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.

Swapan Kumar Sikder

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., >40^0C) 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.

CONTENTS

CHAPTER 4
REMOVAL OF HEAVY METALS USING SODIUM DEOXYCHOLATE: EFFECT OF OPERATING PARAMETERS

CHAPTER 5

LIST OF FIGURES

LIST OF TABLES

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