UNIVERSITI PUTRA MALAYSIA

HEAVY METALS BIOSORPTION BY POWDERED RHIZOPUS OLIGOSPORUS BIOMASS

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BY

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Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of Master of Science in the Faculty of Engineering, Universiti Putra Malaysia.

December 1997

ACKNOWLEDGEMENTS

First of all, I wish to express my utmost thanks and appreciation to my chairman, Dr Fakhru'l-Razi Ahmadun and members of the Supervisory Committee, Dr Arbakariya Ariff and Dr Mohd Ali Hassan for their guidance and enlightening advice throughout the duration of this study

I also wish to express my sincere appreciation to Mr Rosli, Mdm Renuga, Mdm Aluyah, Ms Madihah and Ms Rosfarizan for their assistance and help during my laboratory work

Lastly, I wish to express my whole-hearted thanks to my family members for giving me support and love

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LIST OF ABBREVIATIONS

b	Dissociation constant
C_{eq}	Concentration of metal in solution at equilibrium
C_i	Initial heavy metal concentration
n	Freundlich constant
k	Freundlich constant
m	Amount of biomass
q	Concentration of metal uptake per unit weight of biomass
Q	Maximum concentration of metal uptake per unit weight of biomass in forming a complete mono-layer on cell surface
v	The volume of heavy metal bearing solution

Abstract of this thesis submitted to the Senate of Universiti Putra Malaysia in partial fulfilment of the requirements for the degree of Master of Science.

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December 1997

Chairman: Dr. Fakhrul'l-Razi Ahmadun

Faculty: Faculty of Engineering

The biosorption of several metals by powdered biomass of *Rhizopus oligosporus* was investigated. Cells of *Rhizopus oligosporus* were cultured, harvested, washed, oven dried and mixed in solutions containing lead, copper, cadmium and aluminium ions. After an equilibration period, the biomass was separated from the metal bearing solution and the content of heavy metals were determined by an Atomic Adsorption Spectrophotometer. The biosorption of metal ions was increased with increasing initial concentration of heavy metal. The heavy metal uptake capacity increased in the order: copper (73.50 mg/g) > lead (60.90 mg/g) > cadmium (30.15 mg/g) > aluminium (26.60 mg/g). Langmuir Adsorption Model was suitable for describing the biosorption of lead, cadmium, aluminium and copper. Reciprocal Langmuir Transformation and Scatchard analysis revealed that different types of binding sites are involved in the biosorption process. pH regulation of the process can enhance the biosorption capacity for all metals tested The optimum pH for lead, cadmium, aluminium and copper are 5, 4, 4 and 6 respectively The possibility for desorbing the metals from loaded biomass using HCl and NaOH were tested The desorption efficiency for HCl and NaOH increased with increasing concentration of HCl and NaOH HCl wass more efficient than NaOH The possibility of removing heavy metal from industrial wastes was also investigated For electroplating wastes, the heavy metals uptake capacities increased in the order lead (0 44 mg/g) > cadmium (0 11 mg/g) > copper (0 09 mg/g) For aluminium wastes, the heavy metals uptake capacities increased in the order cadmium (0 12 mg/g) > copper (0 10 mg/g)

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia untuk memenuhi sebahagian daripada syarat untuk mendapat Ijazah Master Sains

BIOSERAPAN LOGAM OLEH SERBUK KERING KULAT *RHIZOPUS OLIGOSPORUS*

Oleh

LING TAU CHUAN

Disember 1997

Pengerusi Dr Fakrul'l-Razi Ahmadun

Fakulti Fakulti Kejuruteraan

Keupayaan dan kecekapan serbuk kering *Rhizopus oligosporus* sel untuk menyerap beberapa logam seperti plumbum, kadmium, aluminium dan kuprum telah dikaji Sel *Rhizopus oligosporus* dikulturakan, dituai, dibilas dengan air suling dan dikeringkan dengan menggunakan oven Serbuk kering sel ditindakbalaskan dengan larutan yang mengandungi kepekatan logam tertentu Setelah mencapai keseimbangan, serbuk kering sel akan dipisahkan daripada larutan secara turasan Kandungan logam akhir akan ditentukan dengan menggunakan Atomic Adsorption Spectrophotometer Adalah didapati bahawa logam yang diserap adalah bertambah dengan bertambahnya kepekatan logam permulaan Jumlah logam yang diserap oleh sel disusun secara menaik ialah kuprum (73 50 mg/g) > plumbum (60 90 mg/g) > kadmium (30 15 mg/g) > aluminium (26 60 mg/g) Langmuir Adsorption Model adalah sesuai untuk menerangkan tindak balas bioserapan ini Analisis Reciprocal Langmuir

Transformation dan Scatchard menunjukkan lebih daripada sejenis tapak aktif terlibat dalam bioserapan Kawalan pH didapati dapat memperbanyakkan jumlah kuantiti logam yang diserap pH yang optimum untuk plumbum, kadmium, aluminium dan kuprum masing-masing ialah 5, 4, 4 dan 6 Logam yang telah diserap oleh sel juga dapat dikeluarkan daripada tapak aktif sel dengan menggunakan HCl dan NaOH Adalah didapati HCl lebih berkesan Lagipun, sel juga dapat menyerap logam-logam yang terdapat pada sisa industri Untuk sisa electroplating, jumlah logam yang diserap disusun secara menaik ialah plumbum (0 44 mg/g) > kadmium (0 11 mg/g) > kuprum (0 09 mg/g) Untuk sisa aluminium pula, jumlah logam yang diserap disusun secara menaik ialah kadmium (0 12 mg/g) > kuprum (0 10 mg/g)

CHAPTER I

INTRODUCTION

The rapid pace of industrialisation has increased the number of heavy metal polluting sources in the manufacturing sector significantly The main heavy metals polluting sources are effluents from industries such as textile industry, basic steel works, electroplating, batteries and metal finishing The most common heavy metal contaminants are lead, cadmium, copper, chromium and aluminium Two kinds of methods used to treat heavy metal waste commercially now are physical and chemical processes However, biological methods increasingly appear as an alternative to the chemical and physical methods which have been proven to be inefficient when used to treat high volume but low metals concentration effluents (Schmiechen et al , 1992)

The diverse physiological metabolic and characteristics of micro-organisms such as fungi, algae, bacteria and yeast and their ability to thrive in a variety of environment may be exploited for the purpose of removing heavy metals from aqueous industrial effluent and metals recovering from industrial processes

A number of mechanisms take place during the removal of heavy metals from aquatic solutions by these microbial biomass These mechanisms include complexation, coordination, adsorption and ion exchange These mechanisms can be divided into two phases namely, passive and active process Various parameters such as biomass concentration, biomass characteristic, types of heavy metals, heavy metals concentration, solution pH and growth media affect these mechanisms, thus affecting biosorption process

The aims of this study are as follows

1 To investigate the ability of powdered biomass of *Rhizopus oligosporus* to adsorb lead, cadmium, copper and aluminium

2 To study the effect of biomass concentration and solution pH on biosorption capacity

3 To analyse the kinetics of biosorption of various heavy metals by powdered biomass of *Rhizopus oligosporus* using several sorption isotherms models such as Langmuir Model, Scatchard plots and Reciprocal transformation of the Langmuir model

4 To study the possibilities of desorbing the metals from loaded biomass and heavy metal removal from industrial effluent such as electroplating wastes and aluminium wastes by biomass

CHAPTER II

LITERATURE REVIEW

Heavy Metal Pollution and Toxicity

Heavy metals are defined as metals having a density greater than 5 g/l or having an atomic number greater than that of iron (Passaw et al , 1961) Phipps (1976) defined toxic heavy metals as `elements which have neither an essential nor beneficial but positively catastrophic effect on normal metabolic functions, even when present in only small amounts Generally, they consist of forty elements in the Periodic Table except those in Groups I and II Heavy metals are widely used in textile, electroplating, basic steel works and metal finishing industries Heavy metals enter our body through inhalation, food chain and drinking water Several million peoples world-wide suffer currently from sub-clinical heavy metals poisoning due to metal contamination of foods and beverages which were identified as major contributors (Nriagu, 1988) High level heavy metal exposure can cause numerous disorders such as growth retardation, morbidity and pathological changes

Lead

Lead is one of the most useful heavy metals used in modern industries such as batteries and electrical, electroplating, ceramic glazes and gasoline industries. There are a variety of these industries in Malaysia. Despite its value, lead is also a very toxic metal. Elevated levels of lead in marine environment can be traced to industrial discharges from these industries (Table 1). These industries are the main polluter in the manufacturing sector and are the industries have low compliance rate with the Environmental Quality (Sewage and Industrial Effluents) Regulation 1979 (*Environmental Quality Report 1994*).

High-level lead exposure can cause neurological disorders such as muscular tremor, fatigue and headache. Furthermore, it also can damage the kidneys and nerves system. Low-level exposure can cause central systems cause central nervous systems disorder. Exposure to small amounts of lead also can seriously affect mental development.

Table 1

Lead Pollution in Malaysia

Cases	**References**
Lead level as high as 3 0 µg/g accumulated in anchovies tissues	Almah et al (1992)
It was found that lead level in many rivers had exceeded the Interim National Water Quality Standards for class III	Environmental Quality Report 1994 Department of Environment, Malaysia (1995)
Lead was one of the main polluter which polluted the marine environment	Environmental Quality Report 1993 Department of Environment, Malaysia (1994)

Copper

Copper is mainly released into the environment by industrial wastes and this caused a serious health hazard Copper is widely used in electroplating, metal finishing and chemical industries (Cherimisinoff, 1995) In Malaysia, there are a lot of industries based on electronic and chemical processes Inevitably, these industries has caused a pollution problem Proper system to treat the wastes from these industries are much desired Furthermore, the indiscriminate disposal of effluent from these small and medium industries will worsen the pollution problem Cooper ion is released into the water and finally enter into human body through the food chain It is deposited in the pancreas, brain and liver which cause “Wilson’s disease” It was found that copper level in several rivers in Malaysia had exceeded the Interim National Water Quality Standards for Class III (Environmental Quality Report, 1994)

Cadmium

Cadmium is widely used in paint pigments, plastics and electroplating industries (Cherimisinoff, 1995) The mismanagement of effluent from these types of industry can cause a serious health hazard When cadmium enter into the human body it bounds to some soft tissues such as kidneys and livers This will cause serious long term and short term effects A disease known as "Itai-Itai" in Japan is associated with cadmium poisoning which caused multiple fractures arising from osteomalacia (Murata et al , 1970) The intensification of industrialisation in Malaysia has increased cadmium polluting problem (Table 2)

Table 2

Cadmium Pollution in Malaysia

Cases	References
Cadmium levels accumulated in fish tissues increased significantly	Babji et al (1986)
Cadmium levels were found to have exceeded the standard of 0 01 mg/l in 3 rivers in Terengganu namely, Sungai Terengganu (0 017 mg/l), Sungai Setiu (0 024 mg/l) and Sungai Dungun (0 014 mg/l)	Environment Quality Report 1993 Department of Environment, Malaysia (1994)
Cadmium levels was found in the coastal waters of Malaysia (0 013 mg/l)	Environment Quality Report 1990 Department of Environment, Malaysia (1991)
Cadmium level as high as 0 04 µg/g was found in rice in various areas of Asia	Watanabe et al (1989)

Aluminium

Aluminium is one of the heavy metals widely used in aluminium anodising industry and electroplating industry At present, treatment technology for aluminium removal is essentially limited to chemical precipitation by pH adjustment However, increasing public awareness of the detrimental consequences associated with the existence of aluminium in the environment has led to significant concern by the public (Wengtsson et al , 1995) Furthermore, aluminium hydroxide (Alum) is normally used to treat water and subsequently used as drinking water The alum enhanced the sedimentation rate of suspended solids However, the alum residues left in tap water will cause health problem Aluminium poisoning giving rise to tremors, loss of memory and jerking have first reported in 1921 and there is evidence that aluminium can be a neurotoxin (Albery, 1996)

Physical and Chemical Treatment of Heavy Metal Wastes

Carbon Adsorption

Heavy metals may be removed from aqueous waste with activated carbon by adsorption of the chemical substances on to a carbon matrix However, the use of adsorption by activated carbon need a high capital investment and inefficient (Schmiechen et al , 1992) The disposal of carbon contaminated with heavy metals can cause a serious impact on environment Furthermore, the operating cost involved to reactivate carbon is very high For example, energy requirements for systems employing thermal reaction is 14,000 - 18,600 KJ/Kg of carbon (Edward and Johnson, 1986)

Chemical Precipitation

Precipitation processes using sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) and calcium carbonate ($CaCO_3$) are a cheaper method The energy consumption and associated costs are low as compared with other methods However, this method is judged that has minimal potential for the heavy metal purification application (Schmiechen et al , 1992) This is because non target materials are precipitated together with the heavy metal thus affecting the heavy metal recovery process Furthermore, this process is a time-dependent physical process (Cheremisnoff, 1995)

Evaporation

Evaporation is the process that heats the liquids, vents the vapours and concentrates the heavy waste into a slurry form The major disadvantages of evaporation are high capital investment and operating cost It has been proven to be inefficient in treating aqueous hazardous wastes containing moderately volatile organic substances (Edward and Johnson, 1986)

Incineration and Air Stripping

Incineration is a high temperature oxidation process The air stripping is a process in which water at elevated temperatures is used to separate volatile components of a liquid The major disadvantages of incineration and air stripping methods are the releases of additional toxic materials such as dioxin (Levin and Geact, 1993) Dioxin is both a potent carcinogen and chemical that