# STUDY ON HEAVY METAL ADSORPTION BY CHITOSAN BIOPOLYMER

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Thesis submitted in partial fulfillment of the requirements for the degree

Master of Science in Materials Science and Engineering

Department of Materials Science and Engineering

University of Moratuwa Sri Lanka

August 2015

#### **Declaration**

I declare that this is my own work and this thesis with the title "Study on Heavy metal Adsorption by Chitosan Biopolymer" does not incorporate without acknowledgement any material previously submitted for a Degree or Diploma in any other University or Institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written or orally communicated by another person except where due reference is made in the text.

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#### **Abstract**

Heavy metal pollution is a serious problem to aquatic ecosystems because some of these metals are potentially toxic even at very low concentrations. Chitosan, a biopolymer produced from crustacean shells, has applications in various areas, particularly in drinking water and wastewater treatment due to its ability to remove metallic ions from solutions. The purpose of this research work was to study the adsorption of cadmium and lead ions into chitosan, produced from shrimp shells at the laboratory level. Shrimp type "penaeus monodon" (giant tiger prawn) was used to synthesis the chitosan. The main characteristic properties such as degree of deacetylation (DD); the amount of amine groups in chitosan, viscosity, crystallinity and thermal analysis were done by using Fourier transform infrared spectroscopy, Brookfield viscometer, X-ray spectroscopy, thermo gravimetric analysis (TGA) and differential thermal analysis (DTA). Chitosan, with a degree of deacetylation between 80% - 95% was used in the experimental part and the flake sizes were smaller than 0.25mm. Experimental work involved the determination of the adsorption isotherms and kinetic studies for each metallic ion in a batch system.

Effect of Degree of deacetylation (DD) of the chitosan, effect of initial pH of the metal ion solution, effect of particle size, effect of initial heavy metal concentration, and effect of chitosan dosage were studied. The results showed that the adsorption capacity depends strongly on pH of the solution, DD of chitosan and slightly depends on the particle size. According to the results, pH values at 6.5 for cadmium and pH values at 4.5 for lead show higher adsorption capacity. High DD chitosan showed higher adsorption capacity mainly due to the higher number of active amino groups in high DD sampleronic Theses & Dissertations

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Simplified kinetic models such as pseudo-first-order, pseudo-second-order, Elovich model and intra-particle diffusion model were used to determine the rate limiting step. Both linear and non-linear According to the kinetic models pseudo second order model best described the adsorption process. Both linear and non-linear models and Elovich model best described the adsorption process. Multilinearity in the intraparticle diffusion model suggested that the adsorption of heavy metal consists of two major steps, due to the different pore sizes of chitosan.

Equilibrium experimental data were analyzed by using two different isotherm models namely, Langmuir and Freundlich. According to the results, adsorption process of cadmium and lead heavy metals is heterogeneous and multilayer adsorption as it best fit with the Freundlich isotherm model. According to the thermodynamic experiments, adsorption process is favorable and physical adsorption was predominant in the adsorption process. Desorption of the heavy metals was possible by using different regeneration solutions.

Key words: Chitosan, Heavy metals, Isotherm, Kinetics, Adsorption

### Acknowledgment

My foremost sincere gratitude is expressed to my supervisor, Dr. S.U. Adikary who gave me the opportunity to carry out this research work and for the immense help and guidance given throughout the project work.

I would also like to thank Dr. P.G. Rathnasiri, progress review committee chair, and Dr. N.M.V.K. Liyanage, M.Sc coordinator of the department, for providing correct guidance through the project work. I also like to express my sincere gratitude to Dr. D.A.S. Amarasinghe, who provided valuable instructions during my research work.

I also like to express my sincere gratitude to senate research committee (SRC) grant of University of Moratuwa, for providing financial assistantship to this research work (Grant No. SRC/LT/2012/12).

In addition to that, I like to express my thanks to all the academic staff members of the Department of Materials Science and Engineering, University of Moratuwa for their assistance and contribution to my research work.

University of Moratuwa, Sri Lanka.

I would be express my sincere gratitude to Mr. D.M.R.K. Dissanayake, PhD www.lib.mrt.ac.lk student at Department of Chemistry, University of Colombo for his excellent support and contribution during my research work.

I also like to thank Mr. K.G.N Thilawala, Mrs. K.A.D. Rathnayake, Mr. H.V.H.H. Senavirathne for their support during my research work.

I am grateful to Mr. S.D. Karunaratna and Mr. Abeyarathne and other nonacademic staff members of the Department of Materials Engineering, for their assistance and contribution to my research work.

In conclusion, I would like to express my pardon if I have inadvertently omitted the name of those to whom thanks is due.

J.M. Unagolla

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# List of terms, abbreviations and symbols

| DA               | Degree of acetylation   |
|------------------|---|
| DD               | Degree of deacetylation   |
| DTA              | Differential Thermal Analysis   |
| FTIR             | Fourier Transform Infrared Spectroscopy   |
| NMR              | Nuclear Magnetic Resonance  |
| PFO              | Pseudo first order  |
| PSO              | Pseudo second order   |
| TGA              | Thermogravimetry Analysis   |
| Ce               | liquid phase adsorbate concentration in equilibrium (mg/L)                                |
| $C_0$            | Initial metal ion concentration of the solution (mg/L) University of Moratuwa, Sri Lanka. |
| $\mathbf{C}_{t}$ | Metalled concentration of the solution at issertations www.lib.mrt.ac.lk                  |
| $C_{\mathrm{f}}$ | Final metal ion concentration of the solution (mg/L)                                      |
| $\mathbf{K}_1$   | Pseudo first order rate constant (min <sup>-1</sup> )                                     |
| $K_2$            | Pseudo second order rate constant (g/mg.min)  |
| $K_{d}$          | Distribution ratio (L/g)  |
| $K_{\mathrm{F}}$ | Freundlich constant   |
| $K_{\rm i}$      | Intra-particle diffusion rate constant (mg/gmin <sup>0.5</sup> )                          |
| $K_{L}$          | Langmuir constant   |
| m                | Mass of the adsorbent (g)   |
| $q_{e}$          | Adsorption capacity at equilibrium (mg/g)   |

- q<sub>t</sub> Adsorption capacity at time t (mg/g)
- $q_{m}$  Monolayer adsorption capacity (mg/g)
- R<sub>L</sub> Langmuir separation factor
- R Universal gas constant (8.314 J/mol.K)
- T Absolute solution temperature (K)
- V Volume of the aqueous metal ion solution (L)
- $\Delta G^0$  Standard state Gibbs free energy change
- ΔH<sup>0</sup> Standard state Enthalpy change
- $\Delta S^0$  Standard state Entropy change
- $\alpha$ ,  $\beta$  Elovich constants
- 1/n heterogeneity factor Theses & Dissertations www.lib.mrt.ac.lk