ADSORPTION-DESORPTION CHARACTERISTICS OF PHENOXYACETIC ACIDS AND CHLOROPHENOLS IN A VOLCANIC SOIL

A thesis presented in partial fulfilment of the
requirements for the degree of *Doctor of Philosophy*
in Process and Environmental Technology Department at Massey University,
Palmerston North, New Zealand.

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1994

To my Late Father

ABSTRACT

A study on the adsorption and desorption behaviour of 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), 2-methyl-4-chlorophenoxyacetic acid (MCPA), 2,4-dichlorophenol (2,4-DCP), 2,4,5-trichlorophenol (2,4,5-TCP) and *para*-chloro-*ortho*-cresol (PCOC), found in high concentrations in a New Zealand landfill. Volcanic soil with an organic matter content of 8.7% was used as adsorbent.

Results of studies to determine the equilibrium sorption behaviour for each chemical showed the adsorption data for both phenoxyacetic acids and chlorophenols could be described by a Freundlich-type isotherm equation, the adsorption capacity followed the order: 2,4,5-T > MCPA > 2,4-D > 2,4,5-TCP > PCOC > 2,4-DCP at all pH and temperature values. Sorption capacity decreased with increasing pH and temperature; the heat of adsorption values indicating chemicals were adsorbed either by physical or hydrogen bonding to the soil surface. Results show only 2-4% of the total surface was occupied indicating chemical adsorption to specific sites present in the soil organic matter. The desorption results indicate isotherm parameters were dependent on the amount of each chemical adsorbed onto the soil. A linear relationship was developed to obtain the desorption parameters from the adsorption isotherm parameters. Desorption experimental results reveal that all the solutes adsorbed could not be desorbed, indicating a fraction of the chemical was resistant to desorption.

A modified Freundlich-type equation described the competitive equilibrium adsorption and desorption of 2,4-D-MCPA, 2,4-D-PCOC and MCPA-PCOC mixtures. The model incorporated competition coefficients and was found to fit measured data, satisfactorily. The competition coefficients were linearly related to the initial concentration of the solutes in case of adsorption, and on the amount of chemical adsorbed for desorption. The results showed that the adsorption capacity of each solute decreased by about 8-12% in presence of the other competing solutes. However, in case of MCPA, the capacity decreased by 31% in the presence of 2,4-D. The desorption results reveal that 2,4-D and MCPA desorbed to a lesser extent in the bicomponent system compared to the corresponding single solute system. Similarly, the desorption of

PCOC was less in the presence of 2,4-D than of MCPA compared to single solute system.

A spinning basket reactor determined the kinetics of sorption for phenoxyacetic acids and chlorophenols. The film-mass transfer coefficients determined from the initial uptake rate data for the first 45 seconds, while the surface diffusion coefficients were obtained by fitting the experimental results with a homogeneous surface diffusion model solution. The desorption diffusion coefficients were found to be of the same order of magnitude as those of adsorption diffusion coefficients. The bicomponent surface diffusion coefficients were found to be slightly smaller (less than 10%) than single solute surface diffusion coefficients and this was due to competition between the solutes.

A surface diffusion model based on equilibrium sorption, film-mass transfer and surface diffusion coefficient along with dispersion was used to predict the soil column data. All the parameters in the model were determined from independent experiments or calculated from literature correlations. The results from the column studies indicate that an increase in the concentration and flow rate resulted in the solutes moving faster in the column. A significant tailing of the chemical was observed at low concentrations for all the solutes. The results indicate that sorption played a dominant role in the transport of chemicals in columns. The breakthrough and elution for phenoxyacetic acids was in the order: 2,4-D > MCPA > 2,4,5-T. For chlorophenols the order was: 2,4-DCP > PCOC > 2,4,5-TCP. The HSDM also used to predict the adsorption and desorption of bicomponent mixtures and the results indicated that the breakthrough and elution occurred earlier than in single solute systems. The order of breakthrough and elution was PCOC > 2,4-D > MCPA.

To conclude, this thesis presents a detailed investigation of the adsorption and desorption characteristics of phenoxyacetic acids and chlorophenols for single and dual component systems in a volcanic soil. This study has identified the mechanisms and processes responsible for the leaching of the chemicals and can be used in remediation of a contaminated soil.

PUBLICATIONS

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ACKNOWLEDGEMENTS

I would like to express heartfelt thanks to Assoc. Prof. S.M. Rao Bhamidimarri and Dr. G. V. Bhaskar for their supervision and criticisms throughout this work.

I am grateful to Dr. G.V. Bhaskar for valuable assistance in numerical analysis and writing the Fortran programs for bi-solute systems.

The assistance of John Alger, Bruce Collins and Wayne Mallet, the workshop staff in the Biotechnology Department for constructing and maintaining the equipment.

Thanks are extended for the assistance of the laboratory staff, Ann-Marie and Janice in obtaining chemicals.

The financial support of Massey University is gratefully acknowledged.

Thanks are also to Peter Gray, Chemical Engineering Department, University of Queensland, for determining the surface area of the soil.

I wish to extend my appreciation to Pinthita Mungkarndee, Dianesius Wongso, Peter Setter and Robert Petrie, Tania, Cryn, Roger, Patty Ratumaitavuki, Ranjan Sharma, Graham Manderson, Sachin Davankar, Venkat and Jyothi, Srinivas, Prabhakar and Mike Sahayam for their friendship and sense of humour.

I also thank Celia and Barry Robertson, Ian Maddox and Noemi for their friendship and hospitality.

Finally, my sincere thanks to my late father and mother, brothers, sisters and to my wife *Gayatri* to whom I will be forever indebted for their guidance and support throughout my life.

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