). Thus, the main reason of flux decline with increasing S/M ratio was the CP effect due to NaDC. The postulate put forward by Huang *et al.* (1994) is thus less likely than the CP postulate.

The initial permeate fluxes in the presence of free residual NaDC were 30-50% of the pure water flux (expts. 14-17), which were lower than the flux obtained in the absence of free residual NaDC (62% of the pure water flux). At high feed metal concentrations, the initial permeate fluxes were further lower (e.g., 28-38% of the pure water flux in expts. 21-22) because of increased CP by the increased free residual deoxycholate ions, and the decline in flux with elapsed time was also higher because of increased membrane fouling by the increased amounts of insoluble $Ni(DC)_2$. For example, the theoretical amounts of insoluble $Ni(DC)_2$ for 1 mM and 10 mM feed Ni (400 ml feed) are 320 mg and 3440 mg respectively (expts. 14 and 21).

At the S/M ratio of 2, the additional sieving effect offered by CP (due to free NaDC) was absent. Hence, the nickel removal without free residual NaDC was relatively low (76.3%), and the soluble $Ni(DC)_2$ that passed through the membrane contributed to permeate nickel. The permeate nickel concentration of 14 mg/L at the S/M of 2 corresponded to 201 mg/L of $Ni(DC)_2$, which would be approximately equal to the solubility value of $Ni(DC)_2$ in the presence of 2 mM NaCl. However, the 24-hour solubility of $Ni(DC)_2$ in 2 mM NaCl solution was experimentally determined to be 158 mg/L (11 mg/L Ni) as shown in Table 4.17. The reason for higher permeate Ni (i.e. 14 mg/L) in this case, compared to that from the solubility contribution (i.e. 11 mg/L Ni), may be due to 6-hour equilibration instead of 24-hour and the value would be lower if a 24-hour equilibration time was used. An additional consideration may be the common ion effect, which is discussed in the following paragraph.

In the case of PBCC5 membrane, an increase in free residual NaDC from 0 to 0.5 mM and from 0.5 mM to 3 mM increases the nickel removal from 76.3% to 94.2% and from 94.2 to 99.7% respectively. The free residual NaDC increases with the increasing S/M ratio since the feed Ni concentration is fixed at 1 mM. Thus, the free residual NaDC plays a very important role in removing Ni ions (Fig. 4.6). The reason for increasing nickel removal with the increasing free residual NaDC is that the solubility of $Ni(DC)_2$ decreases with increasing deoxycholate anions due to the common ion effect. The increased free residual NaDC drives the equilibrium to the right in the equation:

$$Ni^{2+} + 2(DC^-) \rightleftharpoons Ni(DC)_2.$$

At a high feed Ni concentration (at the S/M of 2.5), the free residual NaDC concentration after reaction with nickel was also high. For example, the free residual NaDC concentrations for 10 mM and 20 mM feed Ni were 5 mM and 10 mM respectively (expts. 21 and 22). The high concentration of free residual NaDC reduced the solubility of $Ni(DC)_2$ to a low value giving the observed low permeate Ni concentrations (the Ni removal was greater than 99.9% in each case). Therefore, a S/M of 2.5 was sufficient when the feed Ni concentration was high.

Hence, depending on the feed nickel concentration, different S/M ratios should be used to ensure sufficient free deoxycholate anions for driving soluble $Ni(DC)_2$ into insoluble $Ni(DC)_2$. The experimental evidence suggests that a S/M of 5 is required for 1 mM feed Ni, but a S/M of 2.5 is sufficient for a feed Ni of 10 mM.

Membrane type/material/MWCO

The material comprising the membrane has significant effects on the removal of metal ions by surfactant-based UF, and it can be observed from the results of experiments 14 and 20. PBCC5 and YM3 membranes are made of polyethersulphone (PES) and regenerated cellulose (RC) respectively. Under identical conditions, their nickel rejections are also significantly different with rejections of 94.2% and 69.5% for the PBCC5 and the YM3 respectively. The YM3 membrane has a lower MWCO (3,000 daltons) than the PBCC5 (5,000 daltons), yet the PBCC5 membrane offers a much higher nickel rejection than the YM3. The results strongly indicate that a PES membrane is more effective in NaDC-mediated metal removal than a RC membrane. The flux decline over the course of the two runs is more marked for the PES membrane than for the RC membrane. The flux for the PES membrane starts with about 50% of the pure water flux and ends up with 25-35% of the pure water flux. On the other hand, the flux for the RC membrane starts with 90% of the water flux and ends up with 80-85% of the pure water flux.

Polyethersulphone Regenerated cellulose

Fig. 4.7 Structures of polyethersulphone and regenerated cellulose (Cheryan 1998)

The permeate fluxes of the PES membranes clearly indicate that significant membrane fouling and concentration polarisation do not occur in the YM3 case in contrast to the PBCC5 case. Kim *et al.* (1994) also reported that RC membranes were more diffusive and less susceptible to fouling compared to PES membranes. Hence, residual free deoxycholate ions have no or little effects on the RC membrane, but cause a significant CP on the PES membrane. Moreover, the permeate nickel concentration from the YM3 at the S/M of 2.5 is higher than that of the PBCC5 at the S/M of 2.0, which supports the postulate of no CP due to NaDC on the YM3 membrane.

The absence of significant CP in the YM3 case indicates that the soluble $Ni(DC)_2$ has no or little CP effect on the RC membrane. In the PBCC5 case, CP effects are present even in the absence of free NaDC (expt. 18) as evidenced from the initial permeate flux value (62% of pure water flux) when the soluble $Ni(DC)_2$ was 201 mg/L (14 mg/L Ni). This indicates that soluble $Ni(DC)_2$ has some effect on the PES membrane. However, in most cases the S/M ratio is adjusted to 2.5 or greater for maximising the formation of precipitate (i.e. metal removal) where the amounts of soluble $Ni(DC)_2$ are small and thus, CP of soluble $Ni(DC)_2$ plays a small or negligible role in UF through the PES membranes.

From Fig. 4.7, it is apparent that the PES membrane, because of the aromatic group, is more hydrophobic than the RC membrane. According to Cheryan (1998) the hydrophobicity of PES membranes can make them prone to fouling because of their tendency to interact strongly with a variety of solutes in comparison to the more hydrophilic RC membranes. PES membranes usually adsorb hydrophobic or amphoteric components and hence, the steroidal hydrophobic region of the deoxycholate is likely to interact strongly with a hydrophobic PES membrane. The chemical nature of the membrane thus affects solute-membrane interactions (i.e. fouling), which are related mainly to hydrophobicity and surface roughness. For aqueous feeds, hydrophilic membranes offer less adsorption effects and higher process fluxes (Cheryan 1998) because of their broader pore size distributions compared to hydrophobic membranes (Kim *et al.* 1994). Thus, the YM3 flux (expt. 20) was 90% of the pure water flux, while the PBCC5 flux was 50% of the pure water flux.

The membrane pore size is also important for effective removal of metal ions. A lower MWCO polyethersulphone membrane (PBCC5) was found to have more metal removal capacity than a higher MWCO polyethersulphone membrane (PM10 or PM30). It is evident from the permeate nickel concentrations of 3.4 mg/L, 4.2 mg/L and 6.0 mg/L from PBCC5, PM10 and PM30 membranes respectively with rejections of 94.2%, 92.9% and 89.8% respectively (expts. 8, 14 and 19). As expected, the larger pore size of the PM30 membrane allowed more $Ni(DC)_2$ to pass through with the permeate and contributed to the permeate nickel concentration. However, the process flux for the higher MWCO membrane was higher because of its larger pure water flux. For example, the initial permeate fluxes in PBCC5 and PM30 membranes were 131 $L/h/m^2$ and 200 $L/h/m^2$ respectively (expts. 14 and 19).

PBCC5 and PM30 membranes were used for a high feed metal concentration of 10 mM and the experiments were operated under identical conditions (expts. 21 and 23). The nickel rejection was over 99.9% in each case. The free residual NaDC concentration in the feed after reacting with nickel was high (5 mM) and it is postulated this lowered the solubility of $Ni(DC)_2$ to a great extent from the mass action consideration (p. 114).

The observation that a precipitate forms on mixing high concentration nickel feeds with NaDC suggests that microfiltration (MF) membranes can offer good separation/removal of metal ions. The results of two cross-flow MF experiments (shown in Table 4.3) indicate that the apparent Ni removal/rejection by MF (88.3% and 99.5% for low and high feed Ni respectively) was comparable to the Ni removal by filtration with No. 1 Whatman filter papers (expt. 34 and 35). For example, the MF permeate nickel of 1.6 mg/L from a 5 mM feed Ni was comparable to filtrate Ni of 1.9 mg/L from a 10 mM feed Ni. This means that MF operation is simply an ordinary filtration for any feed Ni and calls into question the contention of Huang *et al.* (1994) that micellar-enhanced actual UF was operative in the removal of metal ions from a solution using NaDC as the surfactant.

Table 4.3

Cross-flow MF of Ni/NaDC system

Expt. No	S/M	Feed Ni (mg/L)	Permeate Ni (mg/L)	Initial permeate flux as % of PWF	Rejection (%)
24	2.5	59	6.9	80	88.3
25	2.5	300	1.6	18	99.5

[Membrane area =0.031 m^2; pore size= 0.2 μm; equilibration time= 24 hours; pure water flux =1375 $L/h/m^2$; flow velocity = 1 m/sec; pressure = 100 kPa; recirculation rate = $3.73x10^{-4}$ m^3/sec]

Temperature and pH

The Ni/NaDC feed mixtures of all experiments discussed previously had a pH of 6.5-7.2 and the UF was operated at room temperature (14-22^{0}C). The temperature so far reported by previous researchers was 30^{0}C (Huang *et al.* 1994; Scamehorn *et al.* 1989; Scamehorn *et al.* 1994) or room temperature (Hong *et al.* 1998) for usual surfactant-based UF operations to successfully remove heavy metal ions from aqueous solutions.

The pH value at or below which DCA precipitates from a Ni/NaDC mixture was investigated. It was found that DCA started to precipitate at a pH of nearly 6 and precipitated entirely at a pH of 4 or less.

$$Ni^{2+} + 2(DC) \xrightarrow[pH \leq 4]{2H^{+}} Ni^{2+} + 2DCA$$

As a result of DCA formation through protonation, the metal ions are released in the solution. Therefore, operations with NaDC are inappropriate at low pH values. Ahmadi *et al.* (1995) reported that when the pH was lowered from 6 to 3, no significant binding between deoxycholate and metal ions (Cd, Cu, Ni, Pb and Zn) occurred due to a reduction in sorption behaviour. A number of researchers reported the strong effects of pH on the metal rejection using reagents other than the NaDC. Uludag *et al.* (1997) reported that there existed a pH value above which stable polymer-metal cation complexes formed, depending on the polymer and cation type. They maintained a pH of 5 for separating mercury (99% retention) from aqueous solutions by continuous polymer-enhanced UF using polyethyleneimine (PEI) as the complexing agent. Paulenova *et al.* (1996) also found that cadmium recovery using sodium dodecyl sulphate (SDS) as a surfactant, n-butanol as a co-surfactant and 8-hydroxyquinoline as an extractant increased with pH, and the recovery was quantitative (>95%) at a pH of 4 or greater. However, the effects of high pH have not yet been reported in the literature.

The experimental results presented in Table 4.4 refer to the effects of high temperature and high pH on the UF performance of Ni/NaDC mixtures.

Table 4.4

Temperature and pH effects on UF of Ni/NaDC system (1 mM Ni)

Expt. No	S/M	pH	Temp (^{0}C)	Equilibration time (h)	Permeate Ni (mg/L)	Initial permeate flux as % of PWF	Rejection (%)
26	5	7	20	3	0.28*	33	99.5
27	5	7	50	3	0.31*	105	99.5
28	5	7	50	24	1.3	74	97.8
29	5	10	50	3	0.082*	108	99.9
30	5	10	50	24	0.14*	97	99.8
31	5	10	20	3	0.061*	55	99.9
32	5	10	20	24	0.056*	57	99.9
33	2.5	10	20	3	0.063*	60	99.9

[PBCC5 membrane, *permeates concentrated 5-10 times prior to colorimetric measurement]

The results clearly indicate that at the pH of 7, a high operating temperature (50^{0}C) has no significant effects on the Ni rejection/removal for a short equilibration time (e.g., 3 hours), but the Ni rejection decreases when a prolonged stirring (e.g., 24 hours) is allowed before UF. This was evident from the constant nickel rejection of 99.5% at 20^{0}C and 50^{0}C after 3-hour equilibration (expts. 26 and 27), and a decrease in Ni rejection from 99.7% at 20^{0}C to 97.8% at 50^{0}C after 24-hour equilibration (expts. 17 and 28). However, the permeate nickel concentration significantly increased at the high temperature for 24-hour equilibration. The increase in permeate nickel concentration with increasing temperature might be due to a reduction in the solubility of nickel deoxycholate. The diffusivity of a solute increases with temperature (Cheryan 1998) and this may be another reason for the higher Ni concentration in the permeate at 50^{0}C.

At 50^{0}C (at pH 7), the pure water flux increased to 1.5-2 times and the permeate flux increased to 2-3 times the respective values at room temperature (20^{0}C). According to

Cheryan (1998) the flux becomes doubled by a temperature rise of 30-45^{0}C due to a reduction in fluid density and viscosity. It is supported by the viscosity and density of water at 20^{0}C and 50^{0}C, which are 1.002 cP and 0.5470 cP respectively, and 0.9982 g/cm^3 and 0.9880 g/cm^3 respectively (Lide 2002). The particulate nature of nickel deoxycholate also might change at the high temperature since it showed less membrane fouling. Thus, the increase in flux with temperature is mainly due to a reduction in fluid viscosity, and also due to a change in the particulate nature of nickel deoxycholate. It can be noted that there should not be any change of membrane properties at 50^{0}C because the PBCC5 membrane can withstand this temperature according to the manufacturer (Amicon Corporation).

The influence of temperature on the metal rejection by MEUF was also reported by Sadaoui *et al.* (1998). They found that the cadmium rejection by SDS was constant in the experimental temperature range of 20-40^{0}C, and chromium rejection by cetyltrimethylammonium bromide decreased slightly with increasing temperature in the experimental range of 30-45^{0}C. The flux increased by about 50% for cadmium and 30% for chromium with a tubular membrane (MWCO 15,000 daltons) composed of zirconium. According to these researchers, the influence of temperature on the metal rejection was linked to cmc variations of free surfactant ion concentrations with temperature. However, in the present study, the free NaDC concentration (i.e. 3 mM) was below the cmc and hence, the present results could not be explained by the postulate put forward by Sadaoui *et al.* (1998).

UF at a pH of 10 removed almost all the Ni ions from the solution for any equilibration time at room temperature and even at high temperature (50^{0}C). The Ni rejection was 99.9% almost in all cases (expts. 29-33). The turbid Ni/NaDC mixture at normal pH (~7) became almost clear when the pH was raised to 10 or greater by using NaOH. Nearly transparent small colloidal particles were found in the clear solution, which looked different from the usual nickel deoxycholate aggregates. UF of such a clear solution resulted in less membrane fouling because of less precipitate formation as evidenced by faster fluxes (33% and 55% of the pure water flux at pH 7 and 10 respectively, expts. 26 and 31).

The reasons for very low permeate Ni at pH 10 were investigated. Experiments were performed at pH 10 and 7 with 400 ml feed mixtures containing 1 mM Ni (expts. 33 and 11). The insoluble materials in both retentates were measured after filtering out the solids and air-drying. Calculations for DCA in the retentate solids were made on the assumption that the solids were nickel deoxycholate. The results show that a smaller amount of retentate solids (60 mg) was obtained at pH 10 compared to that at pH 7 (260 mg). Theoretically, the insoluble materials in the retentate would be 37 mg $Ni(OH)_2$ at pH 10, provided all the nickel in the solids was converted to hydroxide, and 303 mg $Ni(DC)_2$ at pH 7. The results indicate that at pH 10, all Ni did not precipitate as hydroxide. About 10% (40 mg) of the total feed DCA (393 mg) was recovered from the retentate solids at pH 10, which adds further supports to the above explanation. The amounts of DCA in the permeates were also measured by acidification and weighing of the precipitated DCA (permeate plus calculated amount in the liquid phase of retentate). At pH 10, about 53% (210 mg) of the total feed DCA was found in the total liquid phase compared to 17% at pH 7. The DCA results indicate that at pH 10, most of the Ni was not bound to deoxycholate. The possibility was the decomposition of $Ni(DC)_2$ to $Ni(OH)_2$ with concomitant formation of NaDC as the pH was raised from 7 to 10.

$$\underset{\text{(insoluble)}}{Ni(DC)_2} + 2\,Na^+ + 2OH^- \longrightarrow \underset{\text{(insoluble)}}{Ni(OH)_2} + 2NaDC$$

Hence, a high temperature has no noticeable effects in UF of Ni with NaDC (for shorter equilibration time), but a high pH has. At the high pH, the S/M ratio is not relevant for metal removal since the operation is essentially the precipitation and filtration of nickel hydroxide. The results at high pH would be similar to hydroxide precipitation of metals as discussed under "Chemical precipitation" in the Literature Review.

Precipitation of nickel by NaDC

Since a solid precipitate was formed virtually instantly when the nickel and NaDC solutions were mixed, it was of interest to determine the contribution of precipitation to the lowering of nickel level in the liquid phase. The slurries, after 24-hour equilibration time, were vacuum-filtered using No. 1 Whatman filter papers, or centrifuged when filtration proved difficult, and the filtrates or supernatants (or centrates) were analysed for nickel. The results are presented in Table 4.5. The results show that a good quality of filtrate was obtained from a S/M ratio of 5.0 (0.8 mg/L filtrate Ni) rather than 2.5 (6.7 mg/L filtrate Ni) when the Ni concentration in the feed was low (e.g., 1 mM).

Table 4.5

Residual nickel concentrations in liquid phase after precipitation

Expt No	S/M	Feed Ni (mg/L)	Filtrate Ni (mg/L)	% Ni removal	I (M)	Comment
34	2.5	59	6.7	88.6	2.5x10^{-3}	Fast filtration
35	2.5	600	1.9	99.7	25.6x10^{-3}	Fast filtration
36	2.5	1200	2.0	99.8	51.1x10^{-3}	Fast filtration
37	5.0	59	0.82	98.6	5.0x10^{-3}	Fast filtration
38	5.0	600	3.3	99.5	51.1x10^{-3}	Difficult & slow filtration
39	5.0	600	3.1	99.5	51.1x10^{-3}	Centrifugation necessary
40	5.0	1200	6.7	99.4	102.2x10^{-3}	Difficult & slow filtration
41	5.0	1200	7.1	99.4	102.2x10^{-3}	Centrifugation necessary
42	5.0	2400	14	99.4	204.4x10^{-3}	Filtration difficult, so centrifugation followed by filtration

[Equilibration time = 24 hours, I = feed ionic strength (in M) from eq 4.1]

The Ni removal was very good (99.7-99.8%) at the S/M of 2.5 with 10 and 20 mM feed Ni giving filtrate Ni concentrations of 1.9 and 2.0 mg/L respectively (expts. 35 and 36). When the S/M was increased to 5.0 in the above cases, the filtrate Ni concentrations increased to 3.3 and 6.7 mg/L respectively (expts. 38 and 40). The results thus clearly indicate that the filtrate quality at high feed Ni was better when a S/M ratio of 2.5 was used instead of 5. The filtration (i.e. vacuum-filtration) rate at high feed nickel was faster at the S/M of 2.5, indicating that the precipitate particle size might be larger than that at low Ni concentrations. However, at the S/M of 5.0 for high feed nickel, the filtration was very difficult because the rate of permeation was very slow, resulting in extremely low filtrate volumes or fines passed through the filter papers. These difficulties made centrifugation necessary to produce clear supernatant liquids.

The increasing ionic strength resulting from free residual NaDC and sodium chloride (NaCl) was thought responsible for the observed increase in Ni concentrations at the S/M of 5 (at high feed Ni). In such cases, the ionic strength of the liquid phase of feed mixture was predominant over the mass action effect. The ionic strength (I) of a solution is half of the sum of the products of the concentration of each ion multiplied by the square of its valency and is expressed by the equation (Vogel 1961):

$$I = 0.5\sum c_i z_i^2 \qquad (4.1)$$

where c_i is the ionic concentration in gram-molecules/L (i.e. M) and z_i is the valency of the ion concerned. The ionic strength of 1200 mg/L feed Ni with NaDC is 102×10^{-3}M and 51×10^{-3}M at the S/M ratios of 5.0 and 2.5 respectively, where the big difference between the two ionic strengths is due to the higher additional NaDC in the former case. When a 59 mg/L feed Ni is used, the difference between the ionic strengths at the S/M ratios of 2.5 and 5 is low since the difference in the amount of NaDC is small (Table 4.6).

The UF and filtration results suggest that the S/M ratios of 5.0 and 2.5 should be used for low (e.g., 1 mM) and high (e.g., 10 mM) feed nickel concentrations respectively irrespective of filtration or so called MEUF. The results also indicate that the precipitation of nickel by NaDC can remove a major proportion of Ni ions (greater than 98.5%) from the solution and the precipitate can be removed from the liquid phase by the classical filtration techniques in most cases. In those instances where filtration proved difficult, optimisation of parameters to attain maximum particle size may obviate the problem.

Experiments 43-44 (Table 4.6) were carried out to study the effects of UF on the filtrate resulting from the precipitation of nickel by NaDC where PES membranes (PBCC5 and PM10) were used. Permeate nickel concentrations of 4.4 mg/L and 4.7 mg/L were obtained for the PBCC5 and PM10 membranes respectively. The results show that UF of filtrates removed a part (about 35%) of Ni ions remaining in the filtrates. The permeate Ni concentrations of 4.4 mg/L and 4.7 mg/L for the PBCC5 and PM10 membranes respectively indicate that more insoluble $Ni(DC)_2$ were formed from soluble $Ni(DC)_2$ in the filtrates over the course of UF runs. This was supported by the visual observation of turbidity development in the retentate towards the end of a run. The permeate Ni concentrations of 4.4 mg/L and 4.7 mg/L correspond to 63 mg/L and 67 mg/L of soluble $Ni(DC)_2$, which would be approximately equal to the solubility of $Ni(DC)_2$ in the presence of 0.5 mM NaDC and 2 mM NaCl. The solubility of $Ni(DC)_2$ in 0.5 mM NaDC and 2 mM NaCl solution was experimentally determined as 61 mg/L, which also supports the above explanation.

It was observed that compared to UF alone, the total time required for UF of filtrates was significantly shorter (nearly a half for the PBCC5 membrane). The results of experiments 43-44 also indicate that the total Ni removal by a combination of filtration and UF of filtrates was 1.5-1.7% lower than the UF alone from an identical initial feed mixture. This was because of the higher run time of the UF alone, which allowed the formation of more insoluble $Ni(DC)_2$ compared to UF of filtrates.

Table 4.6

UF of filtrates of Ni/NaDC mixtures (1 mM Ni)

Expt. No	Mem-brane	Filtrate Ni (mg/L)	Added DCA (mM)	Perme-ate Ni (mg/L)	Permeate flux (L/h/m^2)	Removal by filtration (%)	Total removal (%)
43	PBCC 5	6.8	0	4.4	48	88.5	92.5
44	PM 10	6.7	0	4.7	53	88.6	92.0
45	YM 3	6.8	0	6.1	91	88.5	89.7
46	PBCC 5	6.9	1	1.8	29	88.3	96.7
47	PBCC 5	6.2	3	1.1	19	89.5	98.1
48	PBCC 5	6.3	5	0.21*	31	89.3	99.6
49	PM 10	6.7	5	0.82	30	88.6	98.6
50	YM 3	6.6	5	3.3	94	88.8	94.4
51	PBCC 5	6.5	5	0.044*	47	89.0	99.9

[Initial S/M=2.5 and initial feed Ni=59 mg/L, filtration after 24-hour equilibration time, UF immediately after DCA addition except expt. 51, *permeates concentrated 10 times prior to colorimetric measurement]

The permeate fluxes in the aforementioned experiments (expts. 43-44) were about 50% of the pure water flux and those were almost unchanged until at the end of the runs. Concentration polarisation due to 0.5 mM NaDC and fouling by smaller amounts of $Ni(DC)_2$ might cause the observed decline in flux at the start of UF of filtrates, but in the absence of a significant fouling layer, a further reduction in flux with elapsed time was absent. The similar initial permeate fluxes (about 50% of pure water flux) from UF of filtrates immediately after filtration and UF alone (24-hour equilibration for the initial feed in both cases) indicate that the effects of free residual NaDC are similar whether the insoluble $Ni(DC)_2$ are filtered out or not.

Experiment 45 is the UF of filtrate using a YM3 membrane giving a permeate nickel concentration of 6.1 mg/L. The result shows that UF of filtrate by the YM3 membrane removed only a small part (10%) of Ni ions remaining in the filtrate compared to 35% by the PES membranes. This means that a smaller amount of insoluble $Ni(DC)_2$ was rejected in the YM3 case compared to the PBCC5 and PM10 cases. This confirms the previous results that the PES membrane has higher metal removal capacity than the RC membrane. As previously reported in the section ***Membrane material/MWCO***, there was little or no concentration polarisation at the YM3 membrane surface since the permeate flux was only 10% lower than the pure water flux.

The vacuum-filtration with No. 1 Whatman filter paper produced a better effluent quality (6.8 mg/L Ni) than by the UF with YM3 (17 mg/L Ni, expt. 20). Pressure facilitated solute transport of $Ni(DC)_2$ can possibly explain this result. Surfactant-based UF has a pool of insoluble $Ni(DC)_2$. During UF, the insoluble nickel deoxycholate aggregates are transported to the membrane surface. Though the effect of pressure on the solubility of a solid is small (Maron and Prutton 1965), the high pressure at the YM3 membrane surface may exceed the limit for the solubility of nickel deoxycholate at 1 bar. In such a situation, some nickel deoxycholate precipitate may be re-dissolved and transported with the permeate giving the observed high permeate Ni. The soluble $Ni(DC)_2$ in the permeate would be converted into insoluble $Ni(DC)_2$ precipitate, but the process would be slow as was discussed previously. Moreover, the analysis of the permeate was done a short period after the UF and this length of time was not sufficient for the formation of a significant amount of insoluble precipitate. As a result, the Ni concentration in the permeate was measured high in such a YM3 case.

The NaDC concentration in the filtrate can be raised to or over its cmc by adding extra amounts of NaDC to it. This process can be called 'augmentation'. Experiments 46-50 (Table 4.6) represent the augmented UF results, which clearly indicate that augmentation increases the Ni removal (i.e. decreases the Ni concentration in the permeate). Augmentation also decreases the flux of the PES membrane. The increasing free NaDC, which would lead to increased concentration polarisation, was responsible for the flux decline and this was evident from Fig 4.3. The increase in free NaDC also reduced the solubility of $Ni(DC)_2$ due to increased deoxycholate ions (i.e. the common ion effect) as discussed previously and thereby, the permeate Ni decreased. This effect thus operates in concert with the effect of increased CP. For example, the permeate quality was excellent with 0.2 mg/L Ni when 5 mM NaDC was added for augmentation in the PBCC5 experiment (expt. 48). PM10 and YM3 membranes also showed improved Ni removals over that of the usual UF runs when the filtrates were augmented by 5 mM NaDC (expts. 49 and 50), although in the latter case the common ion effect alone was operative.

In the cases above the augmented solutions, which appeared to be homogeneous, were not stirred for any equilibration time before UF (i.e. UF was started immediately after augmentation). Experiment 51 gives the augmented UF result where the augmented solution was stirred for 24 hours before UF was commenced. It was observed that the initially clear augmented solution became slightly turbid nearly 30 minutes after augmentation and changed to an opaque white about after 3 hours, indicating formation of $Ni(DC)_2$ precipitate. A permeate Ni concentration of 0.044 mg/L obtained from this experiment indicates that almost all the soluble $Ni(DC)_2$ was converted into insoluble $Ni(DC)_2$. The result suggests that after augmentation of a solution with NaDC, it should be stirred for an equilibration time to obtain the best permeate quality, because of the slow rate of formation of insoluble $Ni(DC)_2$ precipitate, a major part of which is completed about after 3 hours.

4.3.1.2 Copper: Effect of variables on UF of Cu/NaDC system

UF experiments were carried out with copper under various operating conditions. The important variables investigated were S/M ratio, equilibration time, feed metal concentration, membrane MWCO, temperature and pH. The results are given in Table 4.7.

Table 4.7

UF of Cu/NaDC system

Expt. No	Mem-brane	Equilibration time (h)	Feed Cu (mg/L)	Permeate Cu (mg/L)	Initial permeate flux as % of PWF	Rejection (%)
1	PBCC5	3	63.5	0.21	15	99.7[a]
2	PBCC5	24	63.5	0.25	21	99.6[a]
3	PBCC5	24	635	0.044*	7	>99.9[b]
4	PM30	24	635	0.046*	8	>99.9[b]

[*permeates concentrated 10 times prior to AA measurement

a: VCF = 4

b: VCF = 1.33 because the experiments could not be continued untill 300 ml of permeate]

S/M ratio

Huang *et al.* (1994) reported that a S/M ratio of around 2.5 would be optimal for Cu removal by NaDC (over 99.9%). The present experimental results (Table 4.7) also indicate that a S/M ratio of 2.5 would give a very good Cu removal (around 99.7%) at both low and high feed Cu concentrations. It should be noted that the S/M of 2.5 was not sufficient for low feed Ni with NaDC. This can be explained by the low solubility of $Cu(DC)_2$ in water compared to that of $Ni(DC)_2$ (Table 4.18). The S/M ratio for all the reported experiments with Cu/NaDC mixtures was kept at 2.5 unless otherwise stated.

Equilibration time

The mixtures of copper and NaDC solutions were heterogeneous similar to Ni/NaDC mixtures and a gelatinous precipitate was quickly formed. Based on the equilibration time of 3 hours or greater necessary for the Ni/NaDC system, it is assumed that the Cu/NaDC system will require a similar equilibration time. Two UF experiments were carried out with 1 mM feed Cu having 3-hour and 24-hour equilibration times respectively before the ultrafiltration was commenced. Experiments 1-2 (Table 4.7) represent these results for a PBCC5 membrane. The results confirm that a 3-hour equilibration time was sufficient for the Cu/NaDC system and that allowing more than 3-hour equilibration had no significant improvement in Cu removal. In these experiments, the initially deep blue precipitate formed by mixing NaDC with copper did not show a change in colour until after 24 hours.

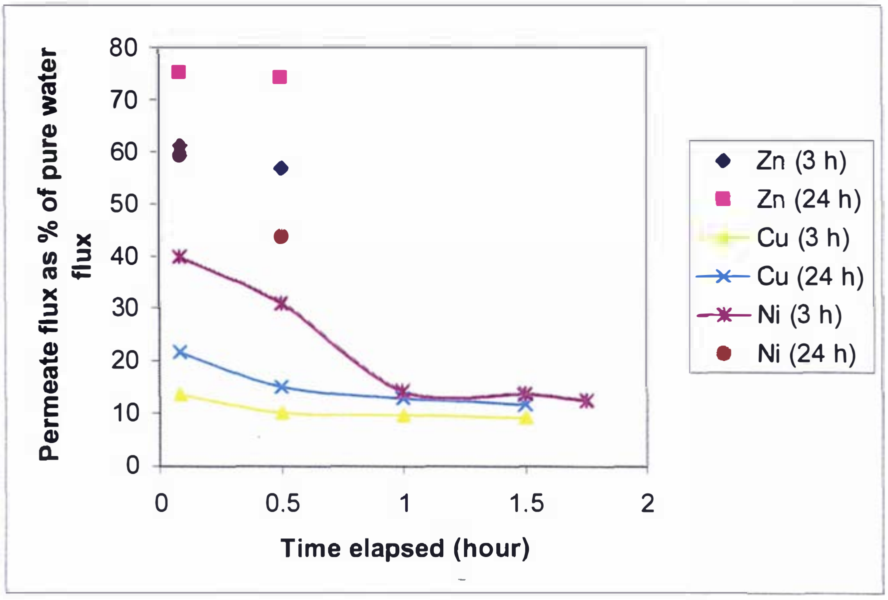


Fig. 4.8 Change in permeate flux with elapsed time in the Ni, Cu and Zn systems with NaDC (PBCC5 membrane)

The permeate fluxes were 15-20% of the pure water flux at the start of UF and continuously decreased with elapsed time until the end of the runs (expts. 1 and 2). In these experiments, the final fluxes were 60% of the initial fluxes and the total UF times was nearly 2 hours. For example, the experiment with 24-hour equilibration time had initial and final fluxes of 70 L/h/m^2 and 39 L/h/m^2 respectively, and the total UF time was 1.8 hours. Compared to the Ni/NaDC system, the mode of decline in permeate flux with elapsed time was similar, but the flux values were considerably lower (by about 1.5 times) in the Cu/NaDC system (Fig. 4.8). Though there was concentration polarisation due to 0.5 mM free residual NaDC along with membrane resistance, the observable difference in flux values between the two systems (i.e. Cu and Ni with NaDC) was the nature of the fouling layer. In the copper case, a thick and gelatinous layer of precipitate was found on the membrane surface at the end of the run, but in the nickel case, a relatively thin and non-gelatinous layer was observed under similar conditions. The gelatinous layer in the Cu/NaDC system caused a serious membrane fouling and resulted in extremely low permeate fluxes.

Feed metal concentration

Experiments 2-3 (Table 4.7) refer to the effects of feed Cu concentrations on the removal of Cu ions. Feed mixtures containing 1 mM and 10 mM Cu produced permeate Cu concentrations of 0.25 mg/L and 0.044 mg/L respectively, which corresponded to Cu removals of 99.6% and 99.9% respectively. The difference between two permeate copper concentrations was insignificant in terms of the effluent quality. It can be added that the permeate nickel concentrations were 3.4 mg/L and 0.053 mg/L from 1 mM and 10 mM feed Ni respectively at the S/M of 2.5 (Tables 4.2 and 4.3), where the difference between two permeate Ni concentrations was significant. Thus, the feed Cu concentration has no major effects in Cu removal by NaDC and a similar trend was observed in the case of zinc. The effects of feed concentrations on the effluent quality for different metal/NaDC systems are also shown in Table 4.8.

Table 4.8

Change of permeate metal concentration with feed metal concentration

Feed metal (mM)	Ni in permeate from Ni/NaDC system (mg/L)	Cu in permeate from Cu/NaDC system (mg/L)	Zn in permeate from Zn/NaDC system (mg/L)
1	3.4	0.25	0.26
10	0.053	0.044	0.13

According to Huang *et al.* (1994) Cu is removed by forming only copper deoxycholate complexes at the surfactant concentration below the cmc, but forming both copper deoxycholate complexes and micelles above the cmc. The distinction is not significant in the present cases of Cu with NaDC as seen from the comparable permeate results from two different feed Cu concentrations. This can rather be explained from the viewpoint of the solubility of copper deoxycholate. The 24-hour solubility of $Cu(DC)_2$ in water is 5.6 mg/L (Table 4.17), which corresponds to 0.42 mg/L of Cu. The solubility is expected to be lower in the presence of 0.5 mM NaDC and 2 mM NaCl as was found in the case of Ni. The permeate Cu concentration of 0.25 mg/L from 1 mM feed Cu with 2.5 mM of NaDC supports this expectation. The permeate Cu from a high feed Cu would decrease further because of increasing NaDC concentrations due to the common ion effect. Thus, a 10 mM feed Cu produced a very low permeate Cu (i.e. 0.044 mg/L).

The UF operation of a Cu/NaDC feed mixture containing a high Cu concentration was difficult. When a high concentration Cu solution was mixed with a high concentration NaDC solution, the mixture appeared to be highly viscous as a result of the precipitate formation. UF of such a slurry produced a small permeate volume before fouling reduced the flux almost to zero. For example, a 200 ml of feed mixture containing 10 mM Cu produced only 50 ml of permeate before the flux dropped to a very low value (expts. 3-4, Table 4.7). The initial permeate fluxes in these experiments were much lower (7-8% of the pure water flux) than that of 1 mM feed Cu (21% of the pure water flux). Thus, the VCF was much lower (i.e. 200/150 or 1.33) in these high copprer cases than in 1 mM copper case (i.e. VCF was 4). The increased solids content of the feed and concentration polarisation due to free NaDC were the likely reasons for the extremely low initial permeate flux in the high feed Cu case. The formation of a thick and sticky fouling layer of precipitate on the membrane surface further decreased the flux with elapsed time. The membrane could not be cleaned by the usual cleaning method and was thrown out. Whether such severe fouling would occur in a cross-flow UF operation needs to be tested, since in the cross-flow runs the solids are carried away from the membrane by the shear forces generated by the flow velocity.

Membrane MWCO

Experiments 3-4 (Table 4.7) were performed using two polyethersulphone membranes PBCC5 and PM30 at the same feed metal concentration (i.e. 10 mM) under identical operating conditions. The permeate Cu concentrations and Cu rejections in both cases were the same, because in effect the operation was dominated by the water solubility of $Cu(DC)_2$ and the membranes were functioning as classical filters. The permeate fluxes in these cases were also the same with very low values due to the reasons discussed previously. Therefore, the MWCO of the membrane is not important in such conditions of high feed Cu concentrations.

Temperature and pH

The Cu/NaDC feed mixtures of all previous experiments had a pH of nearly 7 and UF was operated at room temperature (14-22^{0}C). Similar to Ni, DCA was found fully precipitated at a pH of 4 or less. and so operations with NaDC are inappropriate at low pH values.

The experimental results presented in Table 4.9 refer to the effects of high temperature and high pH on the UF performance of Cu/NaDC systems.

Experimental results indicate that at pH 7, a high operating temperature (50^{0}C) had no significant effects on the Cu removal for any equilibration time.

The temperature of 50^{0}C (at pH 7) had major effects on the permeate flux. The permeate fluxes increased to 4-6 times the respective values at room temperature. At the end of UF runs, no gelatinous layer was found onto the membrane surface, and the copper deoxycholate precipitate was mostly in suspension. There were some deposits compacted onto the membrane surface, which indicated some fouling, but the fouling was relatively small compared to that at room temperature. The viscosity and density of water are reduced by 50% and 1% respectively when the temperature increases from 20^{0}C to 50^{0}C.

Hence, at high temperature, this flux increase is not mainly due to a reduction in fluid viscosity and density. The main reason is, probably, that the gelatinous nature of copper deoxycholate at room temperature was changed into particulate nature at 50^{0}C resulting in less fouling. Thus, the increase in flux at 50^{0}C was due mainly to a change in the particulate nature of copper deoxycholate and also due to a reduction in fluid viscosity.

Table 4.9

Temperature and pH effects on UF of Cu/NaDC system (1 mM Cu)

Expt No	pH	Temperature (^{0}C)	Equilibration time (h)	Permeate Cu (mg/L)	Initial permeate flux as % of PWF	Rejection (%)
5	7	50	3	0.18	85	99.7
6	7	50	24	0.35	75	99.5
7	10	50	3	0.059*	108	99.9+
8	10	50	24	0.47	136	99.3
9	10	20	3	0.021*	62	99.9+
10	10	20	24	0.36	73	99.4

[PBCC5 membrane, *permeates concentrated 10 times prior to AA measurement]

UF at a pH of 10 (at room temperature) removed 99.9% of Cu for shorter equilibration time (e.g., 3 hours), but the Cu removal decreased to 99.4%, i.e. the permeate Cu concentration slightly increased when a long equilibration (24 hours) was applied. This might be due to the fact that some $Cu(OH)_2$ precipitate was re-dissolved at prolonged stirring giving the observed higher permeate Cu concentration. At high pH, Cu is removed mainly by the precipitation of $Cu(OH)_2$, which is discussed later. A high pH can also affect the state of hydration and the conformation and shape of the solute molecules, which can affect the diffusivity and the rejection of solutes according to Cheryan (1998).

At any temperature, the mixtures of copper and NaDC solutions appeared to be deep blue at a pH of 7 and UF of such a mixture showed the formation of a visible fouling layer of the same colour on the membrane. When the pH was raised to 10 by using NaOH, the slurries became clear with a light blue colour and appeared to be homogeneous. After 3-hour equilibration, the clear solutions became light grey with small particles, whose appearance differed from the usual $Cu(DC)_2$ solids. Such a solution turned to dark grey after 24-hour equilibration with relatively larger particles (sand-like) of the same colour. The grey particles deposited on the membrane during UF, but did not form any layer and hence, no membrane fouling was observed. This was evidenced by the high permeate flux (over 70% of the pure water flux) and shorter UF time. It was also observed that at the pH of 10, the clear solution with a light blue colour became dark grey quickly (within 2 minutes) when the temperature was raised from 20^0C to 50^0C.

At pH 10, retentate solids of 60 mg were obtained compared to 260 mg at pH 7. The theoretical amounts of insoluble materials in the retentate solids are 37 mg $Cu(OH)_2$ at pH 10 if all Cu in the solids are considered as hydroxide, and 338 mg $Cu(DC)_2$ at pH 7. This means that all Cu did not precipitate as hydroxide at pH 10. The presence of about 8% (30 mg) of the total feed DCA (393 mg) in the retentate solids at pH 10 also supports this explanation. The acidification of permeates for recovering DCA shows that about 66% (260 mg) of the total feed DCA remained in the total liquid phase compared to 17% at pH 7. This means that at pH 10, most of the Cu was bound to species other than the deoxycholate. Similar to Ni, the possibility was the decomposition of $Cu(DC)_2$ to $Cu(OH)_2$ with concomitant formation of NaDC as the pH was raised from 7 to 10.

$$\underset{\text{(insoluble)}}{Cu(DC)_2} + 2\,Na^+ + 2OH^- \longrightarrow \underset{\text{(insoluble)}}{Cu(OH)_2} + 2NaDC$$

Thus, for a short equilibration time, a high temperature has no effects on the copper removal, but a high pH slightly improves the Cu removal. The copper removal slightly decreases at a high temperature or high pH when the equilibration time is long. There is no membrane fouling if a high pH exists with a high temperature that results in a high permeate flux. In such a situation, the operation is essentially the precipitation and filtration of copper hydroxide.

Precipitation of copper by NaDC

A solid precipitate was formed instantly when the copper solution was mixed with the NaDC solution. To determine the contribution of precipitation in removing copper ions from the liquid phase, the slurries were vacuum-filtered using No. 1 Whatman filter papers after 24-hour equilibration time. The results are presented in Table 4.11 (expts. 11-12). The rate of filtration was fast for feed mixtures containing low Cu though a thin layer of precipitate was observed over the filter paper. In the case of high feed Cu, a thick gelatinous layer of precipitate was formed over the filter paper within a few minutes that made the rate of filtration extremely slow and difficult, resulting in low filtrate volumes. The analysis of filtrates showed that the Cu removal by filtration (99.5% and 99.8% for low and high feed Cu respectively) was very similar to that by UF. In other words, UF is not, theoretically, necessary for removing Cu from aqueous streams using NaDC.

The extremely slow filtration rate for mixtures of high copper with NaDC made necessary the centrifugation, but a clear supernatant liquid (centrate) was not obtained. The centrates were blue and lightly turbid, which indicated the presence of significant amounts of Cu. The centrates were then ultrafiltered by a PBCC5 membrane (expts. 13-14). The Cu removal was as high as that from the UF alone. UF of centrates also produced low permeate fluxes (about 10% of the pure water flux) similar to that found in the UF alone (expt.3). The reasons for low permeate fluxes were the significant concentration polarisation caused by free NaDC and the membrane fouling caused by the gelatinous $Cu(DC)_2$ precipitate compacting onto the membrane surface. This also indicates that the insoluble $Cu(DC)_2$ was mostly in colloidal suspension and not precipitated by centrifugation.

Table 4.10

Residual copper concentrations in liquid phase after precipitation

Expt No	Eq. time (h)	Feed Cu (mg/L)	Filtrate Cu (mg/L)	% Cu removal	Comment
11	24	63.5	0.31	99.5	Fast filtration
12	24	635	1.2	99.8	Difficult & slow filtration
13	24	635	n/a	-	Centrifugation/UF -- 0.047* mg/L
14	24	1270	n/a	-	Centrifugation/UF -- 0.17* mg/L

[S/M=2.5, PBCC5 membrane, 24-hour equilibration before filtration or centrifugation, *permeates concentrated 10 times prior to AA measurement]

The filtration results clearly indicate that the precipitation of insoluble $Cu(DC)_2$ is the principal mechanism of Cu removal from the solution. However, the formation of a gelatinous layer severely reduces the rate of permeation of fluid through the filter paper as well as the membrane, particularly when the feed concentration is high. This makes both the filtration and UF difficult. In this situation, optimisation of parameters particularly temperature would reduce the formation of the gel layer and obviate the problem.

4.3.1.3 Zinc: Effect of variables on UF of Zn/NaDC system

Experiments were carried out with zinc under various conditions. The important variables investigated were S/M ratio, equilibration time, feed metal concentration, membrane type/MWCO, temperature and pH. The results are given in Table 4.11.

Table 4.11

UF of Zn/NaDC system

Expt. No	Memb-rane	Equilibration time (h)	Feed Zn (mg/L)	Permeate Zn (mg/L)	Initial permeate as % of PWF	Rejec-tion (%)
1	PBCC5	3	65	0.20	59	99.7
2	PBCC5	24	65	0.26	75	99.6
3	PBCC5	24	650	0.13	31	99.9+
4	PM30	24	650	0.15	51	99.9+
5	XM100	24	650	0.23	53	99.9+

S/M ratio

According to the work of Huang *et al.* (1994), a S/M ratio of around 2.5 is optimal for Zn removal by NaDC (over 99.9%). The present experimental results (Table 4.11) also showed that a S/M ratio of 2.5 was sufficient for a Zn removal of 99.6% or greater. Hence, the S/M ratio for the zinc system with NaDC was kept at 2.5 unless otherwise stated.

Equilibration time

Similar to Ni and Cu systems with NaDC, the Zn/NaDC system was heterogeneous with the formation of precipitate. UF experiments were carried out with Zn/NaDC mixtures (1 mM Zn) having 3-hour and 24-hour equilibration times respectively, using a PBCC5 membrane (expts. 1-2 in Table 4.11). The results confirm that a 3-hour equilibration time was sufficient for Zn/NaDC mixtures and, allowing more time for equilibration, had no improvement in the Zn rejection. In these experiments, the feed mixtures appeared to be clear (i.e. homogeneous) after mixing, but changed to light white in about 15 minutes and to total white after over 1 hour.

The initial permeate fluxes of Zn/NaDC mixtures were 60-75% of the pure water flux and the final fluxes were 96-99% of the initial fluxes (expts. 1-2). The total UF time was about 30 minutes in each case. Hence, there was no significant decline in flux with elapsed time indicating little or no contribution of fouling. Compared to Ni and Cu systems with NaDC, the decline in flux with elapsed time and the total UF time were considerably low in the Zn/NaDC system (Fig. 4.8). Since the permeate flux of 0.5 mM NaDC solution was about 77% of the pure water flux (Fig. 4.3), the low value of the initial permeate flux compared to the pure water flux in the present Zn/NaDC experiments would result from concentration polarisation of 0.5 mM free residual NaDC and the membrane resistance. At the end of the run, lots of small particles were found in the retentate, but those were not compacted onto the membrane surface, which supports little or no membrane fouling.

Feed metal concentration

The effects of feed Zn concentrations on the Zn removal can be explained from the results of experiments 2 and 3. Feed mixtures containing 1 mM and 10 mM Zn resulted in permeate Zn concentrations of 0.26 mg/L and 0.13 mg/L respectively, which corresponded to Zn removals of 99.6% and 99.9% respectively. The difference between two permeate Zn concentrations was negligible in terms of the effluent quality. The effects of feed concentrations on the effluent quality are also shown in Table 4.8.

The 24-hour solubility of $Zn(DC)_2$ in water was determined to be 6.0 mg/L, which corresponded to 0.46 mg/L of Zn. Similar to $Cu(DC)_2$, the solubility of $Zn(DC)_2$ in the presence of 0.5 mM NaDC and 2 mM NaCl would be lower, and the solubility would further decrease with increasing NaDC concentrations due to the common ion effect. The similar low permeate Zn concentrations from two different feed concentrations support this explanation. Thus, the effect of feed Zn concentrations was not significant in the case of Zn with NaDC as was seen in the copper case.

The UF operation of Zn/NaDC mixtures was not difficult from the flux consideration, even at the high feed concentration that was in contrast to the high feed Cu situation. The initial and final permeate fluxes at 10 mM feed Zn were 31% and 13% of the pure water flux respectively (expt. 3). The increased solids content of the feed and concentration polarisation due to free residual NaDC were the likely reasons for the low initial permeate fluxes. The further reduction in flux with elapsed time was due to the formation of a fouling layer of precipitate on the membrane surface. The membrane fouling in the high feed Zn case was less severe than Cu and even Ni, and the Zn rejection was as high as the Cu rejection.

Membrane MWCO

UF experiments were carried out with PBCC5, PM30 and XM100 membranes for Zn/NaDC mixtures containing 10 mM Zn under identical conditions (expts. 3-5). The Zn removals in all cases were almost the same (over 99.9%). The results indicate that at high feed zinc concentrations, precipitation/insolubilisation was the only mechanism involved in zinc removal and the UF membrane had no major role in rejecting Zn, but only acted as a classical filter.

Temperature and pH

The Zn/NaDC feed mixtures of all previous experiments had a pH of 6.5-7.5 and UF was operated at room temperature (14-22^{0}C). DCA was fully precipitated at a pH of 4 or less releasing the metal ions in the solution. Hence, operations of Zn with NaDC are inappropriate at low pH values. The experimental results presented in Table 4.12 refer to the effects of high temperature and high pH on the UF performance of Zn/NaDC mixtures.

Table 4.12

Temperature and pH effects on UF of Zn/NaDC system (1 mM Zn)

Expt No	pH	Temp (^{0}C)	Equilibration time (h)	Permeate Zn (mg/L)	Initial permeate flux as % of PWF	Rejection (%)
6	7	50	3	0.35	123	99.5
7	7	50	24	0.30	146	99.5
8	10	50	3	0.55	104	99.2
9	10	50	24	0.42	125	99.4
10	10	20	3	0.48	69	99.3
11	10	20	24	0.20	70	99.7

[PBCC 5 membrane]

Experimental results indicate that at pH 7, a high operating temperature (50^{0}C) had no significant effects on the Zn removal for any equilibration time.

At 50^{0}C, the permeate fluxes increased to around 2 times the respective fluxes at room temperature. It might be due mainly to a reduction in the viscosity of the feed solution since the viscosity of water is reduced by 50% when the temperature increases from 20^{0}C to 50^{0}C.

Though the permeate Zn concentration at a pH of 10 slightly increased for shorter equilibration time and decreased for prolonged equilibration time, the changes were negligible in terms of the metal removal. This indicates that a high pH has no significant effects on the Zn rejection, which is similar to the high temperature case.

At any temperature, the mixtures of zinc and NaDC solutions at a pH of nearly 7 appeared to be white after 3-hour or 24-hour equilibration and before UF. At the end of UF of such a white mixture, a large quantity of particles were found in the turbid retentate, which were not compacted onto the membrane surface as discussed previously. When the pH was raised to 10 by using NaOH, the mixtures became clear with the presence of nearly transparent small colloidal particles, which appeared to be different from the usual $Zn(DC)_2$ solids. UF of such a clear mixture did not show any deposition on the membrane and any membrane fouling since the permeate fluxes (70% of the pure water flux) and the total UF time were similar to those found at normal conditions.

The insoluble materials in the retentates at pH 10 and 7 were 70 mg and 330 mg respectively. Theoretically, the insoluble materials in the retentate solids are 39 mg $Zn(OH)_2$ at pH 10, provided all the Zn in the solids is converted to hydroxide, and 338 mg $Zn(DC)_2$ at pH 7. The results thus indicate that at pH 10, all Zn did not precipitate as hydroxide since about 8% (33 mg) of total feed DCA (393 mg) was recovered from the retentate solids. In addition, about 57% (227 mg) of the total feed DCA was found in the total liquid phase at pH 10 compared to 18% at pH 7. The results indicate that at pH 10, most of the zinc deoxycholate was converted to zinc hydroxide. As in the cases of Ni and Cu, the possibility was the decomposition of $Zn(DC)_2$ to $Zn(OH)_2$ with concomitant formation of NaDC as the pH was raised from 7 to 10.

$$\underset{\text{(insoluble)}}{Zn(DC)_2} + 2\,Na^+ + 2OH^- \longrightarrow \underset{\text{(insoluble)}}{Zn(OH)_2} + 2NaDC$$

Thus, at pH 10, the UF operation of the Zn/NaDC mixture is simply the precipitation and filtration of zinc hydroxide.

Precipitation of Zn by NaDC

The mixtures of zinc and NaDC solutions were vacuum-filtered using No. 1 Whatman filter papers after 24-hour equilibration time. The results (expts. 12-14 in Table 4.13) show that the rate of filtration was fast for a feed mixture containing low Zn, and resulted in a high Zn removal (99.7%), which was very similar to the UF results. Filtration was very difficult at high feed Zn concentrations because a significant quantity of precipitate passed through the filter paper. The analysis of a clear filtrate, which was obtained after filtering the dense feed several times on the same filter paper, indicated that the Zn removal was over 99.5%.

Table 4.13

Residual zinc concentrations in liquid phase after precipitation

Expt. No	Feed Zn (mg/L)	Filtrate Zn (mg/L)	Zn removal (%)	Comment
12	65	0.20	99.7	Fast filtration
13	650	0.45	99.9+	Fines in filtrate
14	1300	0.74	99.9+	Fines in filtrate
15	65	0.25	99.6	Centrifugation
16	650	0.82	99.9	Centrifugation
17	1300	0.56	99.9+	Centrifugation

[S/M=2.5, PBCC5 membrane]

The difficulty in filtration of Zn/NaDC mixtures containing high zinc concentrations made necessary the centrifugation that produced a clear supernatant and very good zinc removal as shown in Table 4.13. The filtration and centrifugation results thus indicated that precipitation of zinc as zinc deoxycholate was the main mechanism for zinc removal.

Comparing the filtrate zinc concentration with the permeate zinc concentration in Table 4.11, both UF and filtration were equally effective in separating the precipitate from the liquid phase for feeds having low zinc. Since fines consistently pass through the No. 1 Whatman filter paper at high feed zinc concentrations, this suggests that, if adopted as a practical operation, a membrane operation of some sort, probably microfiltration will be necessary.

The centrifuged supernatants from Zn/NaDC mixtures containing different Zn concentrations were ultrafiltered by a PBCC5 membrane. The results (shown in Table 4.14) indicate that the Zn rejections by UF of supernatants were similar to that from the

UF alone. A small proportion of Zn remaining in the supernatants was in suspension as fine $Zn(DC)_2$ particles and was removed by ultrafiltration. Hence, it can be concluded that the precipitation of $Zn(DC)_2$ can remove a major proportion of Zn (greater than 99.5%) from the solution. The precipitate can be separated or removed from solution by both classical filtration and centrifugation for low feed Zn, but only by centrifugation for high feed Zn.

Table 4.14

UF of supernatants from Zn/NaDC mixtures

Expt. No	Initial Zn (mg/L)	Supernatant Zn (mg/L)	Permeate Zn (mg/L)	Initial permeate flux as % of PWF	Total Zn removal (%)
18	65	0.25	0.13	74	99.8
19	650	0.82	0.13	69	99.9+
20	1300	0.56	0.11	43	99.9+

[Initial S/M=2.5 after 24-hour equilibration]

4.3.2.4 Conclusion

Ultrafiltration experiments, using sodium deoxycholate as the surfactant, have been carried out to remove nickel, copper and zinc ions from a single metal component aqueous solution. As far as the permeate flux is concerned, the hydrophobic polyethersulphone membranes (e.g., PBCC5, PM10 and PM30) are more vulnerable to flux decline than the hydrophilic regenerated cellulose membranes (e.g., YM3) due mainly to concentration polarisation of free deoxycholate ions and membrane fouling by metal deoxycholates. The initial permeate fluxes in the copper/NaDC, nickel/NaDC and zinc/NaDC systems are 20%, 50% and 75% of the pure water flux respectively (for 1 mM metal at the S/M of 2.5 using the PBCC5 membrane and after 24-hour equilibration). The final fluxes of these systems are 12%, 25% and 70% of the pure water flux respectively.

The degrees of membrane fouling by three different metal deoxycholates are not the same as evidenced by the flux decline caused by them. The membrane fouling by copper deoxycholate is much more severe than by nickel deoxycholate at any feed concentration, whereas zinc deoxycholate shows significant membrane fouling only at high feed concentrations, which is significantly less than that by copper and nickel deoxycholates.

Polyethersulphone membranes are much more effective than regenerated cellulose membranes for removing metal ions by NaDC and their pore sizes (i.e. MWCO) are not important when dealing with high feed metal concentrations. The metal removal efficiency of polyethersulphone membranes can be improved by controlling such factors as equilibration time, S/M ratio, feed concentration and pH.

The experimental evidence clearly indicates that when NaDC is used as the surfactant, precipitation of insoluble metal deoxycholate is the principal mechanism operative in metal removal. However, the formation of insoluble metal deoxycholate from soluble metal deoxycholate is slow in the later stages of the reaction because of the low concentration of solute components. Hence, an equilibration time of 3 hours or greater is required for maximising the formation of precipitate. Because of the low solubility of copper and zinc deoxycholates in water, a S/M ratio of 2.5 is sufficient for their significant removals (over 99.5%) at any concentrations. The solubility of nickel deoxycholate is relatively high (about 19 times that the copper deoxycholate) and therefore, a S/M of greater than 2.5 is required for low feed nickel (e.g., a S/M of 5 is required for 1 mM feed nickel) to achieve over 99.5% of nickel removal. However, for high feed nickel, a S/M of 2.5 is sufficient. The higher feed concentration gives a higher metal removal because of increased free deoxycholate ion concentrations that reduce the solubility of metal deoxycholate due to the common ion effect. Though feed metal concentrations are of minor significance in regards to removal of copper and zinc ions, UF is very difficult at high feed copper concentrations because of the extremely low permeate fluxes. This is a result of the gelatinous nature of the precipitated copper deoxycholate at room temperature.

Though precipitation of metal deoxycholate removes most of the metal ions (>98.5% for nickel, >99.5% for copper and zinc) from the target solutions, the precipitate cannot be removed from the solution by classical filtration techniques in most cases when the feed concentrations are high, particularly for copper and zinc. In those instances, centrifugation followed by ultrafiltration is an effective laboratory process. Where the precipitate can be removed, UF can remove a large proportion of the metal remaining in the solution.

A high temperature does not significantly affect the removal of metal ions by NaDC since the increase in solubility of metal deoxycholate with increasing temperature is very slight. A high pH (e.g., 10) in the feed mixture increases largely the removal of nickel ions than at neutral pH (i.e. 7), but the removals of copper and zinc ions are almost the same at pH 7 or 10. The formation and precipitation of metal hydroxide rather than metal deoxycholate becomes the principal mechanism of metal removal at the high pH where the S/M ratio is not relevant and the process becomes simply the filtration of metal hydroxide. Metal hydroxide does not appear to foul the UF membrane as reflected by high permeate fluxes.

4.3.2 Two-metal systems: Separation of individual metals

Huang *et al.* (1994) and Hong *et al.* (1998) reported that when the quantity of a surfactant was limited in a mixture of metal ions, competitive binding occurred between them because of their differential affinity for the surfactant. According to Huang *et al.* (1994), the affinity of Cu, Ni, Zn, Pb and Cd ions for deoxycholate anions is in the order of Pb>Cu>Cd>Zn>Ni. Therefore, individual metals can be separated in principle from their mixtures by NaDC. In a mixture of two divalent metals, the moles of NaDC required should be just twice the moles of the higher affinity metal, which would then precipitate upon forming insoluble metal deoxycholate. The precipitate can be separated from the liquid phase by ultrafiltration or ordinary filtration. The binary systems investigated were Cu/Ni, Cu/Zn and Zn/Ni.

The separation of two metals is expressed quantitatively by 'the separation factor'. Akita *et al.* (1999) defined the separation factor (α) in equation 2.18 as below.

$$\alpha = \frac{[C_r/C_p]_{\text{higher rejected metal}}}{[C_r/C_p]_{\text{lower rejected metal}}} \tag{2.18}$$

where C_r and C_p denote the retentate metal concentration (in mg/L) and permeate metal concentration (in mg/L) respectively.

The above equation has been modified as follows to include the total mass rejected or permeated and used to calcultate the separation factor (α) in the present research. This approach, while arithmatically gives identical results to the Equation 2.18, is more appropriate in the calculation of α for experiments including classical filtration.

$$\alpha = \frac{[\text{total mass in retentate/total mass in permeate}]_{\text{higher rejected metal}}}{[\text{total mass in retentate/total mass in permeate}]_{\text{lower rejected metal}}}$$

$$= \frac{[(C_r.V_r)/(C_p.V_p)]_{\text{higher rejected metal}}}{[(C_r.V_r)/(C_p.V_p)]_{\text{lower rejected metal}}} \tag{4.2}$$

where V_r and V_p are the retentate volume (in L) and permeate volume (in L) respectively.

4.3.2.1 Cu/Ni system with NaDC

Influence of equilibration time on rejection and separation

Similar to single-metal systems, sufficient equilibration time may be required for the two-metal systems. The influence of equilibration time on the Cu/Ni system with NaDC was studied by carrying out a series of experiments with feed mixtures containing 2.5 mM of each metal and 5.0 mM of NaDC, and having different equilibration times. The results (given in Table 4.15) indicate that a 3-hour equilibration is required for this binary system. However, an equilibration time of greater than 3 hours has been found to have no benefit in terms of separation or metal rejection.

Table 4.15

UF of Cu/Ni system with NaDC after different equilibration times

Exp No	Eq. time	Cu concentration (mg/L)			Ni concentration (mg/L)			α (eq. 4.2)	% Cu rejection
		Feed	C_p	C_r	Feed	C_p	C_r		
1	3-hr	159	2.3	1203	147	142	178	417 (426)	99
2	6-hr	159	2.4	1190	147	142	176	400 (408)	99
3	12-hr	159	2.6	1188	147	141	176	366 (360)	98
4	24-hr	159	3.0	1187	147	140	178	311 (298)	98
5	24-hr	159	6.0*	1164	147	137	190	140 (129)	96

[C_p = permeate metal concentration, C_r = retentate metal concentration, feed NaDC = 5.0 mM, UF permeate volume, V_p = 350 ml, UF retentate volume, V_r = 50 ml, membrane = PBCC5, * white precipitate in the feed before UF, ( ) = where retentate con. was calculated from mass balance considering the permeate con. accurate]

The colour of the precipitate formed in a Cu/Ni system with NaDC was usually blue, which became light blue after a long equilibration (e.g., 24 hours). On a few occasions, the blue colour turned into almost white after 24-hour equilibration and resulted in a higher permeate copper concentration (6 mg/L or greater). This means that the white form of precipitate is more soluble than the blue form. It has been found that the conversion of blue precipitate into white form reduces the efficiency of separation. This can be explained by the fact that the white form of copper deoxycholate is associated with 2.5 molecules of water compared to 4.5 molecules with the blue form, as discussed later in the section ***Solubility test***. Hence, the white form of copper deoxycholate is less hydrated than the blue form. Unfortunately there is no information in the literature to verify this result. From a practical point of view, a 3-hour equilibration time precludes the formation of the more hydrated form. This time has been used in further investigations. To determine the metal contents of retentate solids, the 6-hour equilibration experiment (expt. 2, Table 4.15) was followed by six cycles of batch diafiltration to remove all the metal present in the liquid phase of the retentate. The analysis of the final retentate showed that it contained 72% copper and 0.2% nickel of the initial metal concentrations. This indicated that a significant amount of copper was bound to the precipitate solids along with a small amount of nickel. The Cu:Ni molar ratio in the solids was 332:1, while in the starting solution this ratio was 1:1. Thus, acidification of the precipitate would give a solution containing 99.7% copper and 0.3% nickel. However, the actual metal contents of solids might be more than the measured amounts because six diafiltration runs reduced some of the metals due to the solubility effect.

The actual metal contents in the retentate solids were determined for the 3-hour equilibration experiment (expt. 1, Table 4.15) where the retentate containing the precipitate was vacuum-filtered. The solids, after washing, were dissolved in water in the presence of ammonia and then acidified to precipitate the DCA. The liquid phase, after filtering out the DCA, was analysed for copper and nickel. The results show that the Cu:Ni molar ratio in the solids was 99:1. Thus, acidification of the solids would give a solution containing 99% copper and 1% nickel.

Influence of feed metal concentration

Experiments mentioned in Table 4.16 refer to the influence of feed metal concentrations on the separation of copper and nickel from their mixtures. The results clearly indicate that, provided the ratio of NaDC to copper remains constant, a change in the feed metal concentration does not significantly change the Cu rejection, but does affect the separation factor. The vacuum-filtration of an identical feed mixture produces a similar effluent Cu concentration to the UF permeate, but the separation factor is lower than that from UF. As in the single-metal systems, the precipitation of insoluble metal deoxycholate is most likely the mechanism of separation.

Experimental results (Table 4.16) also indicate that the permeate Cu concentration increases with increasing feed Cu concentration. This may be explained by the effects of soluble electrolytes (i.e. nickel chloride and sodium sulphate). The concentrations of these electrolytes increase with increasing concentrations of feed components, which, in turn, increase the ionic strength of the medium. Glasstone and Lewis (1965) gave an equation:

$$K_s = S^2 f_{\pm}^2 \tag{4.3}$$

where K_s is the solubility product of the salt, S is the solubility of the salt, and $f_{\pm}$ is the mean activity coefficient of the salt components (as ions). The increased ionic strength would reduce the activity coefficient and thereby, increase the solubility since the solubility product is constant. The solubility of copper deoxycholate thus increases with increasing feed Cu concentrations giving the observed higher permeate Cu concentrations.

The initial and final permeate fluxes were 80-90% and 70-85% of the pure water flux respectively (expts. 1-6), indicating that only a slight decline in flux with elapsed time was observed under the present operating conditions. The high initial permeate flux may be explained by the absence of concentration polarisation since there was no free residual NaDC in the system. The slight decline in flux with elapsed time indicates little membrane fouling. Since the precipitate, though mainly copper deoxycholate, contains 1% Ni, it may be conjectured that the presence of nickel affects the particulate nature of the precipitate making it less gelatinous than pure $Cu(DC)_2$ in the Cu/NaDC system. This would thus explain the reason of less membrane fouling in the Cu/Ni/NaDC system. In cobalt and nickel separation using a micelle-solubilised hydrophobic ligand 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHPNA) with a nonionic surfactant polyoxyethylene nonyl phenyl ether with 10 ethylene oxide units (PONPE10) at a S/M of 40, similar trends in permeate flux decline were observed by Akita *et al.* (1999), in other words, there was no significant decline in permeate flux with elapsed time.

Table 4.16

UF and filtration of Cu/Ni system with NaDC

Exp No	Expt	Cu concentration (mg/L)			Ni concentration (mg/L)			α (eq. 4.2)	% Cu rejection
		Feed	C_p	C_r	Feed	C_p	C_r		
6	UF	79	1.1	614	73	70	89	439 (423)	99
1	UF	159	2.3	1203	147	142	178	417 (426)	99
7	Filtr.	159	3.3	2079	147	138	258	(337)	(98)
8	UF	317	6.4	2260	293	282	335	297 (297)	98

[C_p = permeate metal concentration, C_r = retentate metal concentration, NaDC/Cu = 2; UF permeate volume, V_p = 350 ml, UF retentate volume, V_r = 50 ml, filtrate volume, V_p of expt. 7 = 370 ml, membrane = PBCC5, equilibration time = 3 hours, ( ) = where retentate con. was calculated from mass balance considering the permeate con. accurate]

Influence of pH

In all previous Cu/Ni binary experiments, the NaDC solution had a pH of 7-8 before mixing with the metal solutions and the final pH of the feed mixture was 5.3-5.5. When the final pH of a similar feed mixture (2.5 mM of each metal and 5 mM NaDC) was raised to 10 by adding 10 M NaOH, it was observed that the mixture became clear with light blue colour and with the presence of small colloidal particles. UF of such a slurry showed a faster initial flux (over 95% of the pure water flux), which was unchanged during the entire course of the run. As previously discussed for the single metals, the difference may be attributed to the formation of metal hydroxides, which do not foul the membrane. The permeate from the feed pH of 10 experiment was almost free of any metals (<0.1 mg/L for both Cu and Ni), which indicated that almost all ions of both metals were removed from the solution. The result thus suggests that a high pH has no selectivity for separating the copper and nickel ions from their mixtures.

An experiment was performed with a similar feed mixture where the pH of the NaDC solution was raised to 10 before mixing and the Cu/Ni solution was slowly added (for 15 minutes) to the NaDC solution to precipitate one metal. The final pH of the mixture was found to be 5.7, and the permeate Cu and Ni concentrations were 5.4 mg/L and 137 mg/L respectively. The feed pH of 5.7 was slightly higher than usual, but gave a slightly lower Cu rejection (i.e. 96%). The effects of low feed pH on separation were not studied since DCA completely precipitated at a pH of 4 or less. The experimental results suggest that when pH is raised from around 5.5 to higher values, the separation efficiency decreases and reaches virtually zero at a pH of nearly 10.

Akita *et al.* (1999) reported that the separation of cobalt and nickel by using a micelle-solubilised hydrophobic ligand EHPNA with a nonionic surfactant PONPE10 changed with pH. They observed that the separation factor (α) was nearly 0 at pH 3, which reached a maximum of 13.7 at a pH of around 5.5, but decreased again beyond the pH of 5.5. The influence of pH on the separation observed by Akita *et al.* (1999) is similar to that found in the present experiments where there is a relatively narrow pH window (i.e. 5.5-6.0) between release of metal cation under acid condition and metal hydroxide formation.

Selectivity of separation

It is evident from the experimental results that at a pH of around 5.5 and with sufficient equilibration time (>3 hours), the separation of copper and nickel from their mixtures is very good with a maximum separation factor of 417. A retentate solid with a Cu:Ni molar ratio of 332:1 (with 99.7% Cu and 0.3% Ni) has been obtained that can be considered as almost free of Ni.

Cu/Ni separations by UF or using bile salts have not previously been reported. The separation of two heavy metals by MEUF was reported by Akita *et al.* (1999) where cobalt and nickel ions were separated by using a micelle-solubilised hydrophobic ligand EHPNA with a nonionic surfactant PONPE10. The separation of cobalt and nickel by

Akita *et al.* (1999) was not high with the highest separation factor being 13.7, whereas the separation factor for Cu/Ni was 417 in the present study.

There are examples of solvent extraction to selectively extract one metal (i.e. Cu) from a mixture of two or more metals. Alguacil and Cobo (1999) used LIX 973N, a reagent consisting of a mixture of hydroxyoximes diluted with an organic solvent to co-extract copper and nickel from ammoniacal ammonium carbonate aqueous media. From a solution containing 3 g/L of Cu, 3 g/L of Ni and 60 g/L of ammonium carbonate, the ammonia present in the loaded organic phase was removed by a pH-controlled scrubbing operation. Thereafter, nickel was stripped at pH 9.8 using aqueous solutions of H_2SO_4 at 1:1 volume phase ratio that yielded nearly 99% total Ni stripping after 3 stages along with 2.47% Cu. Copper was stripped next from the nickel-free organic phase using 180 g/L H_2SO_4 at 1:1 volume phase ratio with 97% total stripping after 3 stages.

A direct comparison between the separations of solvent extraction and UF can be made by calculating the Ni/Cu mass ratios in the effluents. The Ni:Cu mass ratio for the aforementioned solvent extraction after total Ni stripping was 40:1 (i.e. 99/2.47). The Ni:Cu mass ratios for the present UF experiments with 1.25 mM, 2.5 mM and 5 mM metals (Table 4.16) were 64:1, 62:1 and 44:1 respectively. These mass ratios indicate that the UF separation of two metals decreased with increasing starting metal concentrations. However, UF was better than solvent extraction at low metal concentrations.

The two methods (UF and solvent extraction) are different in their principle with both having some advantages and disadvantages. The solvent extraction is capable of dealing with higher metal concentrations (i.e. 3 g/L of Cu and Ni each) and is operative at a high pH range of 9-10.5. However, the operation was not simple since it required a number of stages for both extraction and stripping.

UF is a simple process where a single-stage selective precipitation of metal deoxycholate, based on the affinity of metal ions for the surfactant, is the mechanism of separation.

DCA can be separated from the bound metal ions by acidification and can be reused. Thus, UF possesses the advantages of simplicity over solvent extraction. However, UF has a number of operational difficulties. It is suitable for dilute feed solutions only since the separation factor decreases with increasing feed concentrations. The operation with high metal concentrations is also difficult because large amounts of precipitate foul the membrane and greatly reduce the flux. In addition, UF assisted by NaDC operates for a narrow pH range with the suitable pH lying between 5.3-5.7. The separation efficiency of two metals (e.g., copper and nickel) may change if one of them is changed as evidenced from copper/zinc and zinc/nickel systems, which are discussed later.

Investigations into the basis for separation

The differential affinity of Cu and Ni ions for the deoxycholate anions may result from the differences in solubility or thermodynamic properties of their complexes with DCA. This differential affinity has been studied by investigating the solubility of $Cu(DC)_2$ and $Ni(DC)_2$ complexes, equilibration time effects on a Cu/Ni system with NaDC, and the possible replacement of Ni ions from $Ni(DC)_2$ by Cu ions.

Solubility test

The solubility of $Ni(DC)_2$ and $Cu(DC)_2$ complexes in water were determined by adding the complexes in a known volume of water and shaking continuously. The metal concentrations in the liquid phases were determined after continuous shaking up to 6 days in a thermostated shaker. The $Ni(DC)_2$ and blue $Cu(DC)_2$ complexes were prepared by stirring the metal/NaDC mixtures for 24 hours, then vacuum-filtering and air-drying the precipitates. Another $Cu(DC)_2$ complex, which was almost white, was prepared from a similar Cu/NaDC mixture by 72-hour stirring. The solubility values are shown in Table 4.17 and Fig 4.9.

The solubility results indicate that the maximum solubility for $Ni(DC)_2$ is reached within 2 days, but the solubility of $Cu(DC)_2$ of any form is not achieved even after 6 days. The results also confirm that the nickel deoxycholate has higher water-solubility than the copper deoxycholates (nearly 20 times the solubility of blue copper deoxycholate after 1 day). Out of two types of copper deoxycholates, the white form is almost three times more water-soluble than the blue form. The compositions of both forms of copper deoxycholates were also determined. The white and blue copper deoxycholates were associated with 2.5 molecules and 4.5 molecules of water respectively, suggesting their chemical formulae to be $Cu(DC)_2.2.5H_2O$ and $Cu(DC)_2.4.5H_2O$ respectively. The observed colour change mentioned in the previous section ***influence of equilibration time*** thus may be explained by the transformation of the more hydrated blue form to the less hydrated white form.

Table 4.17

Solubility of $Ni(DC)_2$ and $Cu(DC)_2$ complexes in water

Shaking time (day)	$Ni(DC)_2$ (mg/L)	Blue $Cu(DC)_2$ (mg/L)	White $Cu(DC)_2$ (mg/L)
1	108	5.6	16
2	122	7.2	17
3	122	8.4	19
6	122	12	23

[shaking at 120 rev/min at 33°C, all complexes are considered anhydrous]

The solubility values presented in Table 4.17 were calculated considering the complexes anhydrous. Hence, it can be expected that the blue or white $Cu(DC)_2$ would have the same solubility value. However, the solubility of white $Cu(DC)_2$ was found to be twice or greater than that of blue $Cu(DC)_2$. The difference could not be explained, as a systematic error was unlikely.

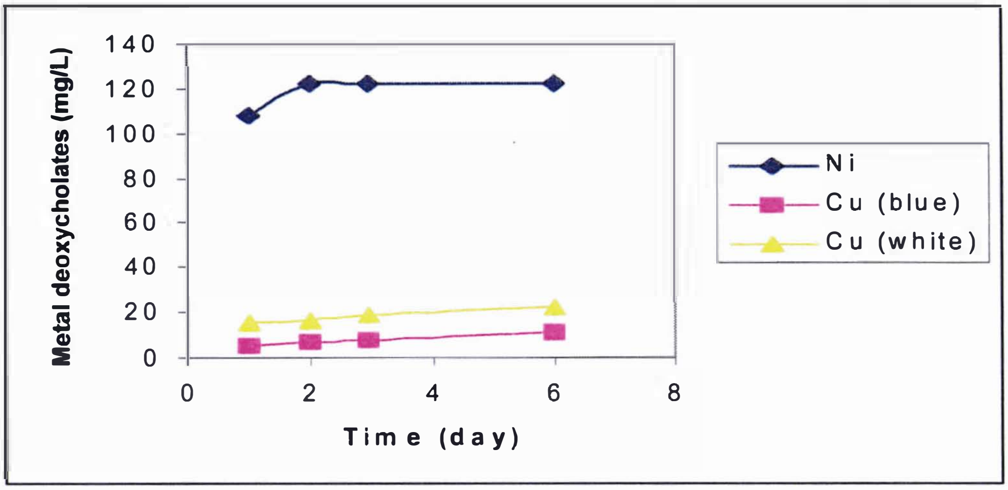


Fig. 4.9 Solubility of $Ni(DC)_2$ and $Cu(DC)_2$ complexes in water

The 24-hour water-solubility of the nickel deoxycholate in the presence of 2 mM NaCl and 2 mM NaCl plus 0.5 mM NaDC was determined as 151 mg/L (10.5 mg/L Ni) and 57 mg/L (4 mg/L Ni) respectively. The results indicate that the solubility of a metal deoxycholate is likely to increase in the presence of NaCl (electrolyte) due to the increased ionic strength of the medium (i.e. salting-in effect) according to Glasstone and Lewis (1965), and decrease in the presence of NaDC due to the common ion effect. The results also suggest that the common ion effect is dominant over the electrolyte effect at low metal concentrations.

Ni ions replacement by Cu ions

Nickel deoxycholate (250 mg; 297×10^{-6} moles) was added to 22.8 mM Cu solution (25 ml; 570×10^{-6} moles). Ten such mixtures were shaken continuously in a thermostated shaker for ten different times and the liquid phases were analysed for Cu and Ni immediately after separation by vacuum-filtration. The results showed that the Ni concentration in the solution was gradually increasing with elapsed time, while the Cu concentration was decreasing. The results also indicate that the Cu ions do replace the Ni ions from Ni(DC)$_2$ and form insoluble Cu(DC)$_2$. These changes of Ni and Cu concentrations are given in Table 4.18.

Table 4.18

Changes of Cu and Ni with elapsed time

Time	Liquid phase Ni		Liquid phase Cu	Cu change	
	mg/L	Micromoles	Mg/L	mg/L	micromoles
0	0	0	1448	0	0
15 min	58	25	1369	79	31
30 min	98	42	1325	123	48
1 hr	157	67	1250	198	78
2 hr	240	102	1160	288	113
6 hr	390	166	1025	423	167
12 hr	470	201	940	508	200
1 day	523	224	867	581	228
2 days	567	242	826	622	246
3 days	607	260	782	666	262
4 days	633	270	767	681	268

Complete displacement of metal from nickel deoxycholate would, theoretically, result in a Ni concentration of 696 mg/L. The changes in Cu and Ni concentrations with elapsed time have been shown graphically in Fig. 4.10. The graph shows that the change in concentration as well as the replacement of Ni ions by Cu ions is relatively fast during the early stages (i.e. up to 12 hours) after which the change is more gradual. Therefore, the order of the reaction is not the same for the whole time range investigated, but different for different time ranges. Fig. 4.10 clearly indicates that no part of the reaction is zero-order (i.e. straight line) and hence, the Ni concentrations (denoted by C) have been used to check the possibility of a first order reaction by a plot of lnC vs time (Fig. 4.11). The graph (Fig. 4.11) shows that the later part of the reaction (i.e. 12-96 hours) is apparently first order, but because the reaction is 90% completed, this apparent fit may be questionable. The initial part of the reaction has been plotted for 1st order and 2nd order reactions as shown in Fig.4.12 and 4.13.

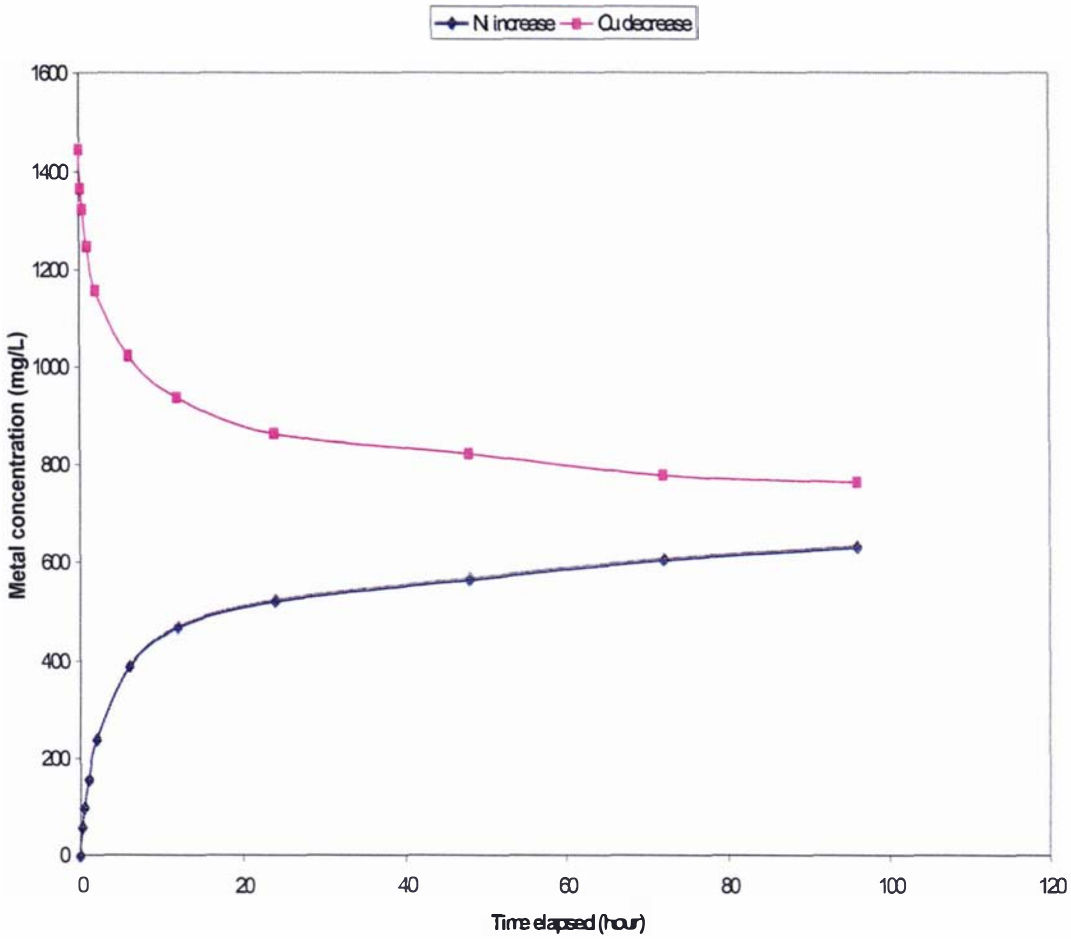


Figure 4.10 Change of Cu and Ni concentrations with elapsed time

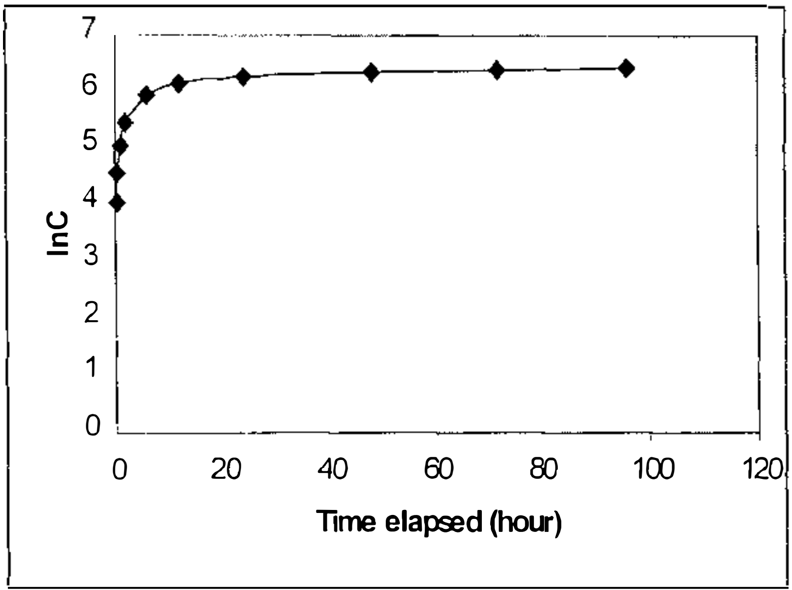


Fig. 4.11 First order plot (lnC vs Time elapsed) of Ni released (0-96 hour)

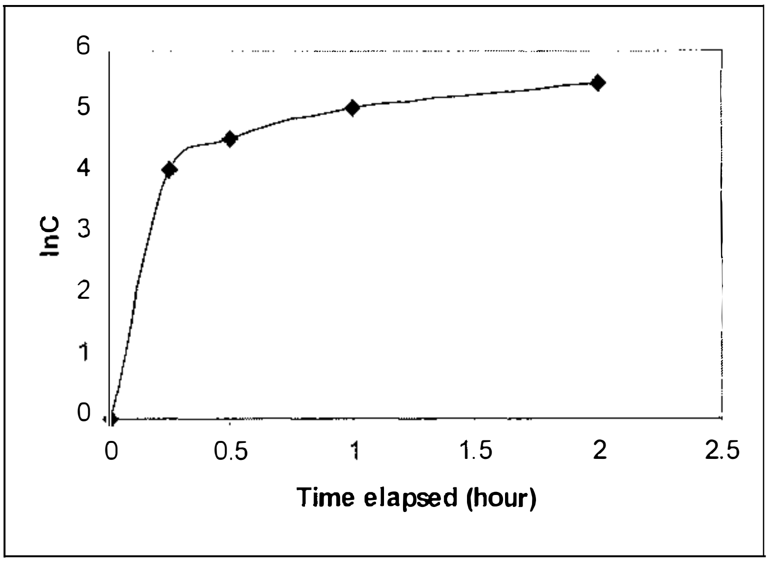


Fig. 4.12 First order plot (lnC vs Time elapsed) of Ni released (0-2 hour) (assuming that some Ni was released into the solution just after mixing)

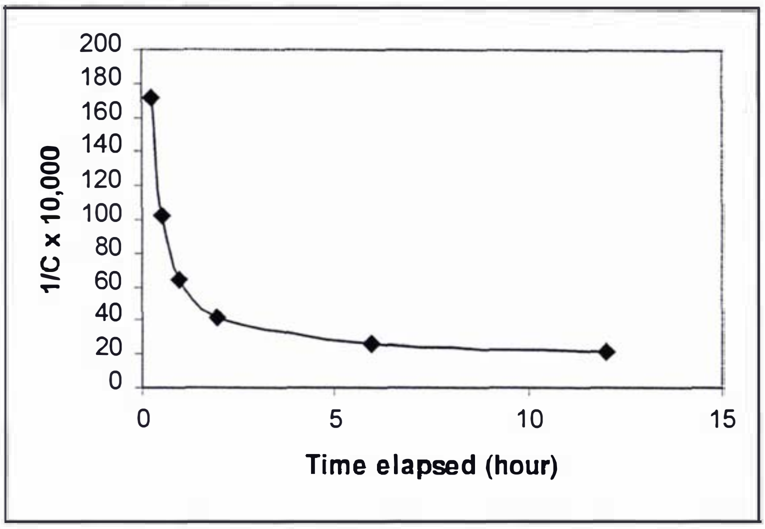


Fig. 4.13 Second order plot (1/C vs Time elapsed) of Ni released (0-12 hour)

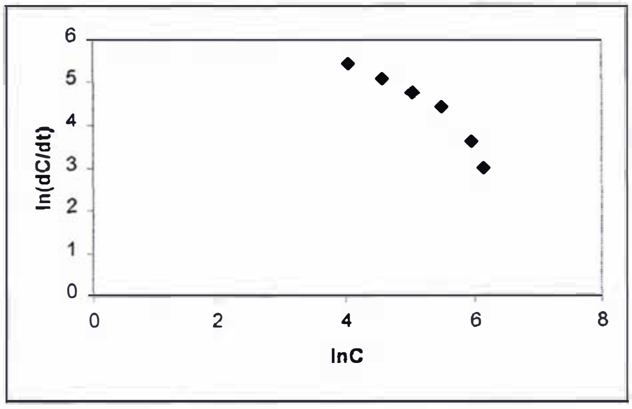


Fig. 4.14 ln(dNi/dt) vs ln(Ni) for the period of 0-12 hours

Graphs of released nickel concentrations with elapsed time (Fig. 4.12, 4.13) suggest that the initial reaction rate is fast and its order is not integral. Its order has been calculated as 2/3 from the plot of ln(dC/dt) vs lnC (Fig. 4.14). Hence, the initial part of the reaction can be expressed by the following equation:

$$dNi/dt = kNi^{2/3}$$

where k is the reaction rate constant.

The order of the reaction (Ni replacement by Cu) can also be determined by using the Cu concentration in large excess compared to Ni (Tinoco *et al.* 1978). The effect of large quantities of Cu on the AA analysis for Ni was investigated. It was found that a 20 mg/L Ni solution was measured to be 17.5 mg/L (i.e. 12.5% less) when present with 50 mM Cu. Therefore, this technique of determining reaction order was not adopted.

Equilibration time effects

A Cu/Ni solution was added to a NaDC solution with the final mixture containing 2.5 mM of each metal and 5 mM of NaDC. Two such mixtures were centrifuged after 30-minute and 24-hour equilibration time respectively. The clear supernatants were separated from the solids and analysed for Cu and Ni. The metal contents in the solids were also determined. The results are given in Table 4.19.

Table 4.19

Centrifugation of Cu/Ni/NaDC mixtures

Equilibration	**Supernatant**				**Solids**	
	metal (mg/L)		metal wt. (mg)		metal wt. (mg)	
	Cu	***Ni***	***Cu***	***Ni***	***Cu***	***Ni***
30-minute	18	125	36	250	265	42
24-hour	3	139	6	278	294	16

[2 L feed, 159 mg/L (316 mg) feed Cu, 147 mg/L (294 mg) feed Ni]

The experimental results indicate that in the early stages of the reaction (i.e. immediately after mixing), some Ni ions were bound to deoxycholate anions along with Cu ions, but the Ni ions were gradually replaced by the Cu ions with elapsed time. The amounts of nickel in the solids (42 mg and 16 mg for 30-minute and 24-hour equilibration time respectively) also support this finding. The UF of a similar feed mixture, after 24-hour equilibration, produced permeate Cu and Ni concentrations of 3 mg/L and 140 mg/L respectively (expt. 4, Table 4.15), which are almost the same as the centrifugation results.

This means that centrifugation or UF remove the insoluble metal deoxycholates to the same extent and hence, UF is not essential to metal removal or separation by NaDC.

An UF experiment was performed using a feed solution (400 ml) containing 10 mM of each metal and 10 mM of NaDC after 24-hour equilibration. The permeate Cu and Ni concentrations were 305 mg/L and 587 mg/L respectively. Since NaDC was limited, no Ni ions were precipitated by the deoxycholate ions.

These results suggest that the selectivity for Cu ions over Ni ions is due to the almost twenty fold difference between the solubility in water of nickel and copper deoxycholates (108 mg/L and 5.6 mg/L respectively, Table 4.17). Since the formation of copper and nickel deoxycholates is an ionic reaction and hence, extremely fast and presumably of the same order of magnitude, the selectivity may be presumed to be not influenced by the kinetics of the system. The experiment with $Ni(DC)_2$ and copper sulphate in which Ni was replaced by Cu supports this explanation. A simple rate equation for the replacement of Ni by Cu was not found.

4.3.2.2 Cu/Zn system with NaDC

Influence of equilibration time

Experiments 2-3 and 5-6 (Table 4.20) refer to the influence of equilibration time on the Cu/Zn system with NaDC. The results indicate that an equilibration time of 3 hours was sufficient for this binary system. An equilibration time greater than 3 hours (e.g., 24 hours) did not significantly improve the separation factor or the metal rejection. The colour of the blue precipitate formed in a Cu/Zn/NaDC system remained unchanged during the course of the experiment.

The metal contents in the retentate solids were determined in the experiments 2 and 3 (Table 4.20) where the retentates containing the precipitate were vacuum-filtered. The washed solids were dissolved in water in the presence of ammonia and then acidified to precipitate the DCA. The liquid phases, after filtering out the DCA, were analysed for copper and zinc. The results show that the Cu:Zn molar ratio in the solids was 2:1 in both cases, while in the starting solution this ratio was 1:1. Thus, acidification of the solids would give a solution containing 67% copper and 33% zinc.

Table 4.20

Cu/Zn/NaDC system with different equilibrations and feed concentrations

Exp No	Expt	Cu concentration (mg/L)			Zn concentration (mg/L)			α (eq. 4.2)	% Cu rejection
		Feed	C_p	C_r	Feed	C_p	C_r		
1	UF	79	23	446	81	54	266	3.9 (4.1)	71
2	UF	159	44	880	163	107	535	4.0 (4.2)	73
3	UF	159	42	890	163	104	540	4.1 (4.2)	73
4	Filtrn.	159	46	1553	163	105	878	(4.0)	73
5	UF	317	79	1614	326	212	1070	4.0 (4.7)	75
6	UF	317	83	1654	326	213	1108	3.8 (4.5)	74

[C_p = permeate metal concentration, C_r = retentate metal concentration, NaDC/Cu = 2; UF *permeate volume*, V_p = 350 ml, UF retentate volume V_r = 50 ml, filtrate volume, V_p of expt. 4 = 370 ml, membrane = PBCC5, equilibration time = 3 hours for expts. 1,2,4,5; 24 hours for expts. 3,6; ( ) = where retentate con. was calculated from mass balance considering the permeate con. accurate]

Influence of feed metal concentration

Experiments 1, 2 and 5 (Table 4.20) refer to the influence of feed metal concentrations on the separation of copper and zinc from their mixtures. The results clearly indicate that the metal concentrations in the feed had no noticeable effects on the separation factor or the rejection of two metals, provided the NaDC/Cu ratio remained constant. A similar feed mixture (2.5 mM of each metal and 5 mM NaDC) was vacuum-filtered (expt. 4, Table 4.21). Analysis of the filtrate showed a similar separation to that by UF. As in the

Cu/Ni/NaDC system, the precipitation of insoluble metal deoxycholates was most likely the mechanism of separation in the Cu/Zn/NaDC system.

The initial permeate fluxes in these experiments (Table 4.20) were 90-98% of the pure water flux, which did not significantly decline with elapsed time. The high initial permeate flux may be due to the absence of concentration polarisation since there was no free residual NaDC in the system. The insignificant decline in flux with elapsed time indicates little or no membrane fouling. Since the precipitate contains 67% Cu along with 33% Zn, it may be conjectured that the presence of zinc affects the particulate nature of the precipitate making it less gelatinous than pure $Cu(DC)_2$ in the Cu/NaDC system. Thus, the system would offer less or no fouling.

It was observed that the permeate Cu increased with increasing feed Cu concentrations. It was evident from the experimental results that the permeate Cu doubled when the feed Cu concentration was doubled. As in the Cu/Ni/NaDC system, the soluble neutral salts (i.e. zinc sulphate and sodium sulphate), not containing a common ion to the copper deoxycholate, increased with increasing concentrations of feed components, which increased the ionic strength of the medium and thereby, increased the solubility of copper deoxycholate giving the observed higher permeate Cu concentrations.

Influence of pH

The Cu/Zn/NaDC feed mixtures of previous experiments (expts. 1-6, Table 4.20) had a pH of around 5.5. In an experiment containing 2.5 mM of each metal and 5 mM of NaDC, the pH of the NaDC solution before mixing was raised to 10 and the Cu/Zn solution was slowly added (for 15 minutes) to it. The final pH of this mixture was 5.7 giving the UF permeate Cu and Zn concentrations of 14 mg/L and 123 mg/L respectively (after 3-hour equilibration). The Cu rejection and the separation factor were increased to 91% and 13 respectively at the pH of 5.7 compared to 73% and 3 respectively at the pH of around 5.5. When the feed pH of a similar experiment was raised to 10 by adding 10M NaOH, the slurry turned to light blue with small colloidal particles. The initial permeate flux at pH 10 was over 95% of the pure water flux that did not significantly decline with elapsed time. The permeate also showed insignificant concentrations of both metals (<0.1 mg/L for both Cu and Zn) at pH 10, indicating that all ions of both metals were precipitated as hydroxides, which did not foul the membrane. Thus, a high pH has no selectivity for separating the copper and zinc ions. As in the Cu/Ni/NaDC system, the separation of metals from the Cu/Zn/NaDC system is also pH dependent.

Selectivity of separation

The experimental results indicate that at a pH of 5.5 and after 3-hour equilibration, the best separation of a copper/zinc mixture by NaDC can be achieved that gives a separation factor of 4.

There is no report in the literature regarding Cu/Zn separations by UF or using bile salts. Fucheng (1996) reported the separation of copper and zinc from their mixtures by solvent extraction using LIX 84 as the copper extractant from the amine solution. This researcher achieved 99.97% of copper extracted along with a small, unspecified amount of zinc at pH 0.7-3.9, while 99.42% of zinc went into the raffinate. The selectivity of Cu/Zn was 1.08×10^6. Unfortunately, there was insufficient data in the abstract to verify the high selectivity value.

Mishonov and Kyuchoukov (1996) developed a mixed extractant Alamine 336/LIX 54 to separate copper and zinc during their transfer from HCl to H_2SO_4 medium. The extractant with extracted metal ions was scrubbed in two steps to remove copper and chloride ions, but zinc passed from Alamine 336 to LIX 54, which was stripped by H_2SO_4. Copper was recovered from the scrubbing solution by the chelating agent LIX 860. However, there was no clear data to compare the separation with the present experimental results.

Thus, the solvent extraction can produce a better Cu/Zn separation than the present UF, but the two methods cannot directly be compared because of the difference in their principles. UF separations are suitable for dilute feed solutions only because of the operational difficulties at high feed concentrations, which are similar to that discussed in the Cu/Ni system with NaDC. In the present study, the UF separation of Cu/Zn was poor (with α=4 and Cu:Zn molar ratio in the solids=2:1) compared to the Cu/Ni separation by UF (with α =417 and Cu:Ni molar ratio in the solids=99:1) using NaDC.

4.3.2.3 Zn/Ni system with NaDC

Table 4.21

Zn/Ni/NaDC system with different equilibration and feed concentration

Exp No	Expt	Zn concentration (mg/L)			Ni concentration (mg/L)			α (eq. 4.2)	% Cu rejection
		Feed	C_p	C_r	Feed	C_p	C_r		
1	UF	81	6	516	73	68	110	51 (64)	93
2	UF	163	16	1068	147	137	238	38 (47)	90
3	UF	163	15	1087	147	137	224	44 (50)	91
4	Filtrn.	163	17	1963	147	135	295	(52)	89
5	UF	326	31	2162	293	265	452	41 (42)	90
6	UF	326	28	2344	293	264	532	42 (46)	92

[C_p = permeate metal concentration, C_r = retentate metal concentration, NaDC/Zn = 2; UF permeate volume, V_p = 350 ml, UF retentate volume V_r = 50 ml, filtrate volume, V_p of expt. 4 = 370 ml, membrane = PBCC5, equilibration time = 3 hours for expts. 1,2,4,5; 24 hours for expts. 3,6; ( ) = where retentate con. was calculated from mass balance considering the permeate con. accurate]

Influence of equilibration time

Experiments 2-3 and 5-6 (Table 4.21) refer to the influence of equilibration time on the Zn/Ni system with NaDC. Similar to Cu/Ni and Cu/Zn systems, a 3-hour equilibration was sufficient for the Zn/Ni system. However, any convenient equilibration time of greater than 3 hours (e.g., up to 24 hours) could be used that would produce similar separation factors.

The metal contents in the retentate solids were determined for the experiments 2 and 3 (Table 4.21) in a similar way as previously described in the Cu/Ni and Cu/Zn systems with NaDC. The results show that the Zn:Ni molar ratio in the solids was 13:1 in both cases, while in the starting solution this ratio was 1:1. Thus, the acidification of the solids would give a solution containing 93% zinc and 7% nickel.

Influence of feed metal concentration

Experiments 1, 2 and 5 (Table 4.21) refer to the influence of feed metal concentrations on the separation of zinc/nickel mixtures. The results clearly indicate that the separation factor as well as the Zn rejection was slightly higher at low feed metal concentrations (e.g., 1.25 mM of each metal) compared to that at higher feed metal concentrations (e.g., 2.5 mM or 5 mM of each metal). A feed mixture containing 2.5 mM of each metal with 5 mM NaDC was vacuum-filtered (expt. 4), and that produced a slightly lower but comparable separation factor as that of the UF. As in the Cu/Ni and Cu/Zn systems, the precipitation of insoluble metal deoxycholates was the mechanism of separation in the Zn/Ni system.

The initial permeate fluxes were 97-98% of the pure water flux and remained almost unchanged until the end of the runs, indicating the absence of concentration polarisation and membrane fouling (expts. 1, 2 and 5 in Table 4.21). There was no free residual NaDC in the system and hence, no concentration polarisation. The precipitate containing 97% Zn and 7% Ni did not foul the membrane and might have a different particulate nature from the precipitate in the single-metal systems.

It was observed that the permeate Zn increased with increasing feed Zn concentrations (i.e. a higher feed Zn produced a higher permeate Zn). As in the Cu/Ni and Cu/Zn systems, the soluble neutral salts (i.e. nickel chloride and sodium sulphate) increased with increasing concentrations of feed components, which increased the ionic strength of the medium and thereby, increased the solubility of zinc deoxycholate giving the observed higher permeate Zn concentrations.

Influence of pH

The Zn/Ni/NaDC feed mixtures of previous experiments (expts. 1-6, Table 4.21) had a pH of 5.5-6.0. In an UF experiment with 2.5 mM of each metal and 5 mM of NaDC, the pH of the NaDC solution before mixing was raised to 10 and the Zn/Ni solution was slowly added (for 20 minutes) to it. The final pH of the mixture was nearly 6.5 and the UF permeate Zn and Ni concentrations were 16 mg/L and 135 mg/L respectively. The metal rejections remained almost the same as those at the pH of 5.5-6.0. The results suggest that the separation of zinc/nickel mixtures was not affected by a slight rise in pH. When the feed pH of a similar experiment was raised to 10 by adding 10 M NaOH, the slurry became almost clear with virtually transparent colloidal particles, and the permeate contained insignificant amounts of both metals (<0.1 mg/L for both Zn and Ni). Thus, a high pH has no selectivity for separating the Zn/Ni mixtures as found in the Cu/Ni and Cu/Zn cases. This is due to the formation of metal hydroxides that do not foul the membrane and results in a consistent permeate flux (over 95% of the pure water flux). In this high pH case, UF acts as simple filtration.

Selectivity of separation

The experimental results indicate that at a pH of 5.5-6.5 and with a 3-hour equilibration, a moderately good separation of zinc/nickel mixtures can be attained by NaDC with a separation factor of around 40.

Zn/Ni separations by UF or using bile salts have not been reported in the literature. Orlov and Stupnikov (1995) reported the selective separation of zinc and nickel from sulphate solutions. The separation was based on the difference in water solubility zinc and nickel sulphides as a function of temperature and pH. From a starting solution with Zn:Ni ratio of 6:1, they obtained the Zn:Ni ratio of 286:1 in the sulphide precipitation at optimum conditions.

In the present experiments, a Zn:Ni molar ratio of 13:1 was obtained in the retentate solids from a starting solution having this ratio of 1:1. The results clearly indicate that the sulphide precipitation produces a much better Zn/Ni separation than the present UF, but the two methods cannot directly be compared because of the difference in their principles. UF separations are suitable for dilute feed solutions only and are subject to other limitations, which are similar to that discussed in the Cu/Ni system with NaDC. However, the Zn/Ni separation under the present experimental conditions is still better than Co/Ni separations by MEUF (α=13.7) reported by Akita *et al.* (1999).

4.3.2.4 Conclusion

To separate individual metal ions from Cu/Ni, Cu/Zn and Zn/Ni systems using NaDC, the precipitation of metal deoxycholates was found to be the dominant mechanism of separation and the precipitates could be separated from the liquid phase by classical filtration. The use of UF was unnecessary as the UF cell was actingsimply as a filter. The separation factors for copper/nickel, copper/zinc and zinc/nickel systems (at 2.5 mM of each metal) were 417, 4 and 40 respectively, indicating that NaDC has very good selectivity for copper over nickel, but poor selectivity for copper over zinc or zinc over nickel. For the maximum separation of two metals from any system, an equilibration time of 3 hours or greater is necessary. The separation factor is not significantly affected by the feed metal concentrations, but is affected by the pH of the feed mixture with the most suitable pH lying between 5.5 and 6.0.

The initial permeate fluxes in all systems were in the range of 80-95% of the pure water flux. There was no significant decline in flux with elapsed time for any system, indicating that fouling was almost absent. This helped to maintain a consistent flux during the entire course of UF runs.

The experimental evidence indicates that separation of copper from copper/nickel systems by NaDC results mainly from the difference in solubility of their deoxycholates in water. It would seem likely that the same effect is operative for copper/zinc and zinc/nickel systems. Since the separation factor of copper/zinc is low, it may be predicted that the water solubility of their deoxycholates will be similar or closer. This is supported by the measured solubility of copper and zinc deoxycholates as 6 mg/L and 5.6 mg/L respectively.

The copper/nickel separation by NaDC is comparable to that from the solvent extraction and can be preferred for dilute solutions for its simplicity as a one-stage operation. Hence, it may have some potential for application on an industrial scale.

In the copper/zinc and zinc/nickel systems with NaDC, the copper:zinc and zinc:nickel molar ratios in the permeates were 1:7 and 1:10 respectively. These separations cannot compete with the solvent extraction separations. Hence, separations of copper/zinc and zinc/nickel systems by NaDC are not suitable for any large-scale applications.

4.3.3 Three-metal (Cu/Zn/Ni) systems

According to Huang *et al.* (1994) the affinity of Cu, Ni and Zn ions for the deoxycholate anions is in the order of Cu>Zn>Ni. Therefore, from a mixture of three, one or two metals can be precipitated by NaDC. The liquid phase or solids containing two metals can be treated as a two-metal system and individual metals can be separated. Thus, in two steps, individual metals can be separated in principle from a Cu/Zn/Ni system using NaDC.

Removal of one metal (i.e. Cu)

A feed mixture containing 2.5 mM of each metal and 5.0 mM of NaDC was stirred for 3 hours and then vacuum-filtered with No. 1 Whatman filter paper. The analysis of the filtrate showed that its Cu, Zn and Ni concentrations were 45 mg/L, 108 mg/L and 147 mg/L respectively with rejections of 72%, 34% and 0% respectively. The Cu and Zn rejections were the same as were obtained in the Cu/Zn system with NaDC.

The metal concentrations in the filtrate also indicated that 28% of the total feed Cu was still present in the liquid phase and hence, the separation of Cu from this ternary system was poor. Because all the nickel remained in the liquid phase, the precipitate solids would contain only copper and zinc, which could be treated as a Cu/Zn system. The separation of Cu/Zn mixtures by NaDC was found to be poor. Moreover, the liquid phase contained significant proportions of all three metals. Therefore, neither the solids nor the liquid phase was further treated.

Removal of two metals (i.e. Cu and Zn)

To remove two metals (i.e. Cu and Zn) from a mixture of Cu, Zn and Ni, the moles of NaDC required should be just twice the total moles of copper and zinc together. Filtration and UF results of such mixtures are presented in Table 4.22.

Table 4.22

Filtration and UF of Cu/Zn/Ni system with NaDC

Expt. No	Equilibration time	Experiment	Feed metal (mg/L)			Filtrate/permeate metal (mg/L)		
	(hour)		Cu	Zn	Ni	Cu	Zn	Ni
1	3	Filtration	159	163	147	2.6	15	124
2	24	Filtration	159	163	147	2.3	14	122
3	3	UF	159	163	147	2.2	14	122

[NaDC=10 mM]

The experimental results show that all three metals were partly rejected with Cu, Zn and Ni rejections of 98%, 91% and 16% respectively. There was no difference in metal rejections for using UF or filtration or different equilibration time. The rejections of three metals from the ternary system were directly comparable to the rejections from the Cu/Ni/NaDC system (99% Cu and 4% Ni) and Zn/Ni/NaDC system (90% Zn and 7% Ni) together. The retentate solids contained good proportions of all three metals and the liquid phase was enriched in zinc and nickel. In addition, the separation of individual metals from the Zn/Ni system was only moderate. Hence, the solids or liquid phase was not further treated.

The above experimental results indicate that the individual metals from a Cu/Zn/Ni system cannot clearly be separated using NaDC. There are few examples in the literature for the recovery of these metals in admixture. Zhang *et al.* (1998) reported the recovery of Cu, Ni and Zn by ammoniacal leaching and selective hydrogen reduction where the percentage recovery of metals was 98-99%. However, the data given are too sparse for a comparison with the NaDC method.

Conclusion

NaDC was used to separate individual metals from a mixture of three metals (copper, zinc and nickel). The experimental evidence indicates that there was co-precipitation of all three metals and thus, the separation of individual metals was not feasible.

4.3.4 Selective precipitation of metals by NaOH

An investigation into the single-metal systems, when the pH of the feed mixture was increased to 10 by the addition of NaOH, suggests that the dominating mechanism of metal removal was the formation of metal hydroxide rather than metal deoxycholate. This observation means that NaOH alone can be used as a precipitant for removing metal ions from aqueous solutions instead of NaDC and also raises the possibility of NaOH for selective separation of a metal from its mixtures with other metals, as was observed in the case of NaDC. The systems of Cu/Ni, Cu/Zn, Zn/Ni and Cu/Zn/Ni with NaOH were studied by ultrafiltering with a PBCC5 membrane to achieve a separation of individual metals.

4.3.4.1 Cu/Ni system with NaOH

An experiment was carried out with a feed mixture containing 2.5 mM of each metal and 5 mM of NaOH after 3-hour equilibration (Expt. 1, Table 4.23). The effluent Cu and Ni concentrations were 3 mg/L and 130 mg/L respectively with Cu and Ni removals of 98% and 12% respectively. Another experiment was carried out with a feed mixture containing 1 mM of each metal and 2 mM of NaOH after 3-hour equilibration (expt. 2, Table 4.24). This also produced similar metal removals (i.e. 98% Cu and 15% Ni) to the previous experiment. The effluent Cu:Ni molar ratios of the systems with 2.5 mM and 1 mM feed metals were 1:47 and 1:42 respectively. The experimental results thus clearly indicate that NaOH selectively removes Cu ions from a mixture of Cu and Ni ions.

Table 4.23

Cu/Ni system with NaOH

Expt No	Feed Cu (mg/L)	Effluent Cu (mg/L)	Feed Ni (mg/L)	Effluent Ni (mg/L)	Effluent Cu:Ni molar ratio	% Cu removal
1	159	3	147	130	1:47	98
2	63	1.3	59	50	1:42	98

[NaOH/Cu = 2; equilibration time = 3 hours]

The feed mixtures of the above experiments, obtained on mixing NaOH with the Cu/Ni solution, became slightly turbid after mixing due to the formation of a colloidal system. After 3-hour equilibration (i.e. before UF), aggregation of the colloids resulted in precipitate formation. There were no noticeable effects of concentration polarisation or membrane fouling during ultrafiltration of these slurries. This was evidenced from the observation that the process flux was almost the same as the pure water flux during the entire course of ultrafiltration. Thus, the operation was simply filtration rather than ultrafiltration.

The selective separation of Cu from Ni by NaOH can be explained by the difference in the solubility products of $Cu(OH)_2$ and $Ni(OH)_2$, which are $6x10^{-20}$ and $1x10^{-14}$ respectively (Vogel 1961, Brown 1964). Thus, $Cu(OH)_2$ is less soluble and will be precipitated before $Ni(OH)_2$. Using the calculation method of Vogel (1961), $Ni(OH)_2$ would be precipitated when the Cu ion concentration is approximately 1/400 part of the Ni ion concentration. (The detailed calculation is presented in Appendix C).

The initial concentrations of both Cu and Ni ions are 2.5 mM in experiment 1 (Table 4.24). Theoretically, $Ni(OH)_2$ would be precipitated when the Cu ion concentration is approximately 0.20 mg/L. This means that an almost complete separation is theoretically possible. However, the separation obtained was not sharp as that theoretically expected since the permeate contained approximately 2% copper and 98% nickel.

Vogel's calculation method can also be applied for the Cu/Ni system with NaDC. From the 1-day solubility of $Ni(DC)_2$ and $Cu(DC)_2$ (108 mg/L and 5.6 mg/L respectively, Table 4.18), their solubility products were calculated as $8.4x10^{-12}$ and $1.2x10^{-15}$ respectively. Hence, $Ni(DC)_2$ would be precipitated when the Cu ion concentration is 1/83 part of the Ni ion concentration. Similar to the NaOH case, a clear separation as that theoretically expected was not obtained by NaDC.

The Cu:Ni molar ratio in the effluent obtained by NaOH is 1:47 compared to 1:67 by NaDC. The Cu removal in both methods was almost the same, but the co-precipitation of Ni by NaOH (i.e. 12%) was higher than that by NaDC (i.e. 4%), which caused the observed difference in the Cu:Ni ratio.

Though the concept of hydroxide precipitation of metals started in early twenties, the literature search could not find any good examples for separation of two metals. Henych *et al.* (1963) reported the removal of metal impurities such as Cu, Co, Pb, Mn, Fe, Zn, As, Cd, Sn, Sb and Bi from sulphate electrolytes in the manufacture of pure cathode nickel. The contaminant metals were converted to insoluble hydroxides after the neutralisation process at pH 6.8-7.0. After the separation of hydroxides, the concentrations of contaminant metals in the clear filtrate were greatly reduced. Unfortunately, the data in the abstract was insufficient to state the efficiency of separation or compete with the present experimental result.

4.3.4.2 Cu/Zn system with NaOH

An experiment was carried out with a feed mixture containing 2.5 mM of each metal and 5 mM NaOH having a 3-hour equilibration time. The Cu and Zn concentrations in the effluent were 1.5 mg/L and 104 mg/L respectively with Cu and Zn removals of 99% and 36% respectively. The Cu:Zn molar ratio in the effluent was 1:67. The experimental results thus clearly indicate that from a mixture of Cu and Zn ions, NaOH can selectively remove Cu ions.

As in the Cu/Ni system, the process flux was almost the same as the pure water flux at the start and the end of "ultrafiltration".

The selective separation of Cu over Zn by NaOH can be explained by the difference in solubility products of $Cu(OH)_2$ and $Zn(OH)_2$, which are $6x10^{-20}$ and $4.5x10^{-17}$ respectively (Vogel 1961). Thus, $Cu(OH)_2$ is less soluble and will be precipitated before $Zn(OH)_2$. Using the calculation method of Vogel (1961), $Zn(OH)_2$ would be precipitated when the Cu ion concentration is approximately 1/27 part of the Zn ion concentration.

The initial concentrations of both Cu and Zn ions are 2.5 mM in the present experiment and theoretically, $Zn(OH)_2$ would be precipitated when the Cu ion concentration is approximately 2.9 mg/L. In the present experiment, the separation was worse than that theoretically expected.

From the 1-day solubility of $Cu(DC)_2$ and $Zn(DC)_2$ (5.6 mg/L and 6.0 mg/L respectively), their solubility products were calculated as $1.2x10^{-15}$ and $1.4x10^{-15}$

respectively. Applying Vogel's calculation method in the Cu/Zn/NaDC system, $Zn(DC)_2$ would be precipitated when the Cu ion concentration is equal to the Zn ion concentration. Theoretically, there would be no separation of two metals ions, but some separation was obtained in the present experiment. This indicates that unspecified factors, other than the solubility products, were responsible in separation of copper and zinc ions from their mixtures by NaOH.

The Cu:Zn molar ratio in the effluent obtained by NaOH is 1:67, which is much superior to that by NaDC (i.e.1:7). Hence, NaOH should be preferred over NaDC to separate Cu and Zn ions from their mixtures. It is surprising that there is apparently no using of this method in the literature for separation on an industrial scale. The simplicity of the operation is fast and constant flux because of the absence of membrane fouling.

4.3.4.3 Zn/Ni system with NaOH

An experiment was carried out with a feed mixture containing 2.5 mM of each metal and 5 mM NaOH having a 3-hour equilibration time. The Zn and Ni concentrations in the effluent were 27 mg/L and 106 mg/L respectively with Zn and Ni removals of 83% and 28% respectively. The Zn:Ni molar ratio in the effluent was 1:4. The experimental results thus indicate that NaOH has some selectivity for removing Zn ions from a mixture of Zn and Ni ions.

As in the previous systems, the separation of solids was a classical filtration, with the UF cell functioning as a simple filter.

The selective separation of Zn over Ni by NaOH can be explained by the difference in solubility products of $Zn(OH)_2$ and $Ni(OH)_2$, which are $4.5x10^{-17}$ and $1x10^{14}$ respectively (Vogel 1961, Brown 1964). Thus, $Zn(OH)_2$ is less soluble and will be precipitated before $Ni(OH)_2$. Using the calculation method of Vogel (1961), $Ni(OH)_2$ would be precipitated when the Zn ion concentration is approximately 1/15 part of the Ni ion concentration. Thus, $Ni(OH)_2$ in the present experiment would precipitate when the Zn ion concentration is approximately 5.4 mg/L. However, the theoretical almost complete separation was not practically obtained.

From the 1-day solubility of $Ni(DC)_2$ and $Zn(DC)_2$ (108 mg/L and 6.0 mg/L respectively), their solubility products were 8.4×10^{-12} and 1.4×10^{-15} respectively. Hence, in the Zn/Ni/NaDC system, $Ni(DC)_2$ would be precipitated when the Zn ion concentration is 1/77 part of the Ni ion concentration. Similar to the Cu/Ni/NaDC case, a theoretical clear separation was not obtained in the Zn/Ni/NaDC system.

The Zn:Ni molar ratio in the effluent obtained by NaOH is 1:4, which was inferior to that by NaDC (i.e.1:10). However, neither NaDC nor NaOH separation of the zinc/nickel mixtures is suitable for application on an industrial scale.

4.3.4.4 Cu/Zn/Ni system with NaOH

An experiment was carried out with a feed mixture containing 1 mM of each metal and 2 mM NaOH having a 3-hour equilibration time. The Cu, Zn and Ni concentrations in the effluent were 1 mg/L, 9 mg/L and 45 mg/L respectively with Cu, Zn and Ni removals of 98%, 86% and 24% respectively. The process flux throughout the experiment was nearly the same as the pure water flux, which indicated that there were no effects of concentration polarisation or membrane fouling.

The result of the Cu/Zn/Ni system suggests that individual metals cannot completely be separated by NaOH, as was observed in the case of NaDC.

4.3.4.5 Conclusion

The separation of individual metal ions from Cu/Ni, Cu/Zn and Zn/Ni mixtures by NaOH was simply filtration rather than ultrafiltration. Starting with 2.5 mM of each metal, the copper:nickel, copper:zinc and zinc:nickel molar ratios in the respective effluents were 1:47, 1:67 and 1:4 respectively. Thus, NaOH showed good selectivity for copper over nickel and zinc, but poor selectivity for zinc over nickel.

Chapter 5

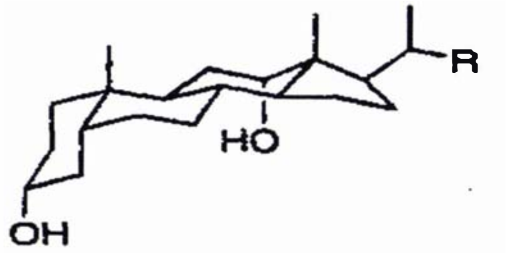
APPLICATION OF SODIUM TAURODEOXYCHOLATE FOR HEAVY METAL SEPARATION

5.1 Introduction

When a heavy metal solution and a NaDC solution are mixed, the mixture is heterogeneous because of precipitation of metal deoxycholate. The insolubilisation plays the major role in metal removal rather than MEUF as reported by Huang *et al.* (1994). Sodium taurodeoxycholate (NaTDC) is a conjugated bile salt thought worthy of investigation because a system was required with a bile acid, which was an example of true (i.e. homogeneous) MEUF. Preliminary tests showed that the mixtures of metal salts (Cu, Ni, Zn) and NaTDC solutions did not form precipitates. NaTDC is also a natural surfactant having a critical micelle concentration (cmc) of 4 mM at 20^0C (Small 1971). The role of NaTDC in separating three heavy metals (Cu, Ni and Zn) from aqueous streams was accordingly studied. The different systems investigated were single-metal systems, two-metal systems (binary) and three-metal systems (ternary).

5.2 Preparation of NaTDC

The structure of NaTDC (Li *et al.* 2000) is:



R= $CH_2CONHCH_2CH_2SO_3Na$

NaTDC was prepared by conjugating DCA with taurine according to the procedure used by Norman (1955). The procedure had the following steps:

DCA (25.5125 g, 65 mmoles) and tri-n-butylamine (15.35 ml, 65 mmoles) were dissolved in dioxan (75 ml) with slight warming. When the DCA was fully dissolved, the mixture was cooled to 10^0C after which ethylchloroformate (6.7 ml, 65 mmoles) was added. After 15 minutes at 10^0C, a solution of taurine (8.95 g, 71.5 mmoles) in*N* NaOH (71.5 ml) was added and the mixture was rapidly stirred. After 15 minutes, the mixture pH was raised to 8-9 (phenolphthalein) by adding NaOH solution. Then the mixture was evaporated *in vacuo* to a syrup that was dissolved in boiling ethanol (120 ml). The solution was filtered after it was cooled to room temperature. Ethyl acetate was added to the clear filtrate to incipient cloudiness and the solution was allowed to stand overnight at 0^0C. The crystals formed overnight were filtered, washed with diethyl ether, air dried and dissolved in 90% ethanol (300 ml). Ether was added to the solution to incipient cloudiness; crystallization began within half an hour and then the mixture was left at 4^0C for a day. The crystals were then washed with 1:1 ethanol: ether, followed by ether, then air-dried. The product was NaTDC, which was dissolved in absolute ethanol and recrystallised in order to remove any associated impurities. The crystals were separated and air-dried. Thus, about 10 g of NaTDC was obtained.

The melting point of NaTDC is 171-5^0C according to Norman (1955). The synthesised NaTDC's melting point was 167-170^0C.

The final product was compared with commercially available NaTDC (Sigma Chemicals Company, USA) using high-pressure liquid chromatography (using a 8NV C_{18} 4 μm Radial-Pak Cartridge column, 60:40 methanol:water as mobile phase, 0.5 ml/min flow rate, Waters 600E system controller and Waters R401 Differential Refractive Index detector). The retention times of the Sigma and synthesised materials were identical (5.0 minutes). Moreover, a mixed sample showed only a single peak.

5.3 Metal separation using NaTDC

All the methodologies used for metal separation by NaTDC were the same as those used for NaDC. In case of a metal/NaTDC system, a 200 ml of feed solution was ultrafiltered until 170 ml of permeate had been collected and the metal concentrations in the samples were analysed by atomic absorption using the GBC Atomic Absorption Spectrophotometer as described for NaDC.

5.4 Results and Discussion

5.4.1 Single-metal systems

5.4.1.1 Nickel: Effect of variables on MEUF of Ni/NaTDC system

A number of MEUF experiments were carried out with nickel. The variables investigated were surfactant-to-metal (S/M) ratio, feed metal concentration and membrane type/MWCO. The MEUF results of Ni/NaTDC solutions are given in Table 5.1.

Equilibration time

A mixture of 1 mM Ni and 2.5 mM NaTDC solutions was stirred for 30 minutes and then allowed to stand for 24 hours. The mixture appeared to be homogeneous without any trace of precipitate. Hence, a 30-minute equilibration time was considered sufficient and used for all for Ni/NaTDC systems investigated.

Table 5.1

MEUF of Ni/NaTDC system

Expt. No	Membrane	S/M	Feed Ni (mg/L)	Permeate Ni (mg/L)	Initial permeate flux (L/h/m^2)	Ni rejection (%)
1	PBCC5	2.5	59	30	117	49
2	PBCC5	3.25	59	22	120	63
3	PBCC5	6.5	59	5.5	128	91
4	PBCC5	8.0	59	3.1	124	95
5	PBCC5	2.0	59	41	159	31
6	PBCC5	6.5	29	6	109	79
7	PBCC5	6.5	117	6	84	95
8	YM3	6.5	59	20	49	66
9	UM2	6.5	59	6	19	90

[Details of all fluxes and total UF times are provided in Appendix A]

S/M ratio and metal rejection at submicellar surfactant concentration

The experimental evidence from the single-metal systems with NaDC indicated that a S/M ratio of 2.5 was sufficient to produce a nickel rejection of greater than 94% from a Ni/NaDC solution and this S/M ratio was thought applicable to the Ni/NaTDC system. A Ni/NaTDC feed solution containing 1 mM nickel at the S/M of 2.5 was ultrafiltered using a PBCC5 membrane. The result (expt. 1, Table 5.1) shows that the nickel rejection/removal was only 49% and hence, a S/M of 2.5 was not sufficient for this system. The reason of low Ni rejection is discussed later. The S/M ratio was then increased to 3.25, 6.5 and 8 to obtain improved nickel rejections. Experiments 2-4 (Table 5.1) represent these results, which clearly indicate that the Ni rejection increased with the increasing S/M ratio. The effects of the S/M ratio on the nickel rejection can also be seen from Fig. 5.1. For example, the Ni rejection increased from 49% to 91% when the S/M ratio was raised from 2.5 to 6.5, but the increase was slight beyond this ratio with 95% Ni rejection at the S/M of 8. Since the Ni concentration in the feed solution was constant (at

1 mM), the increasing S/M ratio increased the free residual NaTDC concentration. The experimental results clearly indicate that the Ni rejection was very good when the free residual NaTDC concentration in the feed solution exceeded its cmc of 4.0 mM, such as at the S/M ratios of 6.5 and 8. Thus, the free residual NaTDC concentration seemed to have a major role in Ni removal.

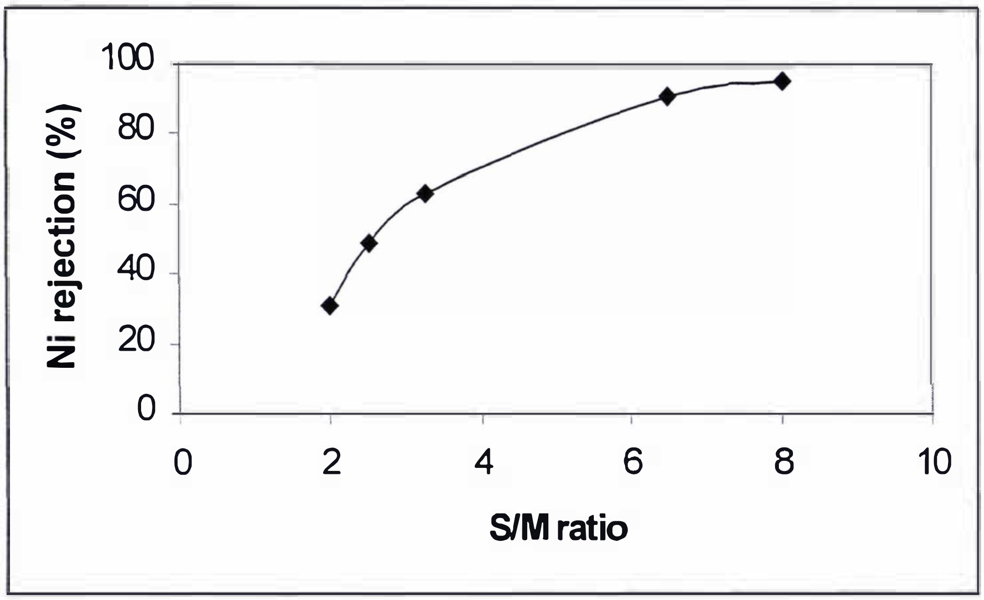


Fig. 5.1 Effects of the S/M ratio on the MEUF performance in the Ni/NaTDC system (PBCC5 membrane)

The result of the S/M ratio of 2 experiment (expt. 5) shows that 31% Ni was removed in the absence of free residual NaTDC. This indicates that the Ni removal by NaTDC depended not only on the free residual NaTDC concentration, but also on the nickel taurodeoxycholate. At the S/M ratio of 2, the reaction may be represented according to the following equilibrium equation:

$$NiCl_2 + 2NaTDC \rightleftharpoons Ni(TDC)_2 + 2NaCl$$

If the reaction is not complete, there will be less than the stoichiometric amount of nickel taurodeoxycholate. This nickel taurodeoxycholate possibly contributes to some concentration polarisation. The initial permeate flux of 48% of the pure water flux in the S/M of 2 experiment, which means 52% less in flux relative to the pure water flux though the free residual NaTDC is absent, supports this explanation. This concentration polarisation should aid in increasing retention of nickel taurodeoxycholate because diffusion through a concentration polarisation or boundary layer is slow according to Cheryan (1998).

The NaTDC present either free or bound contributed to the metal removal. At submicellar concentrations, NaTDC forms primary aggregates with aggregation number 2-7 and these primary aggregates can further agglomerate into larger ones (Li *et al.* 2000; Small 1971). The experimental results suggest that the nickel taurodeoxycholate formed at submicellar NaTDC concentrations was not of a molecular size large enough to remove acceptable amounts of nickel from the aqueous solution. The aggregation number might increase with increasing NaTDC concentrations (i.e. with increasing S/M ratios), as evidenced from the observed increasing metal removals (expts. 1-4). The other possibility was that a full equilibrium towards the right was not achieved even at the S/M of greater than 2 until the free NaTDC exceeded the cmc.

A NaTDC micelle has an aggregation number of 22 (Small 1971) giving it an effective molecular mass of 11,830 daltons, which cannot permeate through the 5,000 daltons cut-off membrane (i.e. PBCC5) and hence, is rejected. Metal ions bound to the micelles are, thereby, rejected. Thus, the nickel rejection is very good at NaTDC concentrations over the cmc. Huang *et al.* (1994) stated that metal was removed by forming metal-surfactant complexes at a surfactant concentration below the cmc, and by forming both metal-surfactant complexes and micelles at a surfactant concentration above the cmc. Though these researchers mentioned (invalidly) this reason in connection with NaDC, it is valid for NaTDC as evidenced from the present experimental results.

The above discussion suggests that at NaTDC concentrations above the cmc, all the Ni ions in the feed should be removed with the appropriate S/M value. However, this was not observed in the present experiments at the S/M of 6.5 as evidenced from the permeate Ni concentration of around 6 mg/L in experiments 3, 7 and 9. Its possible explanation was that some small primary aggregates would still be present in the micellar solution whose molecular size would be lower than the membrane pore size. According to Small (1971), dimers may be present at a bile salt concentration many times greater than the cmc, which supports the above explanation. The present experimental results (expts. 3, 7 and 9) indicate that a significant number of submicellar aggregates might pass through the membrane. This also means that the equilibrium was still not completed at the S/M of 6.5, though a fairly good nickel removal was achieved.

The initial permeate fluxes of 0.5 mM and 4.5 mM NaTDC solutions were determined as 63% and 47% of the pure water flux. The decline in initial flux with increasing NaTDC concentrations may be attributed to concentration polarisation rather than the increasing viscosity of bulk solution, because the viscosities of bile salt solutions at low concentrations are only slightly higher than that of water according to Zakrzewska *et al.* (1990). It was previously explained that concentration polarisation also occurred due to nickel taurodeoxycholate since the initial permeate flux of the S/M of 2 experiment was 48% of the pure water flux. This was in contrast to the Ni/NaDC system where concentration polarisation occurred mainly due to free NaDC as nickel deoxycholate precipitated. The flux of the 0.5 mM NaDC solution was also higher (i.e. 77% of the pure water flux) than the 0.5 mM NaTDC solution, which indicates higher concentration polarisation of NaTDC solutions.

The initial permeate fluxes in the experiments having free NaTDC in the feed solutions (expts. 1-4) were 33-40% of the pure water flux, which decreased by 5-10% over the course of an experiment with the total UF time (for 200 ml feed) of less than 30 minutes. The lower value of the initial permeate flux, compared to the pure water flux indicates that there were significant concentration polarisation effects by free residual NaTDC and nickel taurodeoxycholate. The decline in flux with elapsed time can be explained by a slight fouling effect of nickel taurodeoxycholate. Fouling in the Ni/NaTDC homogeneous system arises when NaTDC or $Ni(TDC)_2$ is adsorbed in internal membrane pores and thereby, the pore size is decreased. This is in contrast to the external fouling in the Ni/NaDC system where insoluble $Ni(DC)_2$ precipitate covers the membrane partially or entirely and reduce the number of functional pores.

From the initial permeate fluxes of all experiment, it could be seen that the flux slightly decreased with increasing S/M ratios (Fig. 5.2). The increasing S/M ratio increased the free NaTDC concentration in the feed, which played a major role in decreasing the flux, probably, through concentration polarisation of the surfactant at the membrane surface.

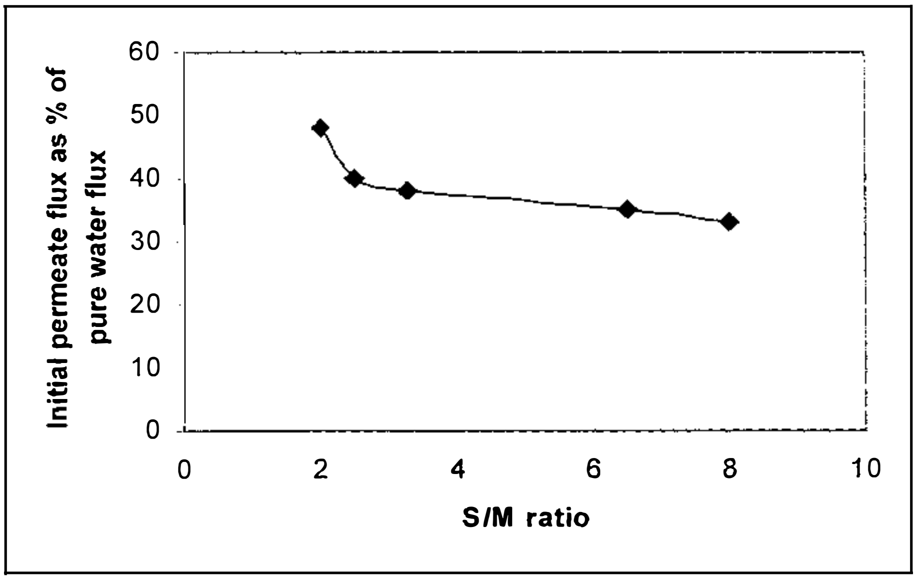


Fig. 5.2 Effects of the S/M ratio on initial permeate flux in the Ni/NaTDC system (PBCC5 membrane)

Although the highest nickel rejection (95%) was obtained at the S/M of 8, it was not considered for further investigation as from an economical point of view that much of NaTDC would be required. The NaTDC is expensive compared to several other organic surfactants and TDCA cannot be precipitated on acidification and recovered from the permeates or retentates because of its high water-solubility. Therefore, the use of NaTDC as a MEUF reagent for industrial applications may not be economically feasible. However, the S/M of 6.5 gave a free NaTDC just over the cmc and should be sufficient for this study. Therefore, the S/M of 6.5 was used for further investigation.

Table 5.2

MEUF of Ni/SDS system

Expt. No	S/M	Feed SDS (mM)	Feed Ni (mg/L)	Permeate Ni (mg/L)	Initial permeate flux (L/h/m^2)	Ni rejection (%)
10	2.5	2.5	59	28	75	53
11	2.5	2.5	117	27	100	77
12	5.0	5.0	117	1.4	109	99

[PBCC5 membrane]

The performance of NaTDC as a surfactant was compared with sodium dodecyl sulphate (SDS), which also produced a homogeneous metal-surfactant solution. At a S/M of 2.5, Ni/SDS feed solutions with 1 mM, 2 mM and 20 mM Ni did not show any precipitate formation when stirred and allowed to stand for 24 hours. MEUF experimental results (Table 5.2) indicate that a S/M of 5 was very good (99% Ni rejection) for the Ni/SDS system rather than 2.5 (77% Ni rejection) for the same feed Ni concentrations. Huang *et al.* (1994) also reported that the optimal S/M ratio for the Ni/SDS system (with 1.2 mM Ni) was 5. In the present experiments, the free residual SDS concentrations were below the cmc of 8.27 mM (Huang *et al.* 1994). Thus, the results indicate that a good nickel removal can be achieved at submicellar free residual SDS concentrations.

Morel *et al.* (1997) reported the rejection of nitrate ions during UF with a cellulose acetate membrane at submicellar surfactant (Hexadecyl Pyridinium Chloride) concentrations. They postulated the progressive covering of the membrane surface by surfactant molecules. At very low surfactant concentrations, surfactant molecules can neutralize the negative sites of the membrane and lie on the surface (Fig. 5.3a). With increasing surfactant concentrations, the tails of the adsorbed surfactant molecules can be directed towards the solution (Fig. 5.3b) because of the hydrophobic interaction between the adsorbed surfactant molecules and the surfactant molecules in solution. The adsorption of ionic surfactant on and within the membrane thus can modify the charge environment of the membrane. According to Morel *et al.* (1997), all the charges in the changed environment produce a potential, which is different from the potential in the electrolyte solution outside the membrane. This potential difference is Donnan potential difference. In case of nitrate ions removal, the counterions of nitrate ions are repelled by the Donnan potential difference and the electroneutrality condition results in the simultaneous rejection of nitrate ions.

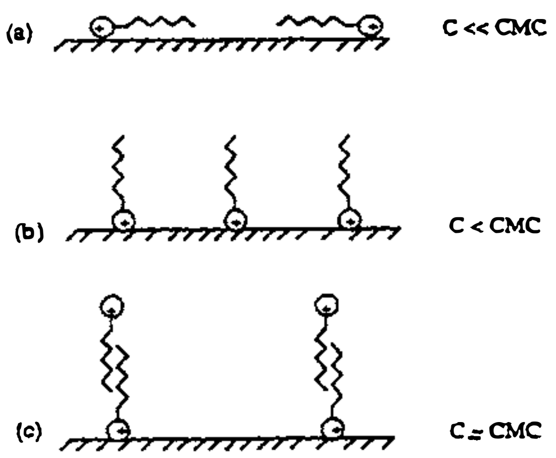


Fig. 5.3 possible arrangements of Hexadecyl Pyridinium Chloride molecules on CA membrane surface (Morel *et al.* 1997).

The Ni removal by submicellar concentrations of SDS can also be explained by the Donnan potential difference, taking into account the reversal of charges for the surfactant and rejected cations. The same agreement may be applied to situations where a significant rejection is observed for submicellar concentrations of NaTDC; for example, experiments 1, 2 and 5 in Table 5.1.

The initial permeate fluxes in the Ni/SDS systems increased with increasing S/M ratios (i.e. 40% and 47% of the pure water flux for expts. 11 and 12 respectively) suggesting that the increasing free residual SDS concentration increased the flux. It was also observed that there was no significant decline in flux with elapsed time. This was in contrast to the fluxes from the Ni/NaTDC system where the permeate flux decreased with increasing S/M ratios (Fig. 5.2) because of increased concentration polarisation.

The increase in initial permeate flux with the increasing S/M ratio in metal/SDS systems was also observed by Huang *et al.* (1994). These authors postulated that the difference in flux behaviour might be due to a different interaction between the metal-surfactant complexes and the membrane surface. However, previous workers (Chong *et al.* 1985) postulated that the surfactant molecules might be adsorbed on the membrane interior “pores” to provide a wetted surface, which would aid the convective flow through the pores and thereby, facilitate the flux increase.

It is difficult to conceive a qualitative change between the membrane and metal-surfactant complexes with increasing surfactant concentration. Indeed, with increasing surfactant concentration, the equilibrium would be expected to be driven towards greater concentrations of metal-surfactant complexes, with increasing adsorption in the internal membrane pores. This would lead to increased membrane fouling and decreased flux. Based on this reasoning, the postulate put forward by Huang *et al.* (1994) seems unlikely. Thus, the postulate by Chong *et al.* (1985) is the more favoured reason until further experimental evidence becomes available.

Feed metal concentration

Experiments 3, 6 and 7 (Table 5.1) and Fig. 5.4 refer to the effects of feed metal concentrations on the nickel rejection at a constant S/M of 6.5. The results clearly indicate that the nickel rejection increased with increasing feed nickel concentrations. The probable reason was that at higher Ni concentrations at the same S/M ratio (i.e. 6.5), the free residual NaTDC and the nickel taurodeoxycholate concentrations were also higher, which gave higher concentration polarisation. Moreover, increased NaTDC might lead to larger aggregates, which would be rejected readily by the membrane along with the bound metal ions.

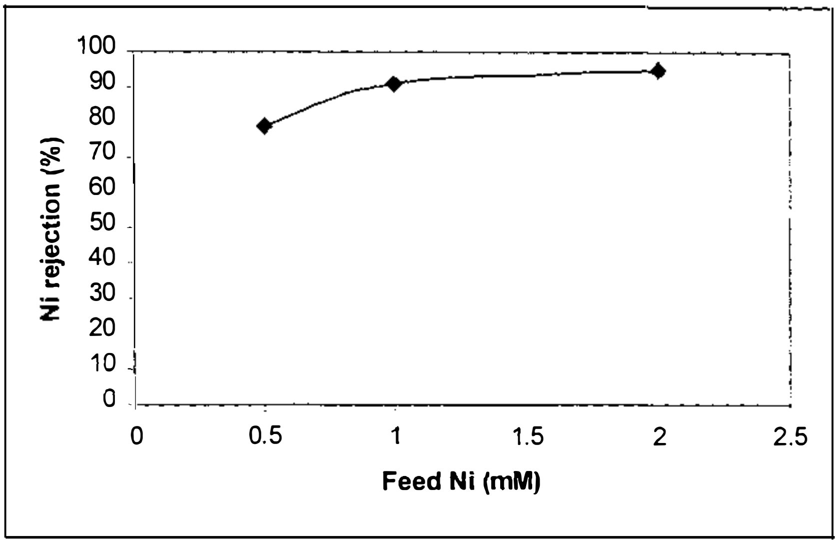


Fig. 5.4 Effects of feed Ni concentrations on the Ni rejection (PBCC5 membrane)

The feed solutions containing 0.5 mM, 1 mM and 2 mM nickel at the S/M of 6.5 had free residual NaTDC concentrations of 2.25 mM, 4.5 mM and 9 mM respectively (calculated based on stoichiometry), indicating that the free residual NaTDC concentration was below the cmc at 0.5 mM nickel concentration in the feed. The nickel rejection increased from 79% to 91% and from 91% to 95% when the feed nickel was increased from 0.5 mM to 1 mM and from 1 mM to 2 mM respectively. Thus, the increase in Ni rejection was high in the former case, but slowed in the later case. The probable reason was that the free residual NaTDC concentration changed from a non-micellar to a micellar state when the rejection increased rapidly, after which the Ni rejection increased due to increased concentration polarisation.

Experimental results also indicate that the permeate nickel did not significantly change with increasing feed nickel concentrations (Fig. 5.11), although the soluble electrolyte (i.e. sodium chloride) concentration increased. The reason is explained later in the section on copper.

Membrane type/MWCO

Experiments 3, 8 and 9 (Table 5.1) represent the effects of membrane type/material on the nickel rejection by MEUF using NaTDC. Three UF membranes – the polyethersulphonic PBCC5, regenerated cellulosic YM3 and polyelectrolyte complex (made of vinylbenzyltrimethylammonium chloride and sodium polystyrene sulphonate) UM2 were used for identical feed solutions, but their nickel rejections of 91%, 95% and 66% respectively were different. The difference in Ni rejections by the membranes was due mainly to the difference in their materials and also might be due to the variation in MWCOs.

YM3 is made of a hydrophilic material that offers lower adsorption effects for hydrophobic materials according to Cheryan (1998). The permeate flux in the YM3 experiment was 98% of the pure water flux and remained constant during the entire course of UF. This suggests that significant concentration polarisation and fouling did not occur in the YM3 membrane. Thus, the additional Ni rejection due to concentration polarisation was absent in the YM3 case giving the observed higher permeate Ni. In contrast, the material comprising the PBCC5 membrane was hydrophobic. Hence, the PBCC5 membrane was prone to fouling and possibly, interacted strongly with hydrophobic materials such as NaDC and NaTDC. The initial permeate flux of the PBCC5 membrane was 35% of the pure water flux and it slightly declined with elapsed time. This indicates that there was significant concentration polarisation and some fouling in the PBCC5 case. The experimental evidence thus suggests that a hydrophobic membrane is much more effective in nickel removal by NaTDC than a hydrophilic one.

The material comprising the UM2 membrane was also hydrophobic. Hence, it behaved similarly as the PBCC5 membrane. The initial permeate flux of the UM2 membrane was 56% of the pure water flux and the decline in flux with elapsed time was slight, indicating little fouling. The initial permeate flux of the PBCC5 membrane was 20% lower than that of the UM2 membrane, which may indicate lower concentration polarisation in the UM2 case. However, the fluxes of two membranes cannot directly be compared because of a large difference in their pure water fluxes, which were about 360 L/h/m^2 for the PBCC5 membrane and 34 L/h/m^2 for the tight membrane UM2.

Similar trends in Ni rejection and flux behaviour were also observed in the Ni/NaDC system for the PBCC5 and YM3 membranes with Ni rejections of 94% and 77% respectively, and initial permeate fluxes of 50% and 90% of the pure water flux respectively. There was little membrane fouling in the YM3 by nickel deoxycholate, but almost none by nickel taurodeoxycholate. On the other hand, the PBCC5 membrane was fouled by insoluble nickel deoxycholate and the degree of fouling was much higher than that by nickel taurodeoxycholate as evidenced from the flux decline with elapsed time. The nickel rejections by the PBCC5 and YM3 membranes in the Ni/NaDC system were also higher than those in the Ni/NaTDC system.

The difference in Ni rejection and flux behaviour between the two systems (i.e. NaDC and NaTDC) was due to their differential solution behaviours. The Ni/NaDC solution was heterogeneous where the precipitation of insoluble nickel deoxycholate was the basis of nickel removal. The nickel deoxycholate aggregates also externally/physically fouled the membrane to a great extent. In contrast, the Ni/NaTDC system was homogeneous where Ni was removed by concentration polarisation of free NaTDC and $Ni(TDC)_2$, and/or Donnan potential difference. The membrane fouling in the Ni/NaTDC system might be caused due to internal pore plugging by NaTDC or $Ni(TDC)_2$ adsorption, and this fouling was considerably lower since the nickel taurodeoxycholate was in solution and true MEUF was occurring .

5.4.1.2 Copper: Effect of variables on MEUF of Cu/NaTDC system

The variables investigated were S/M ratio, feed metal concentration and membrane type/MWCO. The MEUF results of Cu/NaTDC solutions are given in Table 5.3.

Table 5.3

MEUF of Cu/NaTDC system

Expt. No	Membrane	S/M	Feed Cu (mg/L)	Permeate Cu (mg/L)	Permeate flux ($L/h/m^2$)	Cu rejection (%)
1	PBCC5	2.5	63	41	140	35
2	PBCC5	3.25	63	27	125	57
3	PBCC5	6.5	63	5.8	106	91
4	PBCC5	8.0	63	2.1	115	97
5	PBCC5	6.5	32	4.9	75	85
6	PBCC5	6.5	127	8.8	70	93
7	YM3	6.5	63	21	45	67
8	UM2	6.5	63	0.8	11	99

Equilibration time

A mixture of 1 mM Cu and 2.5 mM NaTDC solutions was stirred for 30 minutes and then allowed to stand for 24 hours. The mixture appeared to be homogeneous since no precipitate was observed. Hence, a 30-minute equilibration time was considered to be sufficient for the Cu/NaTDC system and used for all experiments.

S/M ratio

To investigate the effects of S/M ratios on the Cu rejection by NaTDC, MEUF experiments were performed with 1 mM feed Cu solution at different S/M ratios of 2.5, 3.25, 6.5 and 8 using a PBCC5 membrane. The results (expts. 1-4, Table 5.3) clearly indicate that the Cu rejection (35%) was poor at a S/M ratio of 2.5, but increased with increasing S/M ratios. The effects can also be seen from Fig.5.5. The Cu rejections as well as the permeate quality were good at the S/M ratios of 6.5 and 8 with rejections of 91% and 97% respectively. The reason for the improved copper removal with the increasing S/M ratio was similar to that discussed in the previous section on nickel.

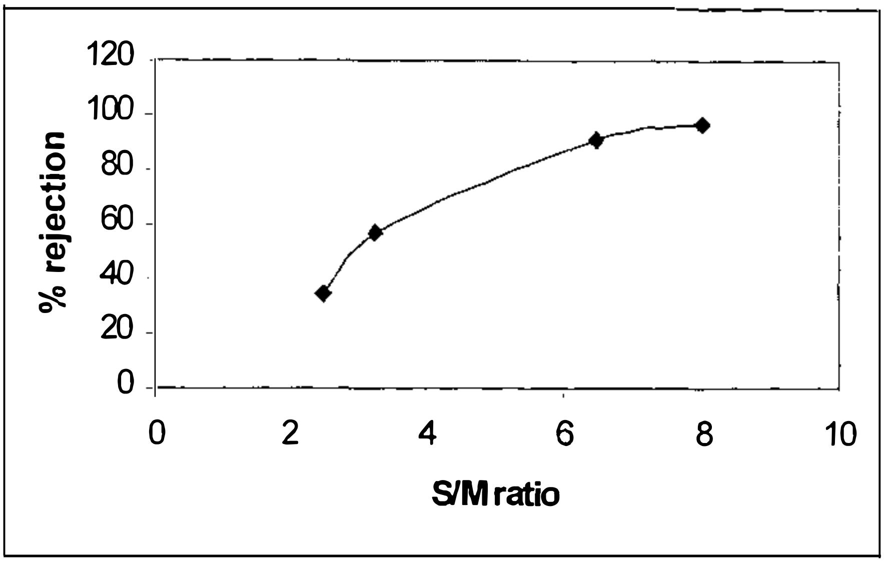


Fig. 5.5 Effects of the S/M ratio on the MEUF performance in the Cu/NaTDC system (PBCC5 membrane).

The initial permeate fluxes in these experiments (expts. 1-4) were 30-40% of the pure water flux, which decreased to 20-30% over the course of an experiment with the total UF time of less than 30 minutes. The low values of initial permeate flux indicated significant concentration polarisation due to free residual NaTDC, and copper taurodeoxycholate as well. The decline in flux with elapsed time might be caused by the fouling effect of copper taurodeoxycholate. However, the decline in flux with elapsed time was higher in the Cu/NaTDC system compared to that in the Ni/NaTDC system, indicating that membrane fouling and concentration polarisation effects were less in the Ni/NaTDC system. Since NaTDC was the same as in the Ni case, the difference might be due to the solubility of $Cu(TDC)_2$ compared to that of $Ni(TDC)_2$.

As in the Ni/NaTDC system, the initial permeate flux in the Cu/NaTDC system decreased with increasing S/M ratios (Fig. 5.6). The increasing S/M ratio increased the free residual NaTDC in the feed, which might increase concentration polarisation and thereby, decrease the flux.

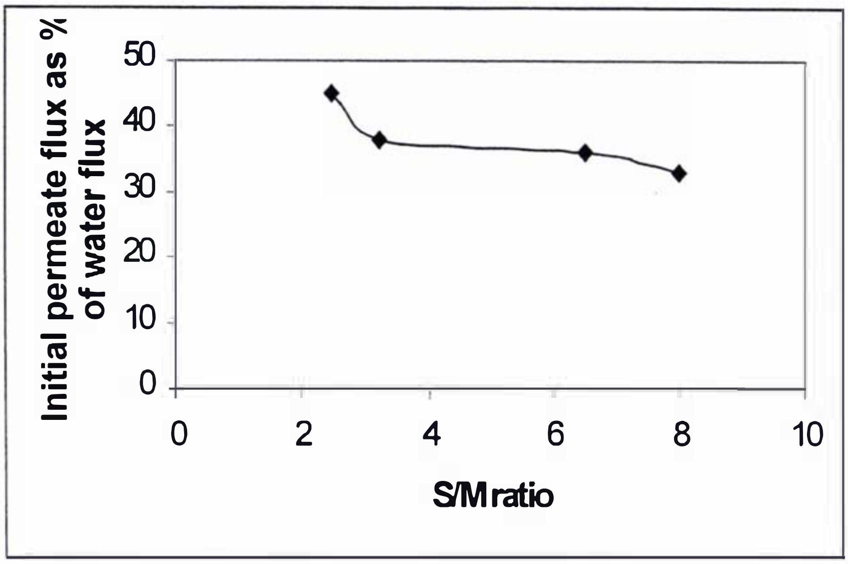


Fig. 5.6 Effects of the S/M ratio on initial permeate flux in the Cu/NaTDC system (PBCC5 membrane).

Although the highest copper rejection (97%) in the present experiments was obtained at a S/M of 8, it was not considered for further investigation as such a high ratio would be uneconomical. The S/M of 6.5 gave a free NaTDC of over its cmc and therefore, was used for further investigation as in the case of Ni.

MEUF results of Cu/NaTDC solutions were compared with those from the Cu/SDS system. At a S/M of 2.5, Cu/SDS feed solutions with 1 mM and 20 mM Cu did not show any precipitate formation when stirred and allowed to stand for 24 hours. This indicates that the Cu/SDS system was homogeneous. The MEUF results of the Cu/SDS solutions indicate that a very good Cu rejection (i.e. 99%) was obtained at the S/M of 5 rather than 2.5 (Table 5.4) as was found in the Ni/SDS system. In the present experiments, the free residual SDS concentrations were below its cmc, indicating good Cu removals at submicellar free residual SDS concentrations. This can be explained by Donnan potential difference as was discussed in the previous section on nickel.

Table 5.4

MEUF of Cu/SDS system

Expt. No	S/M	Feed SDS (mM)	Feed Cu (mg/L)	Permeate Cu (mg/L)	Initial permeate flux (L/h/m^2)	Cu rejection (%)
9	2.5	2.5	63	33	70	48
10	5.0	10	127	1.2	108	99

[PBCC5 membrane]

The initial permeate flux in the Cu/SDS system increased with increasing S/M ratios (i.e. 37% and 45% of the pure water flux at the S/M of 2.5 and 5 respectively) and there was no significant decline in flux with elapsed time. This means that the increasing free SDS concentration increased the flux. This was in contrast to the flux from the Cu/NaTDC system where the permeate flux decreased with increasing S/M ratios (Fig. 5.6) because of increased concentration polarisation.

Huang *et al.* (1994) also observed the increase in flux with increasing S/M ratio for metal/SDS systems. The reason of this flux increase was discussed in the Ni/SDS system.

Feed metal concentration

Experiments 3, 5 and 6 (Table 5.3) and Fig. 5.7 refer to the influence of feed metal concentrations on the copper rejection at a constant S/M of 6.5. The results clearly indicate that the copper rejection increased with increasing feed copper concentrations as was observed in the case of Ni. When the feed Cu concentration increased (at a constant S/M ratio), the free residual NaTDC and the copper taurodeoxycholate concentrations also increased, which gave higher concentration polarisation. The increased NaTDC might produce larger aggregates or micelles, which would be rejected readily by the membrane.

The copper rejection increased rapidly (from 85% to 91%) when the feed copper was increased from 0.5 mM to 1 mM. It may be due to the fact that the free residual NaTDC concentration (calculated based on stoichiometry) changed from a non-micellar to a micellar state, which increased the rejection rapidly. At micellar state, the copper rejection increased slowly with increasing feed copper concentration, probably, due to increased concentration polarisation.

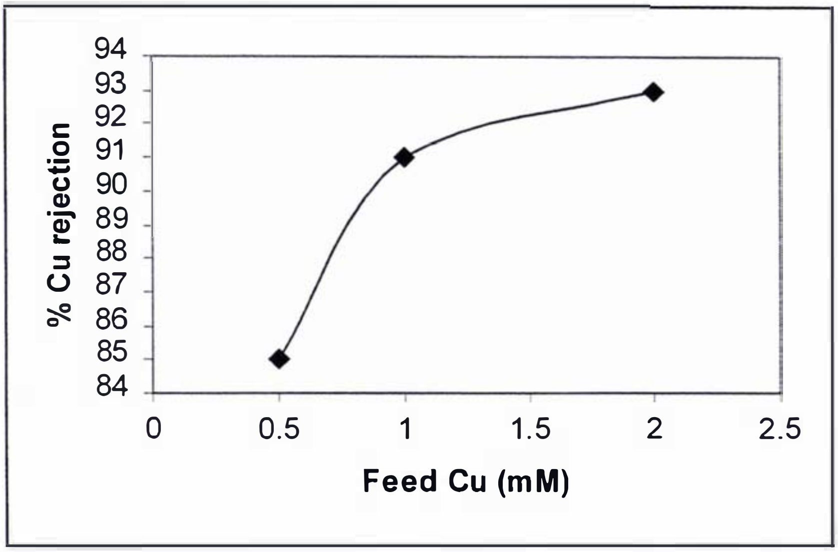


Fig. 5.7 Effects of feed Cu concentrations on the Cu rejection (PBCC5 membrane)

Experimental results also indicate that the permeate Cu concentration increased with increasing feed Cu concentrations (Fig. 5.11). This might be due to the increased soluble electrolyte (i.e. sodium sulphate) concentrations accompanying the increasing concentrations of the feed components, which increased the ionic strength of the medium. Assuming that copper taurodeoxycholate is capable of forming aggregates and micelles, the solubility of copper deoxycholate might be slightly increased or the shape and conformation of the copper deoxycholate aggregates might be affected by the increasing ionic strength, according to Glasstone and Lewis (1963) and Cheryan (1998), giving the observed higher permeate copper concentrations. It would seem likely that the same effects were operative in the case of zinc. In the case of nickel, the permeate nickel did not significantly change with increasing feed nickel concentration, which is in contrast to copper and zinc cases.

One possible way to explain the above results is the *Hard and soft-acid and base (HSAB)* concept. In the metal series of Ni^{2+}, Cu^{2+} and Zn^{2+}, the ionic charge remains the same, but the number of shielding electrons from inner shells increases. Thus, Zn is the most polarisable and Ni is the least. Hence, one should expect that the hardest acid of the three (i.e. Ni^{2+}) would form the strongest bond to the hard base TDC^-. Thus, $Ni(TDC)_2$ appears to be much more stable and thereby, less affected by the increasing ionic strength of the medium compared to $Cu(TDC)_2$ and $Zn(TDC)_2$. This would result in almost unchanged Ni concentration in the permeate.

Membrane type/MWCO

Experiments 3, 7 and 8 (Table 5.3) refer to the effects of membrane type/material on the copper rejection by MEUF using NaTDC. The polyethersulphonic PBCC5, polyelectrolyte complex (made of vinylbenzyltrimethylammonium chloride and sodium polystyrene sulphonate) UM2 and regenerated cellulosic YM3 were used for identical feed solutions, but their copper rejections were different with 91%, 99% and 67% respectively. This difference in Cu rejections is attributed mainly to the difference in their materials as in the case of nickel.

5.4.1.3 Zinc: Effect of variables on MEUF of Zn/NaTDC system

A number of experiments were carried out with zinc. The variables investigated were S/M ratio, feed metal concentration and membrane type/MWCO. The MEUF results of Zn/NaTDC solutions are given in Table 5.5.

A Zn/NaTDC mixture was stirred for 30 minutes and then allowed to stand for 24 hours. No precipitate was observed, indicating that the mixture was homogeneous. Hence, a 30-minute equilibration time was considered sufficient and used in all Zn/NaTDC systems investigated.

Table 5.5

MEUF of Zn/NaTDC system

Expt. No	Membrane	S/M	Feed Zn (mg/L)	Permeate Zn (mg/L)	Initial permeate flux (L/h/m^2)	Zn rejection (%)
1	PBCC5	2.5	65	36	137	45
2	PBCC5	3.25	65	24	143	63
3	PBCC5	6.5	65	4.4	133	93
4	PBCC5	6.5	33	4.1	94	87
5	PBCC5	6.5	130	6.1	81	95
6	YM3	6.5	65	23	48	65
7	UM2	6.5	65	2.3	12	96

S/M ratio

MEUF experiments were carried out with Zn/NaTDC solutions to investigate the effects of the S/M ratio on the Zn rejection. The results (expts. 1-3) indicate that the Zn rejection increased with increasing S/M ratios. The effects can also be seen from Fig. 5.8. Similar trends in metal rejections were also observed for Cu and Ni. As in the cases of Cu and Ni, the zinc rejection was poor with 45% at the S/M of 2.5, but increased to 93% at the S/M ratio of 6.5. Investigation was not made beyond the S/M of 6.5. The possible reasons for improved zinc removal with the increasing S/M ratio was discussed in the previous section on nickel.

The initial and final permeate fluxes in these experiments (expts. 1-3) were 39-44% and 21-30% of the pure water flux respectively. The total UF times in these experiments were less than 30 minutes. The low values of initial permeate flux indicate significant concentration polarisation due to free NaTDC, and zinc taurodeoxycholate as well. The decline in flux with elapsed time might be due to the membrane fouling resulting from zinc taurodeoxycholate. The flux decline with elapsed time was slightly higher in the

Zn/NaTDC system compared to the Ni/NaTDC and Cu/NaTDC systems (Table 5.6), which indicated that the effects of membrane fouling were slightly higher in the Zn/NaTDC system. Since NaTDC was the same in all three systems, the difference might be due to the solubility of $Zn(TDC)_2$ with respect to $Ni(TDC)_2$ and $Cu(TDC)_2$. As in the Ni/NaTDC and Cu/NaTDC systems, the initial permeate flux decreased with increasing S/M ratios in the Zn/NaTDC system (Fig. 5.9)

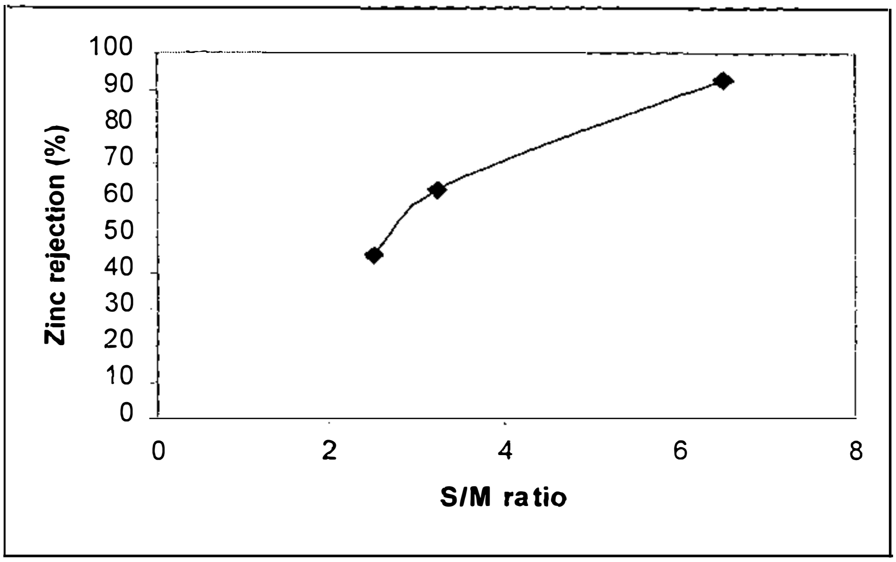


Fig. 5.8 Effects of the S/M ratio on the MEUF performance in the Zn/NaTDC system (PBCC5 membrane).

Table 5.6

Decline in permeate flux with elapsed time (PBCC5; S/M=6.5)

Elapsed time (minute)	Permeate flux as % of pure water flux		
	Ni/NaTDC System	Cu/NaTDC system	Zn/NaTDC system
3	39	33	39
15	33	29	29

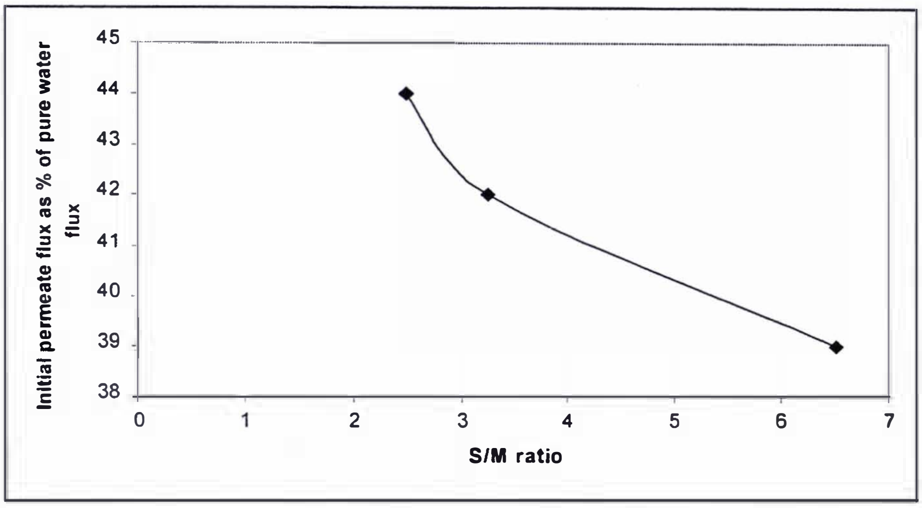


Fig. 5.9 Effects of the S/M ratio on initial flux in the Zn/NaTDC system (PBCC5)

Table 5.7

MEUF of Zn/SDS system

Expt No	S/M	Feed SDS (mM)	Feed Zn (mg/L)	Permeate Zn (mg/L)	Permeate flux (L/h/m^2)	Zn rejection (%)
8	2.5	2.5	65	32	83	51
9	5.0	5.0	130	1.6	116	99

[PBCC5 membrane]

Similar to the Ni/SDS and Cu/SDS systems, the Zn/SDS system was also homogeneous and the zinc rejection was very good (i.e. 99%) at a S/M of 5 rather than 2.5 (Table 5.7). The results also indicate that significant zinc removals can be attained at submicellar free residual SDS concentrations. This can be explained by Donnan potential difference as discussed in the previous section on nickel.

The initial permeate flux in the Zn/SDS system increased with increasing S/M ratios (i.e. 35% and 44% of the pure water flux at the S/M of 2.5 and 5 respectively) and there was no significant decline in flux with elapsed time. This means that the increasing free SDS concentration increased the flux. This is in contrast to the Zn/NaDC and Zn/NaTDC systems where the flux decreased with increasing S/M ratios because of increased concentration polarisation. The reason for the increase in initial flux was discussed in the Ni/SDS system.

Feed metal concentration

Experiments 3-5 (Table 5.5) and Fig. 5.10 refer to the effects of feed metal concentrations on the zinc rejection at a constant S/M of 6.5. The zinc rejection increased with increasing feed zinc concentrations as was observed in cases of Cu and Ni. The zinc rejection in these instances increased because of the increased free NaTDC and zinc taurodeoxycholate concentrations, which would result in higher concentration polarisation effects. The increased NaTDC might have produced larger aggregates or micelles, which were rejected readily by the membrane along with the bound zinc ions.

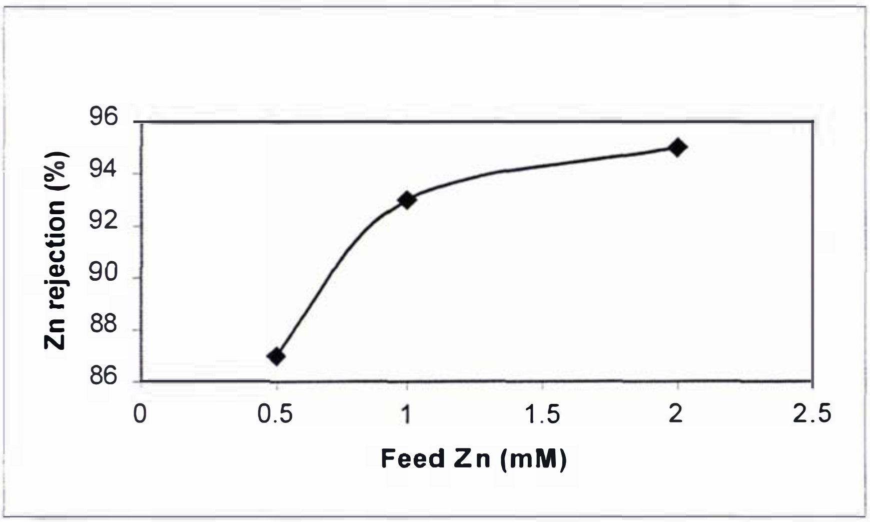


Fig. 5.10 Effects of feed zinc concentrations on the zinc rejection (PBCC5 membrane)

The permeate zinc concentration increased with increasing feed zinc concentrations (Fig. 5.11), similar to the copper case. The reason was the increasing ionic strength of the medium as previously discussed in the section on copper.

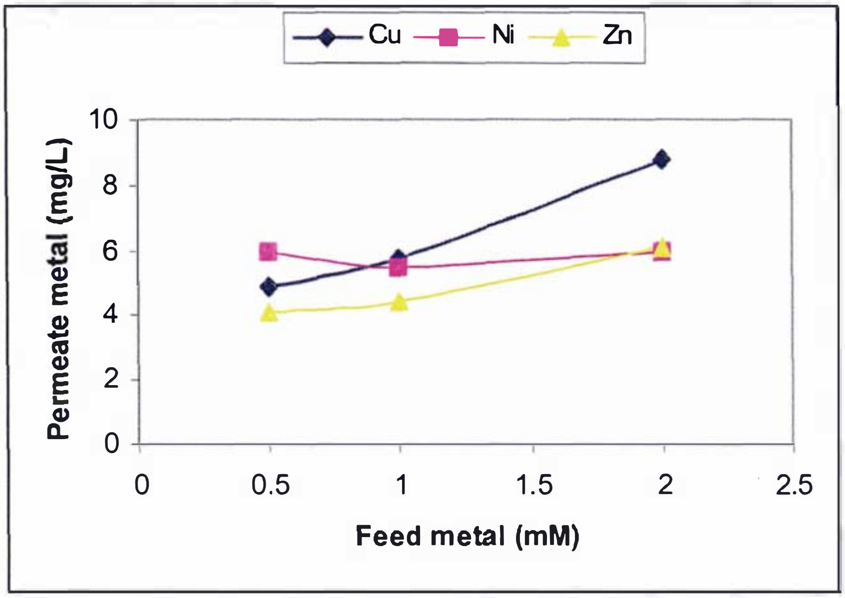


Fig. 5.11 Effects of the increasing feed metal concentration on the permeate metal concentration (PBCC5 membrane)

Membrane type/MWCO

Experiments 3, 6 and 7 (Table 5.5) represent the effects of membrane type/MWCO on the zinc rejection by MEUF using NaTDC. PBCC5, UM2 and YM3 membranes were used for identical feed solutions with zinc rejections of 93%, 96% and 65% respectively. The difference in Zn rejections by the membranes is attributed to the difference in their materials, as previously discussed in the case of nickel.

5.4.1.4 Conclusion

The mixtures of nickel, copper or zinc salts with NaTDC are homogeneous and do not form precipitate. Hence, when NaTDC is used as the surfactant, true MEUF occurs in metal removal in contrast to precipitation in the metal/NaDC system.

Nickel, copper and zinc ions can be removed from the aqueous streams by MEUF using NaTDC as the surfactant. Experimental evidence indicates that the free residual NaTDC concentration in the feed solution should be over its cmc for any significant removal of metal ions and thus, a suitable S/M ratio is very important. A S/M ratio of 6.5 has been found sufficient for a feed containing 1 mM metal that produces nickel, copper and zinc removals of 91%, 91% and 93% respectively. However, such high S/M ratios may not be economical because of the difficulty in recovery of the expensive NaTDC.

Hydrophobic membranes are much more effective than hydrophilic ones for removing metal ions by NaTDC because of the possible absence of significant concentration polarisation in the hydrophilic case.

The initial permeate fluxes in the nickel, copper and zinc systems with NaTDC are 35%, 32% and 39% of the pure water flux respectively (1 mM metal at the S/M of 6.5 and using the PBCC5). These fluxes decrease to around 25% of the pure water flux after an approximately 30-minute run. Under the same conditions, the initial permeate fluxes of the YM3 membrane remain between 90-98% of the pure water flux, which do not decline with elapsed time. The low values of initial flux in the polyethersulphonic PBCC5 membrane can be ascribed to the concentration polarisation effect of free taurodeoxycholate and metal taurodeoxycholate, which appears to be absent in the YM3 case, giving the observed high flux values. There is some membrane fouling in the PBCC5 case since the flux declines with elapsed time. The fouling in the metal/NaTDC system occurs, most likely, due to the effects of metal taurodeoxycholate. However, this fouling appears to be less severe compared to that found in the metal/NaDC system.

5.4.2 Two and three-metal systems: Separation of individual metals

MEUF of single-metal systems (Cu, Ni and Zn) using NaTDC as the surfactant showed that NaTDC can remove the metal ions significantly (with over 90% rejection) from aqueous solutions. However, the selectivity of NaTDC in separating binary or ternary metal systems and the order of affinity of Cu, Ni and Zn ions for the taurodeoxycholate ions are unknown. According to Hong *et al.* (1998) and Huang *et al.* (1994) when the quantity of a surfactant is limited in a mixture of metal ions, competitive binding will occur between them if they have differential affinity for the surfactant. Hence, the individual metals can be separated in principle from their mixtures. Accordingly, MEUF experiments were carried out for Cu/Ni, Cu/Zn, Zn/Ni and Cu/Zn/Ni systems with NaTDC.

5.4.2.1 Cu/Ni system with NaTDC

MEUF experiments were carried out for a Cu/Ni mixture (1 mM each metal) at different NaTDC concentrations. The results are presented in Table 5.8.

Table 5.8

MEUF of Cu/Ni system with NaTDC

Expt No	Membrane	Feed NaTDC (mM)	Permeate Cu (mg/L)	Permeate Ni (mg/L)	Separation factor
1	PBCC5	2	46	44	1.0
2	PBCC5	8.5	7.0	8.3	1.3
3	UM2	2	27	27	1.1

[Feed Cu = 1 mM, feed Ni = 1 mM]

The experimental results clearly indicate that both the Cu and Ni were removed to almost the same extent, indicating that the permeate in each case contained almost the same quantity of each metal irrespective of the NaTDC concentration. When the NaTDC concentration was raised from 2.0 mM to 8.5 mM, metal concentrations in the permeate decreased (expt. 2), but the permeate Cu:Ni molar ratio as well as the separation factor remained unchanged. The tighter UM2 membrane with the same feed metals improved the removal of each metal, but the separation factor remained unchanged (expt. 3). The separation factor in all cases was about 1, which indicated no separation at all. The experimental evidence thus indicates that from a mixture of Cu and Ni, NaTDC cannot separate individual metals.

The initial and final permeate fluxes in the Cu/Ni system with NaTDC (2 mM feed NaTDC) through the PBCC5 membrane (expt. 1) were 31% and 28% of the pure water flux respectively. Only a slight decline in flux with elapsed time was observed under the present operating conditions, which indicates little membrane fouling. Though there was no free NaTDC in the system (expts. 1), the initial permeate flux was still low as indicated in the single-metal systems. This indicates that metal taurodeoxycholates contributed significantly to concentration polarisation, which supports the previous explanation of concentration polarisation due to metal taurodeoxycholate as mentioned in the single-metal systems with NaTDC.

5.4.2.2 Cu/Zn system with NaTDC

A MEUF experiment was carried out with the PBCC5 membrane for a feed solution containing 1 mM of each metal and 2 mM of NaTDC. The concentrations of Cu and Zn in the permeate were 44 mg/L and 53 mg/L respectively giving a separation factor of 1.3. The result thus suggests that NaTDC cannot separate the individual metals from the Cu/Zn mixture as seen in the case of Cu/Ni mixture.

The initial and final permeate fluxes in the Cu/Zn system with NaTDC were 28% and 21% of the pure water flux respectively. The result indicates little membrane fouling. The low initial flux might be caused due to concentration polarisation of metal taurodeoxycholates as previously discussed in the Cu/Ni system with NaTDC.

5.4.2.3 Zn/Ni system with NaTDC

A MEUF experiment was carried out for a feed solution containing 1 mM of Zn and Ni each and 2 mM of NaTDC using a PBCC5 membrane. The concentrations of Zn and Ni in the permeate were 48 mg/L and 47 mg/L respectively with the separation factor of 1.0.

The result suggests that NaTDC has no selectivity to separate individual metals from a Zn/Ni mixture.

The initial and final permeate fluxes of the Zn/Ni and NaTDC system were 36% and 32% of the pure water flux respectively. The reason is similar as previously discussed in the Cu/Ni/NaTDC system.

5.4.2.4 Cu/Zn/Ni system with NaTDC

MEUF experiments were carried out for the three-metal systems (Cu, Zn and Ni) to observe the effects of NaTDC on the separation or removal of metals. The results are shown in Tables 5.9.

Table 5.9

MEUF of Cu/Zn/Ni system with NaTDC

Expt	Feed NaTDC (mM)	Permeate metal (mg/L)			Permeate
No		Cu	Zn	Ni	Cu:Zn:Ni molar ratio
1	2	54	54	47	1 :1 :0.9
2	4	42	42	37	1: 1: 1

[1 mM Cu, 1 mM Zn and 1 mM Ni in the feed]

The experimental results indicate that all three metals were removed almost to the same extent as evidenced from their concentrations in the permeate. This suggests that they should have similar affinity for the taurodeoxycholate ions. The experimental results also indicate that increasing the feed NaTDC increased the removal of metals, but their proportion in the permeate remained almost the same.

The initial and final permeate fluxes in the Cu/Zn/Ni system with NaTDC were about 25% and 20% of the pure water flux respectively. The concentration polarisation of metal taurodeoxycholates was the possible reason of the low initial flux since there was no free residual NaTDC in the system.

5.4.2.5 Conclusion

MEUF experimental results of Cu/Ni, Cu/Zn, Zn/Ni and Cu/Zn/Ni systems with NaTDC strongly suggest that the individual metals cannot be separated from a mixture of metals because ions of all metals have similar removal efficiency, and show similar affinity for the taurodeoxycholate ions. Thus, homogeneous bile acid solutions do not appear to give clear selectivity for two or more metals. This is in contrast to the homogeneous system of SDS with a mixture of metals where Cu, Ni and Zn ions showed differential affinity for SDS in the order of Cu>Ni>Zn according to Huang *et al.* (1994).

The permeate fluxes of the mixtures of metals with NaTDC were similar to those in the single-metal systems and the concentration polarisation of metal taurodeoxycholates was likely the reason for low initial fluxes since there was no free residual NaTDC in the systems.

Chapter 6

APPLICATIONS OF THIS RESEARCH

6.1 Introduction

Removal or separation of heavy metal ions from aqueous solutions by MEUF or surfactant-based ultrafiltration was reported by a number of researchers (Akita *et al.* 1997; Hong *et al.* 1998; Huang *et al.* 1994; Scamehorn *et al.* 1994; Scamehorn *et al.* 1989). Although good metal rejection was claimed in these reports, they did not provide the information regarding solution behaviour or the effects of the key parameters such as membrane material, temperature and pH. Each of the previous researchers used only one value for most parameters and the approach varied between different investigations. The justification for selecting the particular values was also unclear. In order to develop an effective metal separation system based on this concept, additional information on the effects of the key parameters is necessary.

The present research investigated the separation of heavy metals using sodium deoxycholate (NaDC) as the surfactant with the effects of the key process parameters. The applicability of sodium taurodeoxycholate (NaTDC) as a new surfactant was also investigated. It was found that NaTDC has potential as a surfactant to remove heavy metal ions, but its application may not be feasible from an economic point of view as discussed in Chapter 5. A NaDC-mediated separation process is, therefore, proposed with the appropriate values of the parameters based on their observed effects, and the reasoning for selecting the values is provided. Such a process will produce a very good metal rejection with high process flux and, therefore, shorter operation time.

6.2 The NaDC-mediated process

6.2.1 Separation of heavy metals by NaDC

When metal and NaDC solutions are mixed at normal pH (~7) and room temperature, a solid precipitate of insoluble metal deoxycholate forms. It has been found that the precipitate formation is time-dependent. At low metal concentrations, this precipitate can be separated and removed from the solution by filtration with No. 1 Whatman filter paper or by centrifugation. From a single-metal system containing of 1 mM metal with 2.5 mM NaDC, precipitate removal of about 89% nickel and over 99.5% copper and zinc each (after 24-hour equilibration) was found in this research (section 4.3.1).

At high metal concentrations (e.g., 10 mM), the metal deoxycholate precipitate cannot be removed from the solution by filtration or centrifugation in some cases. In the case of nickel, the rate of filtration was fast for the NaDC/nickel ratio of 2.5, producing a clear filtrate. When the NaDC/nickel ratio was increased from 2.5 to 5, filtration was not possible because of extremely low filtration rates or fines passing through the filter paper, but centrifugation (at 15,000 rpm) produced a clear supernatant. In the case of copper, a thick gelatinous layer of precipitate was formed over the filter paper reducing the rate of filtration almost to zero within a few minutes. Centrifugation of copper/NaDC mixture was also not feasible because much of the precipitate remained in colloidal suspension. In the case of zinc, fines consistently passed through the filter paper and so filtration was not possible, but centrifugation produced a clear supernatant. From a single-metal system consisting of 10 mM metal with 25 mM NaDC, filtration/centrifugation removed 99.7% of nickel or zinc from the solution.

UF membranes can also be used to remove the solid precipitate where the UF cell acts as a simple filter. However, the precipitate fouls the membrane, particularly in cases of nickel and copper, and the process flux is significantly reduced as the operation progresses. From the aforementioned single-metal systems (1 mM metal), UF removals of nickel, copper and zinc were 94.2%, 99.6% and 99.6% respectively (using a PBCC5 membrane). The initial permeate fluxes were 50%, 21% and 75% of the pure water flux respectively, and these reduced to 35%, 12% and 74% of the pure water flux respectively at the end of UF runs. At 10 mM metal concentration, the removal was over 99.9% for each case with the initial fluxes of 38%, 7% and 31% respectively of the pure water flux, which reduced finally to 19%, 0% and 13% of the pure water flux respectively.

In UF, a low value of the initial permeate flux relative to the pure water flux may be due to concentration polarization effects of free deoxycholate, and the decline in permeate flux with elapsed time is caused, probably, by the influence of fouling as a result of solids buildup. The UF results thus indicate that there was little or no membrane fouling by zinc deoxycholate at low concentrations, but in other cases fouling was always present. The fouling by copper deoxycholate was more severe than any other case due to the formation of a gelatinous layer over the membrane surface.

Huang *et al.* (1994) reported that the removal of heavy metals using the surfactant NaDC is MEUF. However, the experimental evidence from the present research clearly indicates that precipitation of insoluble metal deoxycholate is the principal mechanism operative in metal removal from aqueous solutions when NaDC is used as surfactant, and this precipitate should effectively be separated or removed from the solution by a solid-liquid separation step. The precipitation depends on the solubility of metal deoxycholate, which may be influenced by other parameters, particularly temperature and pH.

Since different metal cations have differential affinity for the deoxycholate anions (in the order of Cu>Zn>Ni according to Huang *et al.* 1994), NaDC can separate individual metals from a mixture. If the quantity of the surfactant is limited in a two-metal mixture, the higher affinity metal will precipitate as its deoxycholate (Hong *et al.* 1998; Huang *et al.* 1994). UF of copper/nickel, copper/zinc and zinc/nickel systems with NaDC (2.5 mM of each metal with 5 mM NaDC, using a PBCC5 membrane and after 3-hour equilibration, section 4.3.2) produced initial fluxes of 80%, 90% and 95% of the pure water flux respectively, which did not significantly decline with elapsed time. This indicates that there was little or no membrane fouling during UF of two-metal systems, which is in contrast to the single-metal systems of copper and nickel. This may be due to the different particulate nature of the mixture of two different metal deoxycholates from a single metal deoxycholate. However, there was no concentration polarization of NaDC in the two-metal systems because the free residual NaDC was absent. The nickel:copper, zinc:copper and nickel:zinc molar ratios in the respective permeates of the aforementioned cases were 67:1, 2.5:1 and 7.7:1 respectively. Filtration of similar mixtures produced these molar ratios to be 42:1, 2.3:1 and 7.1:1 respectively. The separation of copper/nickel mixture was much better than the other two. As in the single-metal systems, precipitation was the principal mechanism of separation and theoretically, UF was not required.

6.2.2 Selection of parameters

The effectiveness of a process will depend on selecting the appropriate values of key parameters. The parameter values proposed here are based on the experimental evidence from the present research.

Membrane type/material

The performance of a membrane in a separation process is determined by its selectivity and flux (Mulder 1991). The material comprising the membrane determines its properties and the performance it will offer in a separation system.

Surfactant-based UF separations of heavy metals by different research groups used membranes of different materials such as hydrophilic cellulose acetate (Hong *et al.* 1998; Scamehorn *et al.* 1994; Paulenova *et al.* 1996) and hydrophobic anisotropic acrylanitryl (Huang *et al.* 1994). The metal rejection in each case was between 96-99.9%, though the surfactant differed from group to group. Thus, both hydrophilic and hydrophobic membranes appeared to be effective in removing heavy metals. With the exception of Paulenova *et al.* (1996), each group used only one type of membrane material. Paulenova *et al.* (1996) used cellulose acetate, polyacrylanitryl and polysulphone membranes for removing cadmium using SDS as a surfactant, n-butanol as a co-surfactant and 8-

hydroxyquinoline as an extractant. The authors stated that the cellulose acetate membrane was the best of the three, but there was no data presented to substantiate this finding.

The present research compared the performance of hydrophobic polyethersulphone (PES) and hydrophilic regenerated cellulose (RC) membranes. From a mixture of 1 mM nickel with 2.5 mM NaDC (after 24-hour equilibration, section 4.3.1.1), the regenerated cellulosic YM3 membrane produced only 70% metal rejection in contrast to 94% by the polyethersulphonic PBCC5 membrane. The RC membrane produced an initial permeate flux of 90% of the pure water flux that did not significantly decrease with elapsed time. In contrast, the PES membrane produced an initial flux of only 50% of the pure water flux and this decreased further with elapsed time. The difference in flux behaviour of two membranes was presumably due to the PES membrane being subjected to significant concentration polarization and fouling effects, which were less in the RC membrane. Hence, RC membranes are advantageous with higher process flux and less cleaning requirements, which are very desirable for a membrane separation process. Cheryan (1998) reported that RC membranes had low adsorption effects and higher fluxes, which supports the present finding. The metal rejection, which is the prime objective, is far less for a RC membrane where around 30% of metal appears in the effluent. Thus, in spite of operational advantages, using a hydrophilic (e.g., RC) membrane is not appropriate. In contrast, hydrophobic (e.g., PES) membranes, though having significant flux reduction with elapsed time and needing extensive cleaning, are appropriate and more logical to use because of their high metal rejection capability. This finding of hydrophobic over hydrophilic membrane is in contrast to that reported by Paulenova *et al.* (1996), whose findings could have been due to ultrafiltration of a colloidal system, which was presumably minimally adsorbed by the cellulose acetate membrane.

Hydrophobic PES membranes can be selected from a wide range of available MWCOs (5,000-100,000 daltons). A lower MWCO membrane has been found to offer higher metal rejection than a higher MWCO one in the NaDC-mediated system. This is evident from the permeate nickel concentrations of 3.4 mg/L and 6.0 mg/L obtained from the 5,000 daltons cut-off PBCC5 membrane and 30,000 daltons cut-off PM30 membrane respectively, with rejections of 94.2% and 89.8% respectively (1 mM feed Ni with NaDC/Ni ratio of 2.5 and after 24-hour equilibration, from Table 4.2 in section 4.3.2.1). The initial permeate fluxes in those cases were 131 L/h/m^2 and 200 L/h/m^2 respectively (about 50% of the pure water flux). In the aforementioned case of low metal concentration, the rejection of PM30 is around 4% less than the rejection of PBCC5. However, at high metal concentrations (e.g., 10 mM), PBCC5 and PM30 both reject over 99.9% of any metal (copper, nickel or zinc). At 10 mM metal concentration, the initial permeate fluxes of PBCC5 and PM30 were 38% and 54% of the pure water flux respectively for nickel, 31% and 51% of the pure water flux respectively for zinc, and 7% and 8% of the pure water flux respectively for copper. In the high copper case, the initial fluxes of both membranes were very low and they were quickly reduced almost to zero because of the gelatinous nature of copper deoxycholate as discussed previously.

For a large-scale operation, using a higher MWCO membrane is preferable for higher process flux. Though a higher MWCO membrane gives less nickel rejection at low concentrations, the rejection can be increased by increasing the NaDC/nickel (i.e. S/M) ratio that will lower the solubility of nickel deoxycholate and minimise the difference in rejections of two different MWCO membranes. For example, by increasing the NaDC/nickel ratio from 2.5 to 5, the aforementioned nickel rejection of 94.2% increased to 99.7%. However, UF of a high copper/NaDC mixture is not feasible even by increasing the membrane MWCO.

Surfactant-to-metal ratio

In the present research, it was found that the optimal S/M ratio would vary depending on the starting metal concentration, particularly in the case of nickel. At 1 mM starting nickel concentration, the nickel rejection was 94.2% (3.4 mg/L permeate nickel) at the S/M of 2.5, but the rejection increased to 99.7% (0.19 mg/L permeate nickel) when the S/M was increased to 5. Since the metal rejection/removal by NaDC was due mainly to the precipitation of insoluble metal deoxycholate and there was no change between two systems other than the surfactant concentration, the increased rejection with the increased

S/M ratio is ascribed to the decreased solubility of metal deoxycholate with increasing concentrations of deoxycholate ions because of the common ion effect. The solubility of nickel deoxycholate is much higher compared to those of copper and zinc deoxycholates (Table 4.17, section 4.3.2). Therefore, a S/M ratio higher than 2.5 would be required at low nickel concentrations. The experimental evidence suggests that a S/M of 5 or greater is necessary for 1 mM feed nickel, but 2.5 is sufficient for 10 mM feed nickel to obtain a rejection of over 99.5%. Because of the low water-solubility of copper and zinc deoxycholates, a S/M of 2.5 has been found sufficient for copper or zinc at any concentrations with rejections of greater than 99.5%.

Huang *et al.* (1994) also reported that the S/M ratio of 2.5 was not sufficient for removing nickel at a low concentration using NaDC because they obtained only 70% removal at 1.2 mM nickel concentration with this S/M ratio. These authors attributed this to the total NaDC concentration being below the cmc and suggested a higher S/M ratio for low nickel concentrations. In the present research, it was found that precipitation of metal deoxycholate is the mechanism of metal removal and it is not related to the cmc of NaDC, but to the solubility of metal deoxycholate. At low nickel concentrations, a S/M ratio of greater than 2.5 is required to lower the comparatively higher solubility of nickel deoxycholate by the common ion effect. The postulate put forward by Huang *et al.* (1994) is thus less likely than the solubility postulate from this research.

The target of the proposed process is to maximise the removal of heavy metal ions in one unit operation since an additional one will add extra cost to the process. This can be achieved by precipitating all metal ions using extra amounts of NaDC relative to metal ions (i.e. increasing the S/M ratio).

Using a higher S/M ratio (i.e. excess NaDC) can have some negative impact on the proposed process. The DCA complexed with metal ions will precipitate, but the rest will remain in the solution. Thus, a significant amount of the excess NaDC will be lost in the effluent the recovery from which will require handling a larger volume of effluent, adding extra cost to the process. The other effect of adding excess NaDC is the increased sodium (as salts) in the effluent, which may need further treatment before discharge if the limit of Na is exceeded.

Using excess NaDC can also increase the ionic strength of the medium that may increase the solubility of metal deoxycholate (according to Glasstone and Lewis 1963) potentially leading to a higher metal concentration in the effluent. This is evidenced from the filtration nickel results of 1.9 mg/L and 3.3 mg/L at the S/M of 2.5 and 5 respectively (10 mM starting nickel). Therefore, using excess NaDC does not always form more precipitate or remove more metal ions.

Therefore, the suitable S/M ratio should be such that it maximises precipitation as well as metal removal. The present research suggests that the S/M ratio of 2.5 is sufficient for copper and zinc, but the S/M ratio should be 2.5 or greater for nickel, depending on its concentration.

Equilibration time

Uludag *et al.* (1997) reported that a 2-hour mixing time was sufficient to reach complexation equilibria during removal of mercury by polyethyleneimine. Most researchers did not report a specific reaction or mixing time before the UF was commenced.

The present research finds that the equilibration time (i.e. mixing time) is very important for metal removal by NaDC since the metal/NaDC mixture is heterogeneous and forms precipitate. The formation of insoluble metal deoxycholate precipitate from soluble metal deoxycholate is slow, particularly at low solute concentrations. Therefore, sufficient time for equilibration should be allowed to maximise precipitate formation as well as metal removal.

The experimental evidence from this research shows that an equilibration time of at least 3 hours is necessary. The Ni removal and the process flux increase with increasing equilibration time. The nickel rejection of 90% at 3-hour equilibration increased to 94% after 24-hour equilibration (1 mM metal, S/M of 2.5 and PBCC5 membrane, Table 4.2 in section 4.3.1.1). The initial fluxes in these cases were 40% and 50% of the pure water flux respectively, and the total UF times were 1.9 hours and 0.7 hour respectively. Thus, using a 3-hour equilibration time rather than 24-hour gives 4% less nickel rejection and 10% less flux, but it saves 20 hours of total process time. However, the rejection increases as the S/M ratio is increased; as an example, the nickel rejection at 24-hour equilibration increases to 99.7% at the S/M of 5. In such adjusted S/M ratio cases, the difference between 3-hour and 24-hour rejections is very small. In cases of copper and zinc (1 mM), the rejection (99.7%) did not vary between 3-hour and 24-hour equilibrations, but the initial flux increased by 6% for copper and 15% for zinc.

Thus, for any metal, an equilibration time of just over 3 hours would be appropriate provided the S/M ratio is adjusted where necessary, particularly for low nickel concentrations.

Temperature

Previous researchers had used a temperature of 30^0C (Huang *et al.* 1994; Scamehorn *et al.* 1989; Scamehorn *et al.* 1994) or room temperature (Hong *et al.* 1998). In their research, the metal rejection remained between 96-99.9% and the flux was between 60-80% of the pure water flux.

Sadaoui *et al.* (1998) reported the influence of temperature on cadmium removal by SDS and chromium removal by cetyltrimethylammonium bromide (CTAB) using a tubular membrane (MWCO 15,000 daltons) composed of zirconium. The cadmium rejection was constant in the experimental temperature range (20-40^0C), but the chromium rejection decreased slightly with temperature rise in the experimental range (30-45^0C). The flux increased by about 50% for cadmium and 30% for chromium as the temperature was raised from the lowest to the highest value. According to these researchers, the influence of temperature in rejection was linked to cmc variations of free surfactant ion concentrations with temperature. In the present observations, the free surfactant was below the cmc and hence, the results of this research cannot be explained by the hypothesis put forward by Sadaoui *et al.* (1998).

In the present research when the temperature was raised from 20^{0}C to 50^{0}C, the nickel, copper and zinc rejections remained almost unchanged at 99.5%, 99.7% and 99.7% respectively (1 mM metal, S/M is 5 for nickel and 2.5 for copper or zinc, after 3-hour equilibration and using a PBCC5 membrane). These results indicate that the increasing temperature usually does not affect the solubility of metal deoxycholates.

Similar to that found in the literature, the present research also observed that the process flux markedly increases with increasing temperature. The initial flux (expressed as percentage of the pure water flux at 20^{0}C) in the aforementioned 3-hour equilibration observations at 20^{0}C and 50^{0}C were 33% and 104% respectively for nickel, 59% and 123% respectively for zinc, and 15% and 85% respectively for copper. The viscosity of water at 20^{0}C and 50^{0}C are 1.002 cP and 0.5470 cP respectively, and density of 0.9982 g/cm^3 and 0.9880 g/cm^3 respectively (Lide 2002). The fluid viscosity is reduced by about 50% and the density by 1% for this temperature rise. Thus, the increase in flux for zinc and nickel can be explained by a reduction in fluid viscosity at a higher temperature. In the case of copper, other factors along with fluid viscosity reduction were also operative. It was observed that the copper deoxycholate was gelatinous at 20^{0}C and greatly fouled the membrane, but the gel turned into solid particles at 50^{0}C resulting in less fouling. The particulate nature of nickel deoxycholate also might change at high temperature since it showed less fouling. Thus, the increase in flux with temperature results from reduction in fluid viscosity, and a change in the particulate nature of metal deoxycholate.

Operation at room temperature is usual and adopted mostly for economic reasons since the cost of heating energy is significant. Although a high temperature maximises the flux with minimum fouling, it would not make the proposed process economical since it needs at least a 3-hour equilibration time. In the aforementioned nickel and zinc cases, the total operation times including the equilibration time are 4 hours and 3.6 hours respectively at room temperature, and 3.6 hours and 3.2 hours respectively at 50^0C. Hence, operation at 50^0C would save less than 1 hour of operation time, but would require over 3 hours for heating and extra time for cooling the retentate and effluent back to room temperature for further processing. Hence, for nickel and zinc, room temperature is to be selected.

In the aforementioned low copper case, operation at 50^0C would reduce the total operation time from 5 hours to 3.5 hours and hence, still room temperature would be the appropriate selection due to the aforementioned reasons. In the high copper case, operation cannot be completed at room temperature because of the gelatinous precipitate, as discussed previously. At 50^0C, the gelatinous precipitate became particulate and operation could be completed in a short period. Therefore, for high feed copper, a high temperature is to be used. However, a 50^0C temperature may not be necessary for copper; any temperature that would cause the gelatinous nature of the precipitate to change into particulate form as evidenced from the flux increase, would be sufficient. Whether the operation can be done at room temperature in cross-flow UF or MF needs to be tested.

Thus, with the exception of high copper case, all operations should be done at room temperature.

pH

There are only a few reports in the literature on the strong effects of pH on the metal rejection (Paulenova *et al.* 1996; Uludag *et al.* 1997). None of these relate to the use of NaDC. Huang *et al.* (1994) worked with NaDC, but did not study the effects of pH.

This research shows that the separation or removal of heavy metal ions by NaDC strongly depends on the pH of feed mixture. When a NaDC and a metal solution were mixed, the mixture had a pH in the range of 6.5-7.5. A metal rejection of greater than 99.5% was obtained at this pH of 6.5-7.5 (provided the S/M was increased for low nickel concentrations) after 3-hour equilibration at any temperature.

When the pH of a metal/NaDC mixture was lowered to 6, DCA started to precipitate. This finding is similar to other reports found in the literature on bile salts. Small (1971) reported that the free bile acid (e.g., cholic acid) precipitated at a pH of 6.5. Ahmadi*et al.* (1995) also reported that no significant binding between deoxycholate and metal ions occurred when the pH was lowered from 6 to 3 due to a reduction in sorption behaviour. Therefore, a pH below the normal range (i.e. 6.5-7.5) cannot be used in the case of NaDC. When the pH of a similar metal/NaDC mixture was raised to 10, metal ions precipitated as metal hydroxide and DCA appeared into the solution as NaDC. Therefore, a high pH is also not good for metal deoxycholate precipitation.

The effects of low and high pH on metal deoxycholate precipitation can be explained by the following equations (M denotes nickel, copper or zinc):

Acidic condition,
(low pH)

$$M^{2+} + 2(DC^-) \xrightarrow{2H^+} M^{2+} + 2DCA$$

Alkaline condition,
(high pH)

$$M(DC)_2 + 2\,Na^+ + 2OH^- \longrightarrow M(OH)_2 + 2NaDC$$

As an acid is added to lower the pH, an equivalent amount of DCA is precipitated with each successive acid addition. When the pH is increased, the metal deoxycholate decomposes and metal ions precipitate as metal hydroxide.

The considerations arising from the above equations mean that the effectiveness of NaDC as a surfactant is operative over a relatively narrow pH range between precipitation of DCA with release of metal cations under acid condition and metal hydroxide formation under alkaline condition. Therefore, the pH of a metal/NaDC mixture should be kept close to the neutral pH (i.e. 7) to maximise precipitation of insoluble metal deoxycholate.

Pressure

Huang *et al.* (1994) and Uludag *et al.* (1997) reported that pressure had no noticeable effects on the metal rejection, but the process flux varied linearly with the applied pressure.

Huang *et al.* (1994) obtained almost the same metal rejection of 99.9% at pressures of 276 kPa (40 psi) and 552 kPa (80 psi), but the permeate flux increased from45 L/h/m^2 (at 276 kPa) to 110 L/h/m^2 (at 552 kPa) in their study. Although a high operating pressure may cause membrane compaction, they did not observe any membrane compaction between pressures of 138-690 kPa (20-100 psi) on the anisotropic acrylanitryl (RGO3) membrane for a bench-top cross-flow system.

Uludag *et al.* (1997) observed that the mercury rejection by polyethyleneimine was almost constant at 82% in the observed pressure range of 40-140 kPa. The permeate flux was 2 L/h/m^2 at 40 kPa that linearly increased to 8.8 L/h/m^2 at 140 kPa for a laboratory-scale Osmonics Sepa CF Membrane Cell. The authors reported that a high pressure led to higher concentration polarization since it would bring a higher convective transport rate of macromolecules to the membrane surface.

Most of the previous researchers (Hong *et al.* 1998; Huang *et al.* 1994; Scamehorn *et al.* 1994; Scamehorn *et al.* 1989; Paulenova *et al.* 1996) maintained a constant pressure in the range of 276-414 kPa (40-60 psi) for surfactant-based UF operation to successfully remove heavy metal ions from aqueous or waste streams.

For the PES membranes used in this research, the maximum recommended operating pressure was 483 kPa (70 psi) as set by the manufacturer. This research used a pressure of 345 kPa (50 psi) for the stirred cell, which could tolerate a maximum pressure of 518 kPa (75 psi) recommended by Amicon Corporation. The initial permeate fluxes from 1 mM feed metal were 100 L/h/m^2, 33 L/h/m^2 and 167 L/h/m^2 for nickel, copper and zinc respectively (40%, 15% and 60% of the pure water flux respectively) using the PBCC5 membrane and after 3-hour equilibration. However, the flux values will be increased in a cross-flow system, which is adopted for large-scale operations because of reduced concentration polarization and fouling effects due to decreased shear at the membrane surface.

6.2.3 Recovery of DCA

A major proportion of the DCA added in the process (single-metal system) usually remains in the precipitate (since the usual S/M is 2.5) as filtered/centrifuged solids or in the retentate. For example, about 80% of the added DCA remains in the solids and 20% in the total liquid phase at the S/M ratio of 2.5. The DCA fraction in the liquid phase will be increased if a higher S/M ratio is used. Therefore, the DCA remaining in both the solids and the liquid phase should be recovered, and this can be done by acidification (to lower the pH to 4 or less) followed by filtration. Although acidification of the effluent would require handling a large liquid volume, it will still be beneficial since a significant amount of DCA will be recovered. In the present research, about 18% of the added DCA (at the S/M of 2.5) has been recovered from the total liquid phase in the total recovery of about 90%. The recovered DCA can be reused. Hence, after the first cycle, around 10% extra DCA would be needed and the surfactant cost would thus be minimised. However, acidification of the permeate would increase the salt contents (Na salts) in the final effluent, which may cause operational problems or may be unsuitable for disposal. In such a case, the effluent would be treated for salt reduction that would introduce extra costs to the process.

6.2.4 Suggested process for metal separation

Single-metal systems

It has been concluded from the present research (discussed in sections 6.2.1) that heavy metal removal by NaDC is not MEUF, but precipitation of metal deoxycholate. Precipitate formation is sufficient with metal removal of 99% or greater when the pH is close to 7, the S/M ratio is adjusted to 2.5 or greater based on the metal concentration, and the equilibration time is at least 3 hours. Room temperature is sufficient for nickel and zinc, but a higher temperature is required for copper. The precipitate can be removed by filtration, centrifugation or possibly microfiltration since ultrafiltration gives only marginal improvement in effluent quality. The suggested process is shown in Fig. 6.1.

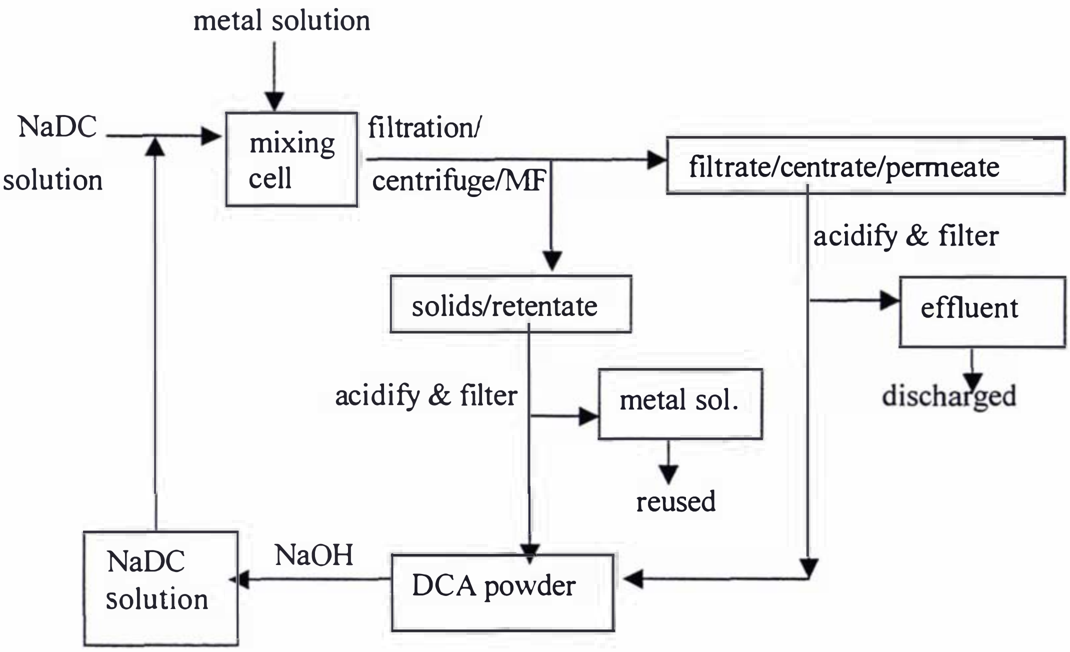


Fig. 6.1 Suggested separation process for single-metal systems

To make the process cost-effective, only one unit operation should be selected for removing the precipitate that would suit any metal at any concentration. Since filtration or centrifugation may not work for all metals at high concentrations, cross-flow MF would be the appropriate selection.

Two-metal systems: separation of copper and nickel mixtures

The present research suggests that separation of copper and nickel from their mixture is good (effluent Cu:Ni molar ratio of 1:42 or greater) if operated in the pH range of 5.5-6.0 at room temperature and after 3-hour equilibration. If the moles of NaDC addition is just twice the moles of copper, copper deoxycholate precipitates and this precipitate can be separated from the solution by simple filtration. Similar to the single-metal system, UF is not necessary, and MF can be used. The suggested process is shown in Fig. 6.2.

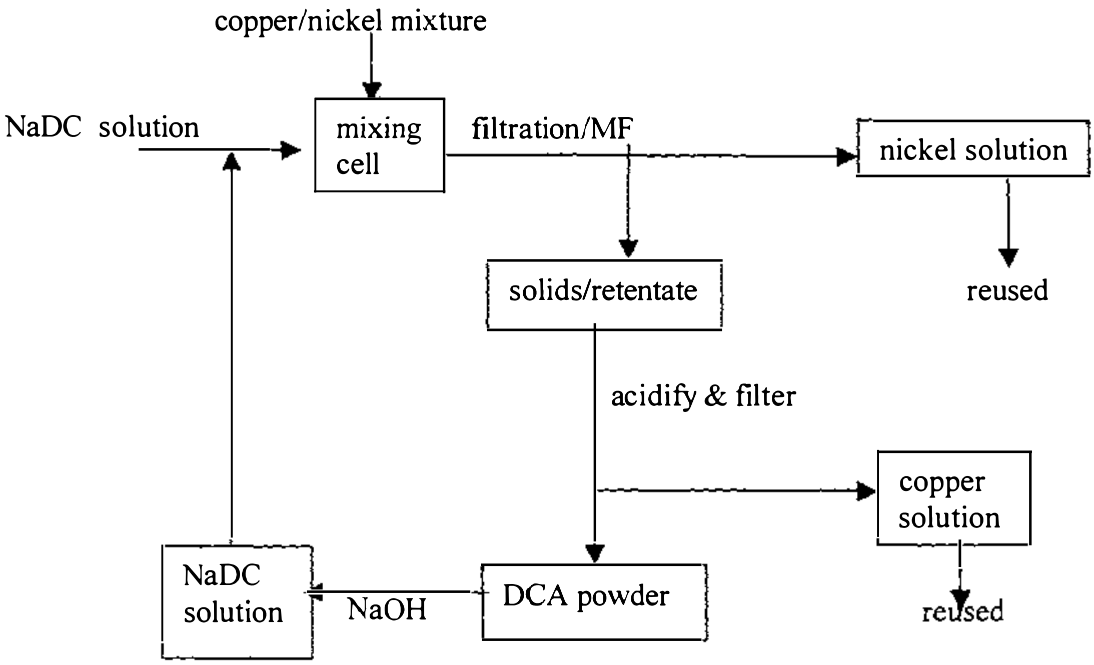


Fig. 6.2 Suggested separation process for copper/nickel mixtures

Comparison of the suggested process with solvent extraction

Surfactant-based separation processes (UF or MF) consume less energy and are environmentally safer than solvent extraction particularly when a natural or biological surfactant is used (Fillipi *et al.* 1998; Hebrant *et al.* 1998). A systematic economic analysis of the suggested process was not done and hence, it could not directly be compared to solvent extraction or any other technique. However, based on the reports of Fillipi *et al.* (1998) and Hebrant *et al.* (1998) as discussed previously, some comparison of the suggested process with solvent extraction can be drawn.

Fillipi *et al.* (1998) reported that a ligand-modified MEUF process requires a 17% higher capital and 43% higher operating costs where the costs of ligand and surfactant were 18%

and 3% respectively of the total operating cost. In the suggested process with DCA, the operating cost would be higher since the DCA cost (US$60/kg) is much higher than the ligand (US$12/kg) and surfactant (US$2.1/kg) used by Fillipi *et al.* (1998). It should be noted that Fillipi *et al.* (1998) assumed a ligand recovery of 75% per cycle. In the suggested DCA process, the DCA recovery was 90% per cycle, but even allowing for that the DCA cost per cycle would be in the order of US$ 6-7 per kg. Thus the DCA process would be costlier than the solvent extraction or the LM-MEUF processes. Hence a more economical biological surfactant or ligand needs to be sought.

6.3 Conclusion

Since the key parameters are optimised for a NaDC-mediated system, the suggested process will offer good process flux, while keeping the metal rejection closer to 100%. UF is not needed, though it works better than filtration and centrifugation. Thus, cross-flow MF would, probably, be the appropriate selection. Other than the high copper case at a higher temperature, all single-metal operations can be done at room temperature. Separation of copper/nickel mixtures can be achieved at room temperature by simple filtration, and MF can also be used similar to the single-metal systems. However, the DCA process would not be economical than the solvent extraction or the LM-MEUF processes.

Recommendations for future work

From this research, the following work with NaDC has been suggested for further study.

Copper deoxycholate is gelatinous at room temperature and forms a gel layer over the filter or membrane surface reducing greatly the permeation rate. This gel layer fouls the membrane to a great extent. The fouling due to copper deoxycholate becomes extremely severe at a high concentration. Since fouling is less in cross-flow operation due to increased shear at the membrane surface, further work is needed to investigate whether such copper deoxycholate fouling occurs in cross-flow MF at room temperature. The MF nickel removal using NaDC was 99.5% (Table 4.4), but copper and zinc removals were not experimented with. Further work in this area is, therefore, suggested.

Chapter 7

SUMMARY AND CONCLUSION

Surfactant-based UF, more commonly known as MEUF, has potential as an effective technique for removing heavy metals from aqueous systems. Metal ions being too small are allowed to be attached to surfactant macromolecules and thus, are rejected by the UF membranes.

Sodium deoxycholate (NaDC) has been used for a major part of this research. NaDC produces a heterogeneous solution with a metal, in contrast to the homogeneous solution of sodium taurodeoxycholate (NaTDC) with a metal.

The present research with sodium deoxycholate (NaDC) shows that the hydrophobic polyethersulphone membranes are much more effective in removing metal ions, but more vulnerable to flux decline through fouling than the hydrophilic regenerated cellulose membranes. Since metal removal is the prime objective, hydrophobic membranes should be selected for the effectiveness of removal.

Concentration polarization occurs mainly due to the presence of free deoxycholate ions, but soluble metal deoxycholate also contributes to some concentration polarization. In contrast, membrane fouling is caused by insoluble metal deoxycholate and the degree of membrane fouling is different for different metal deoxycholates. The fouling becomes much more severe if the metal deoxycholate is gelatinous such as in the case of copper. In such a severe fouling condition, the operation cannot be completed and the membrane cannot be cleaned making it unsuitable for further use.

The precipitation of insoluble metal deoxycholate is the principal mechanism operative in metal removal from the aqueous solution, in contrast to the assertion of MEUF of Huang *et al.* (1994). However, the formation of insoluble metal deoxycholate from soluble metal deoxycholate is slow in the later stages of the reaction because of the low concentration of solute components. Hence, an equilibration time of 3 hours or greater is required for maximising the formation of precipitate.

The solubility of metal deoxycholate in the presence of other components in the solution contributes to the permeate metal concentration. The solubility increases mainly with increasing neutral salts (e.g., NaCl), but decreases with increasing NaDC due to the common ion effect, which is predominant over other effects. Thus, a S/M ratio of 2.5, though sufficient for high metal concentrations, may not be sufficient for low metal concentrations in the feed, particularly in the case of nickel where a higher S/M ratio is necessary.

When the temperature is raised high (up to 50^0C) from room temperature, the metal removal by NaDC is not significantly affected, but the permeate flux is greatly increased. On the other hand, as the pH increases from the normal value (~7), metals are precipitated as metal hydroxide that forms preferentially over metal deoxycholate. Metal hydroxide precipitate does not foul the membrane and results in high permeate flux.

From a single-metal component aqueous solution, a metal removal of greater than 99.9% has been achieved using NaDC with optimisation of parameters. About 90% of the DCA added to the process can be recovered and reused that reduces the material cost.

Different metal ions have differential affinity for the deoxycholate ions, which results mainly from the difference in solubility of their deoxycholates in water. In separating individual metals from their binary mixtures, NaDC shows good selectivity for copper over nickel, but poor selectivity for copper over zinc or zinc over nickel. The best separation of binary mixtures is achieved when the feed pH lies between 5.5 and 6.0. The separation of individual metals from ternary mixture of copper, nickel and zinc is also poor. Therefore, separation of copper and nickel from their mixtures by NaDC can have potential for application on an industrial scale.

The mixture of metal and NaTDC solutions does not show formation of precipitate. Hence, MEUF appears to be the only mechanism for metal separation when NaTDC is used as the surfactant. The membrane fouling is less in the NaTDC case compared to that in the NaDC case. However, NaTDC requires a high S/M ratio for any significant removal of metal ions; for example, a S/M ratio of 8 is required to remove 95% of metal ions. This high S/M ratio makes the process with NaTDC uneconomical since NaTDC is very expensive compared to other surfactants and cannot be easily recovered from the solution. Therefore, although NaTDC has the potential for removing heavy metals from the aqueous solution through MEUF with less membrane fouling, its application as a surfactant may not be feasible from an economic point of view.

Two NaDC-mediated processes are, therefore, proposed based on this research. To separate metal ions from a single-metal aqueous solution, cross-flow MF can be used at room temperature for nickel and zinc and, probably, at a higher temperature for copper. Copper/nickel mixture can be separated by filtration at room temperature, but MF can also be used. Both processes will offer high separation efficiency and reasonable process flux. However, the DCA process would not be economical than the solvent extraction or the LM-MEUF processes as reported in the literature.

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APPENDIX A

Estimate of precision of analytical results

Nickel

The AA spectrophotometer usually measured the nickel concentration at 232 nm wavelength with a working limit of up to 8.0 mg/L. The calibration curve ('absorbance vs time' graph) was produced using 2, 4, 6 and 8 mg/L standard solutions of nickel.

A standard solution containing 3.65 mg/L of nickel was analysed by AA on different days using a calibration curve generated on that particular day. The nickel concentrations (in mg/L) were 3.35, 3.39, 3.41, 3.46, 3.48, 3.51, 3.54, 3.58, 3.59 and 3.47. The average value (x) and standard deviation (s) of this set of data were 3.478 and 0.0796 respectively. The average value can be reported together with the confidence limits (e.g., 95%) as $x \pm ts/\sqrt{n}$ where n is the number of observations and t is the appropriate value of Student's t for (n-1) degrees of freedom (Kellner *et al.* 1998). Hence, with the 95% confidence limit, the average value of the aforementioned set of data becomes
$3.478 \pm 2.26*0.0796/\sqrt{10} = 3.478$ ● 0.057.

To indicate the precision of the result instead of a specific estimate, the "significant figure convention" has been found more appropriate (Kellner *et al.* 1998) and applied to report the present experimental results. The significant figures contain all the digits known with certainty plus the first uncertain digit (Kellner *et al.* 1998; Pecsok *et al.* 1976; Skoog *et al.* 1988). In the aforementioned set of data, no digits after the decimal point are certain. Taking one decimal as the uncertain digit, two significant figures are appropriate to report the above result. Hence, the average value can be reported with the 95% confidence limit as 3.5± 0.1.

The AA method measured the theoretical nickel concentration (i.e. 3.65 mg/L) to be 3.5 mg/L, which was about 5% lower and might be due to systematic errors. This lower value made an alternative method necessary for obtaining better nickel results. Since the colorimetric dimethylglyoxime method was available for measuring the nickel concentrations, it was used in this research as an alternative to the AA method. The standard sample containing 3.65 mg/L of nickel was analysed by the colorimetric method that gave the nickel concentrations (in mg/L) of 3.58, 3.62, 3.66, 3.65 and 3.59. The average value and the standard deviation of this set of data were 3.62 and 0.04 respectively. With the 95% confidence limit, the average value of the set of data can be written as 3.62 ± 2.78*0.04/√5 = 3.62 ± 0.05. According to the "significant figure convention", this result can be presented with two significant figures as 3.6 ± 0.1.

Table A.1

Comparison between the AA and the colorimetric results of nickel

Sample	AA results (mg/L) (x ± ts/√n)	Colorimetric results (mg/L) (x ± ts/√n)
3.65 mg/L Ni solution	3.48 ± 0.06 = 3.5± 0.1	3.62± 0.05=3.6 ± 0.1
MEUF permeate	4.81± 0.07 = 4.8± 0.1	5.07± 0.06=5.1 ± 0.1

The AA method and colorimetric methods were compared by the results of two identical samples shown in Table 4.1. The nickel concentrations measured by the colorimetric method were found to be 3-5% higher than the AA results. The colorimetric method thus appeared to be more accurate for measuring the nickel concentration and was used for samples from the single-metal systems of nickel.

In colorimetric analysis, the permeate samples were not diluted when their nickel concentrations fell within the range of calibration graph (0-20 mg/L). The presence of DCA was thought to affect the formation of colour complexes and thereby, the final concentration measurements. A MEUF permeate sample was analysed with and without removing DCA, and their nickel concentrations with the 95% confidence limit were 11.3±0.2 mg/L and 11.8±0.2 mg/L respectively. This indicated that the final nickel concentration was slightly lower when DCA was present. The theoretical DCA concentration in the aforementioned permeate sample (containing DCA) was about 0.5 mM and it was reduced to 0.1 mM during colorimetric analysis since 5 ml of sample was diluted to 25 ml. A higher reduction in nickel concentration might be obtained if a higher amount of DCA were present. Therefore, any DCA present was precipitated and filtered out before the sample was ready for colorimetric analysis.

Based on the "significant figure convention" and above results, the concentration values obtained directly from AA analysis (i.e. 0.5-8 mg/L) or colorimetric analysis (i.e. 0.5-20 mg/L) can be reported as the average values with two significant figures. Numerical calculations such as addition, subtraction, multiplication and division have been used alone or in combination to report the experimental results from the directly measured values. The examples are rejection ratio and separation factor, where the uncertainty associated with individual numbers can be significant. According to Cleland (1983), the resultant uncertainty in adding or subtracting numbers is the square root of the sum of squares of the individual uncertainties and the resultant uncertainty in multiplying or dividing numbers is the square root of the sum of squares of percentage uncertainties in the individual numbers. Zeros between nonzero digits have been considered significant irrespective of the decimal point (Kellner *et al.* 1998).

Using the above convention, the rejection (expresses as percentage) in experiment 14 (Table 4.2) is calculated as [{(59.0±0.2)-(3.4±0.1)}/(59.0±0.2)]*100= 94.2 ± 0.5. Since the uncertainty is ±0.5, the rejection may be reported by the nearest round figure (i.e. without decimal places). Nevertheless, this would lead to any rejection of greater than 99.5% to 100%, which would not be appropriate because all the permeates reported in this research contained small amounts of nickel and in such cases, 100% of nickel was not rejected/removed. Therefore, one consistent decimal place in three significant figures is more appropriate in reporting the rejection.

Samples having high or very low nickel concentrations were diluted or concentrated as required for their analysis by the AA method or colorimetric method. The final concentration values of such samples have also been reported with two significant figures because the concentration or dilution factor contained very minor errors. However, a final nickel concentration of greater than 99 mg/L cannot be reported properly with two significant figures. Hence, in the present research with the light of above conventions, two significant figures have been used irrespective of the decimal position for reporting any nickel concentration of 99 mg/L or less, and round figures (i.e. without decimal places) beyond that.

Copper

The AA analysis of copper was done at 324.7 nm wavelength with a working concentration limit of up to 5 mg/L. The calibration curve was produced using 1, 2, 3 and 5 mg/L standard solutions of copper. A standard solution containing 2.54 mg/L of copper was analysed by AA. The 10 replicates gave an average concentration of 2.499 mg/L with the standard deviation of 0.048. With the 95% confidence limit, the average value can be written as $2.499 \pm 2.26 * 0.048/\sqrt{10} = 2.499 \pm 0.034$.

According to the "significant figure convention" already discussed for nickel, two significant figures have been used to report any copper concentration of 99 mg/L or less, and round figures (i.e. without decimal places) beyond that. The above result thus can be reported with the 95% confidence limit as 2.5 ± 0.03, and the measured value is 98.4% of the theoretical value.

Using the reasoning set out in the previous section on nickel, the copper rejection (expressed as percentage) has been reported with three significant figures.

Zinc

The AA analysis of zinc was done at 213.9 nm wavelength using 0.5, 1.0, 1.5 and 2.0 mg/L standard solutions of zinc for producing the calibration curve. A standard solution containing 1.306 mg/L of zinc was analysed. The 10 replicates gave an average concentration of 1.2769 mg/L with the standard deviation of 0.0225. With the 95% confidence limit, the average value can be written as 1.30 ± 0.02 as previously explained, and the zinc rejection (as percentage) has been reported with three significant figures.

Separation factor

Using the "significant figure convention", the separation factor for the copper/nickel system has been reported with two or three significant figures (i.e. without any decimal place), and with two significant figures for other systems (i.e. copper/zinc and zinc/nickel systems).

APPENDIX B

Details of pure water and permeate fluxes

4.3.2.1 Nickel: Effect of variables on MEUF of Ni/NaDC system

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
1	PM10	127	5	4	23	18	6.2
2	PM10	127	6	5	24	19	4.5
3	PM10	100	8	8	22	22	5.3
4	PM10	107	34	32	19	18	3.5
5	PM10	106	37	35	19	18	3.4
6	PM10	128	51	40	25	20	2.5
7	PM10	125	54	43	31	25	2.2
8	PM10	112	58	52	31	28	2.0
9	PM10	130	73	56	43	33	1.5
10	PBCC5	85	12	14	25	29	6.3
11	PBCC5	249	100	40	30	12	1.9
12	PBCC5	234	116	50	63	27	0.88
13	PBCC5	280	125	45	65	23	0.78
14	PBCC5	260	131	50	90	35	0.71
15	PBCC5	187	76	41	43	23	1.4
16	PBCC5	171	51	30	30	18	1.8
17	PBCC5	171	46	27	42	19	1.9
18	PBCC5	276	171	62	134	49	0.53
19	PM30	420	200	48	125	30	0.51
20	YM3	52	47	90	42	81	1.7

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
21	PBCC5	81	31	38	15	19	4.4
22	PBCC5	60	17	28	v. low	-	-
23	PM30	420	226	54	62	15	0.82
24	MF	1375	1100	80	320	23	0.25
25	MF	1375	242	18	50	4	6.0
26	PBCC5	288	94	33	65	23	0.95
27	PBCC5	156	163*	n/a	n/m	-	0.64
28	PBCC5	156	115*	n/a	n/m	-	0.69
29	PBCC5	151	163*	n/a	n/m	-	0.54
30	PBCC5	156	151*	n/a	140	n/a	0.54
31	PBCC5	156	86	55	n/m	-	1.2
32	PBCC5	151	86	57	n/m	-	1.1
33	PBCC5	234	142	60	n/m	-	0.75
43	PBCC5	234	113	48	108	46	0.71
44	PM10	118	62	53	58	49	1.3
45	YM3	53	48	91	47	89	1.6
46	PBCC5	176	51	29	8	5	5.2
47	PBCC5	186	36	19	12	6	6.2
48	PBCC5	168	52	31	51	30	1.7
49	PM10	66	20	30	19	29	5.7
50	YM3	48	45	94	41	85	1.9
51	PBCC5	172	81	47	41	24	1.2

* at 50^0C

n/m = not measured

n/m = not applicable

p.w.f. = pure water flux

4.3.2.2 Copper: Effect of variables on UF of Cu/NaDC system

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
1	PBCC5	218	33	15	20	9	2.0
2	PBCC5	327	70	21	39	12	1.8
3	PBCC5	327	22	7	v. low	-	-
4	PM30	415	33	8	v. low	-	-
5	PBCC5	218	185*	n/a	n/m	-	0.48
6	PBCC5	159	120*	n/a	117	n/a	0.65
7	PBCC5	370	400*	n/a	n/m	-	0.18
8	PBCC5	352	477*	n/a	n/m	-	0.14
9	PBCC5	337	209	62	n/m	-	0.33
10	PBCC5	330	241	73	n/m	-	0.32

* at 50^{0}C

n/m = not measured

n/m = not applicable

4.3.2.3 Zinc: Effect of variables on UF of Zn/NaDC system

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
1	PBCC5	281	167	59	160	57	0.50
2	PBCC5	312	235	75	230	74	0.33
3	PBCC5	235	73	31	31	13	1.6
4	PM30	410	210	51	78	19	0.53
5	XM100	265	140	53	47	18	1.0
6	PBCC5	390	480*	n/a	n/m	-	0.16
7	PBCC5	343	500*	n/a	n/m	-	0.16
8	PBCC5	374	390*	n/a	n/m	-	0.21
9	PBCC5	343	430*	n/a	n/m	-	0.19
10	PBCC5	343	235	69	n/m	-	0.36
11	PBCC5	343	240	70	n/m	-	0.35
18	PBCC5	304	225	74	179	59	0.37
19	PBCC5	226	155	69	n/m	-	n/m
20	PBCC5	304	130	43	n/m	-	n/m

* at 50^{0}C

n/m = not measured

n/m = not applicable

4.3.3.1 Cu/Ni system with NaDC

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
1	PBCC5	240	200	83	164	68	0.42
2	PBCC5	249	215	86	180	72	0.40
3	PBCC5	360	296	82	265	74	0.33
4	PBCC5	343	309	90	275	80	0.27
5	PBCC5	327	312	95	280	86	0.26
6	PBCC5	208	187	90	170	82	0.55
8	PBCC5	187	140	75	95	51	0.70

4.3.3.2 Cu/Zn system with NaDC

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
1	PBCC5	366	359	98	345	94	0.25
2	PBCC5	152	135	89	120	79	0.71
3	PBCC5	360	348	97	314	87	0.27
5	PBCC5	218	214	98	183	84	0.46
6	PBCC5	265	250	94	245	92	0.38

4.3.3.3 Zn/Ni system with NaDC

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
1	PBCC5	210	206	98	200	95	0.45
2	PBCC5	241	238	98	200	83	0.41
3	PBCC5	327	321	98	300	92	0.30
5	PBCC5	249	244	98	215	86	0.40
6	PBCC5	73	71	97	65	89	1.3

4.3.4 Cu/Zn/Ni system with NaDC

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
3	PBCC5	156	154	99	153	98	0.62

4.3.5.1 Cu/Ni system with NaOH

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
1	PBCC5	163	163	100	156	96	0.55
2	PBCC5	343	343	100	335	98	0.27

4.3.5.2 Cu/Zn system with NaOH

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
1	PBCC5	125	125	100	122	98	0.62

4.3.5.3 Zn/Ni system with NaOH

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
1	PBCC5	122	122	100	115	94	0.70

4.3.5.4 Cu/Zn/Ni system with NaOH

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
1	PBCC5	327	326	100	315	96	0.62

5.4.1.1. Nickel: Effect of variables on MEUF of Ni/NaTDC system

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
1	PBCC5	293	117	40	103	35	0.38
2	PBCC5	320	120	38	93	29	0.41
3	PBCC5	366	128	35	92	25	0.42
4	PBCC5	374	124	33	69	18	0.47
5	PBCC5	328	159	48	127	39	0.32
6	PBCC5	265	109	41	87	33	0.46
7	PBCC5	239	84	35	59	25	0.67
8	YM3	50	49	98	49	98	0.92
9	UM2	34	19	56	16	47	2.6
10	PBCC5	171	75	44	70	41	1.1
11	PBCC5	249	100	40	92	37	0.80
12	PBCC5	234	109	47	102	44	0.80

5.4.1.2. Copper: Effect of variables on MEUF of Cu/NaTDC system

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
1	PBCC5	351	140	40	105	30	0.58
2	PBCC5	359	125	35	87	24	0.41
3	PBCC5	327	106	32	72	22	0.47
4	PBCC5	382	115	30	73	19	0.47
5	PBCC5	226	75	33	55	24	0.68
6	PBCC5	245	70	29	42	17	0.83
7	YM3	50	45	90	45	90	1.0
8	UM2	27	11	41	9	33	3.8
9	PBCC5	187	70	37	41	22	0.95
10	PBCC5	242	108	45	85	35	0.75

5.4.1.3. Zinc: Effect of variables on MEUF of Zn/NaTDC system

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
1	PBCC5	312	137	44	94	30	0.35
2	PBCC5	343	143	42	75	22	0.53
3	PBCC5	343	133	39	72	21	0.41
4	PBCC5	234	94	40	81	35	0.53
5	PBCC5	253	81	32	58	23	0.67
6	YM3	50	48	96	48	96	0.93
7	UM2	23	14	61	12	52	2.7
8	PBCC5	234	83	35	86	37	0.93
9	PBCC5	265	116	44	105	40	0.70

5.4.2.1 Cu/Ni system with NaTDC

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
1	PBCC5	234	73	31	66	28	0.72
2	PBCC5	30	22	73	20	67	2.2
3	PBCC5	187	39	21	32	17	1.3

5.4.2.2 Cu/Zn system with NaTDC

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
1	PBCC5	210	58	28	45	21	1.1

5.4.2.3 Zn/Ni system with NaTDC

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
1	PBCC5	218	78	36	70	32	0.63

5.4.2.4 Cu/Zn/Ni system with NaTDC system

Expt. No	Mem-brane	Pure water flux	Initial permeate flux		Final permeate flux		Total UF time
		L/h/m^2	L/h/m^2	% of p.w.f.	L/h/m^2	% of p.w.f.	hour
1	PBCC5	203	51	25	41	20	1.1
2	PBCC5	198	47	24	38	19	1.2

APPENDIX C

Fractional precipitation calculation

4.3.5 Selective precipitation of metals by NaOH

The solubility products of $Cu(OH)_2 = 6x10^{-20}$ (Vogel 1961)

$Ni(OH)_2 = 1x10^{-14}$ (Brown 1964)

$Zn(OH)_2 = 4.5x10^{-17}$(Vogel 1961)

$Cu(DC)_2 = 1.2x10^{-15}$ (calculated)

$Ni(DC)_2 = 8.4x10^{-12}$ (calculated)

$Zn(DC)_2 = 1.4x10^{-15}$ (calculated)

4.3.5.1 Cu/Ni system

Hydroxides

Being less soluble, $Cu(OH)_2$ will be precipitated before $Ni(OH)_2$ since its solubility product will be first exceeded.

$Ni(OH)_2$ will be precipitated when OH^- ion concentration is

$$> \sqrt{\{(1x10^{14})/[Ni^{++}]\}}$$

and then both hydroxides will be precipitated simultaneously. When $Ni(OH)_2$ commences to precipitate, OH^- ions will be in equilibrium with both hydroxides and then

$$[OH] = \sqrt{\{S_{Cu(OH)2}/[Cu^{++}]\}} = \sqrt{\{S_{Ni(OH)2}/[Ni^{++}]\}}$$

$$\text{and } \{[Cu^{++}]/[Ni^{++}]\}^2 = S_{Cu(OH)2}/S_{Ni(OH)2}$$

$$= 6x10^{-20}/1x10^{-14}$$

Therefore, $[Cu^{++}]/[Ni^{++}] = 1/408$

Hence, $Ni(OH)_2$ would be precipitated when the Cu ion concentration is approximately 1/400 part of the Ni ion concentration.

If the initial concentrations of both Cu and Ni ions are 2.5 mM, then $Ni(OH)_2$ would be precipitated when

$$
\begin{aligned}
[Cu^{++}] &= (1/408)*(2.5/2000)N \\
&= (1/408)*(2.5/2000)*(63.5*1000) \text{ mg/L} \\
&= 0.19 \text{ mg/L}
\end{aligned}
$$

Deoxycholates

When $Ni(DC)_2$ commences to precipitate, then

$$[DC^-] = \surd\{S_{Cu(DC)2}/[Cu^{++}]\} = \surd\{S_{Ni(DC)2}/[Ni^{++}]\}$$

$$
\begin{aligned}
\text{and } \{[Cu^{++}]/[Ni^{++}]\}^2 &= S_{Cu(DC)2}/S_{Ni(DC)2} \\
&= 1.2x10^{-15}/8.4x10^{-12}
\end{aligned}
$$

Thus, $[Cu^{++}]/[Ni^{++}] = 1/83$

Hence, $Ni(DC)_2$ would be precipitated when the Cu ion concentration is approximately 1/83 part of the Ni ion concentration.

If the initial concentrations of both Cu and Ni ions are 2.5 mM, then $Ni(DC)_2$ would be precipitated when

$$
\begin{aligned}
[Cu^{++}] &= (1/83)*(2.5/2000)N \\
&= (1/83)*(2.5/2000)*(63.5*1000) \text{ mg/L} \\
&= 0.96 \text{ mg/L}
\end{aligned}
$$

4.3.5.2 Cu/Zn system

Hydroxides

When $Zn(OH)_2$ commences to precipitate, OH^- ions will be in equilibrium with both hydroxides and then

$$[OH^-] = \surd\{S_{Cu(OH)2}/[Cu^{++}]\} = \surd\{S_{Zn(OH)2}/[Zn^{++}]\}$$

$$\text{and } \{[Cu^{++}]/[Zn^{++}]\}^2 = S_{Cu(OH)2}/S_{Zn(OH)2}$$

$$= 6x10^{-20}/4.5x10^{-17}$$

Thus $[Cu^{++}]/[Zn^{++}] = 1/27$

If the initial concentrations of both Cu and Zn ions are 2.5 mM, then $Zn(OH)_2$ would be precipitated when

$$[Cu^{++}] = (1/27)*(2.5/2000)N$$

$$= (1/27)*(2.5/2000)*(63.5*1000) \text{ mg/L}$$

$$= 2.9 \text{ mg/L}$$

Deoxycholates

When $Zn(DC)_2$ commences to precipitate, then

$$[DC^-] = \surd\{S_{Cu(DC)2}/[Cu^{++}]\} = \surd\{S_{Zn(DC)2}/[Zn^{++}]\}$$

$$\text{and } \{[Cu^{++}]/[Zn^{++}]\}^2 = S_{Cu(DC)2}/S_{Zn(DC)2}$$

$$= 1.2x10^{-15}/1.4x10^{-15}$$

Thus $[Cu^{++}]/[Ni^{++}] = 1/1$

4.3.5.3 Zn/Ni system

Hydroxides

When $Ni(OH)_2$ commences to precipitate, OH^- ions will be in equilibrium with both hydroxides and then

$$[OH^-] = \sqrt{}\{S_{Zn(OH)2}/[Zn^{++}]\} = \sqrt{}\{S_{Ni(OH)2}/[Ni^{++}]\}$$

and $\{[Zn^{++}]/[Ni^{++}]\}^2 = S_{Zn(OH)2}/S_{Ni(OH)2}$

$= 4.5x10^{-17}/1x10^{14}$

Thus $[Zn^{++}]/[Ni^{++}] = 1/15$

If the initial concentrations of both Zn and Ni ions are 2.5 mM, then $Ni(OH)_2$ would be precipitated when

$[Zn^{++}] = (1/15)*(2.5/2000)N$

$= (1/15)*(2.5/2000)*(65.3*1000)$ mg/L

$= 5.4$ mg/L

Deoxycholates

When $Ni(DC)_2$ commences to precipitate, then

$$[DC^-] = \sqrt{}\{S_{Zn(DC)2}/[Zn^{++}]\} = \sqrt{}\{S_{Ni(DC)2}/[Ni^{++}]\}$$

and $\{[Zn^{++}]/[Ni^{++}]\}^2 = S_{Zn(DC)2}/S_{Ni(DC)2}$

$= 1.4x10^{-15}/8.4x10^{12}$

Thus $Cu^{++}]/[Ni^{++}] = 1/77$

If the initial concentrations of both Zn and Ni ions are 2.5 mM, then $Ni(DC)_2$ would be precipitated when

$[Zn^{++}] = (1/77)*(2.5/2000)N$

$= (1/77)*(2.5/2000)*(65.3*1000)$ mg/L

$= 1.1$ mg/L