BIOSORPTION OF HEAVY METALS (Cu, Zn, Cd and Pb) BY MARINE ALGAE BIOMASS

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SCHOOL OF SCIENCE AND TECHNOLOGY
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Prof. Dr. Marcus Jopony _____

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ABSTRACT

BIOSORPTION OF HEAVY METALS (Cu, Zn, Cd and Pb) BY MARINE ALGAE BIOMASS

The use of biological materials or biomass as adsorbent for the removal of heavy metals from aqueous solutions or wastewater is increasingly getting attention. In the present studies, biosorption of heavy metals (i.e Cu, Zn, Cd and Pb) by non-living biomass of marine algae, *Sargassum* sp., was investigated according to batch and column techniques. The experimental variables include contact time, initial metal concentration, biosorbent dosage, metal type, pH, solution composition, biosorbent pre-treatment, flow rate and bed height. The residual concentration of the metals in solution was determined by flame atomic absorption spectroscopy (FAAS). The results showed that the adsorption of all the metals by the biosorbent was rapid and approached maximum within 30 min contact time but attained equilibrium after 120 min. The adsorption obeyed pseudo-2nd order kinetics (R^2 ~ 1.0) with the rate constant, k_2, following the order Pb > Cu ~ Zn > Cd. The amount of each metal adsorbed increased proportionally from approximately 980 µg/g to 4900 µg/g while percentage removal was fairly constant (~ 98 %) with increase in initial metal concentration from 10 µg/mL to 50 µg/mL. The equilibrium adsorption data fitted better to Freundlich isotherm (R^2 = 0.97 – 0.99) compared with Langmuir isotherm (R^2 = 0.74 – 0.88). The calculated maximum monolayer adsorption, q_{max} of the biomass vary according to the type of metal: Cd (16.67 mg/g) > Pb (14.29 mg/g) > Cu = Zn (12.50 mg/g). Percent adsorption increased slightly (i.e 2.32 % - 15.9 %) with increase in the biosorbent dosage from 0.1 to 1.0 g. The adsorption of all the metals increased with increase in pH from pH 2.0 to 4.0, with no further significant increase beyond pH 4.0. Metal removal efficiency was lower in mixed metal solutions compared to single metal solutions. The presence of other metal ions in solution resulted in the reduction of the adsorption of a particular metal in the order Zn > Cu > Cd > Pb, and this was more apparent at high initial metal concentrations. Acid pre-treatment of the biomass resulted in the reduction (14.5 % - 48.8 %) in its efficiency to adsorb the metals. Meanwhile, the results of the column experiments showed that the efficiency of Cu, Zn, Cd and Pb removal decreased with the increase in flow rate but increased with the increase in bed height. Overall, non-living biomass of the locally available marine algae, *Sargassum* sp., have promising potential as biosorbent for the heavy metals Cu, Zn, Cd and Pb.

ABSTRAK

Penggunaan bahan biologi atau biojisim sebagai bahan penjerap untuk menyingkirkan logam berat dari larutan akuas atau air kumbahan semakin mendapat perhatian. Dalam kajian ini, jerapan logam berat (Cu, Zn, Cd dan Pb) oleh biojisim alga laut, Sargassum sp. telah dikaji menggunakan kaedah kelompok dan kaedah turus. Pembolehubah eksperimen termasuklah masa sentuhan, kepekatan asal logam, dos bahan jerapan, jenis logam, pH, komposisi larutan, pra-rawatan bahan jerapan, kadar aliran dan ketinggian turus. Kepekatan akhir logam dalam larutan ditentukan menggunakan spektrokopi serapan atom cahaya (FAAS). Hasil kajian menunjukkan bahawa jerapan untuk semua logam berat berlaku dalam masa yang singkat dan menghampiri maksimum dalam masa sentuhan 30 minit tetapi mencapai keseimbangan selepas 120 minit. Jerapan ini mematuhi kinetik tertib kedua (R^2 ~ 1.0) dengan pemalar kadar k_2 mengikut urutan Pb > Cu ~ Zn > Cd. Amaun setiap logam yang dijerap oleh biojisim Sargassum sp. meningkat secara berkadaran dari sekitar 980 µg/g ke 4900 µg/g manakala peratusan penyingkiran adalah malar (~ 98 %) dengan peningkatan kepekatan awal logam dari 10 µg/mL ke 50 ug/mL. Data keseimbangan jerapan lebih mematuhi isoterma Freundlich (R^2 = 0.97 - 0.99) berbanding isoterma Langmuir (R^2 = 0.74 – 0.88). Nilai kapasiti jerapan maksima, q_{max} adalah berbeza mengikut jenis logam: Cd (16.67 mg/g) > Pb (14.29 mg/g) > Cu = Zn (12.50 mg/g). Peratusan jerapan logam meningkat sedikit sahaja (2.32 % - 15.9 %) *dengan peningkatan amaun biojisim yang digunakan dari 0.1 g sehingga 1.0 g. Jerapan untuk semua logam meningkat dengan peningkatan pH larutan dari pH 2.0 ke pH 4.0, kemudian menjadi malar pada pH > 4.0. Keberkesanan penyingkiran logam adalah rendah dalam larutan campuran logam berbanding logam tunggal. Kehadiran logam lain dalam larutan menyebabkan pengurangan dalam efisiensi jerapan bagi logam spesifik mengikut urutan Zn > Cu > Cd > Pb dan kesan ini lebih ketara pada kepekatan awal logam yang tinggi. Pra-rawatan biojisim alga dengan asid menghasilkan penurunan (14.5 % - 48.8 %) dalam keupayaan untuk menjerap logam. Hasil eksperimen turus menunjukkan bahawa keberkesanan biojisim untuk menyingkirkan logam Cu, Zn, Cd dan Pb menurun dengan peningkatan kadar aliran tetapi meningkat dengan peningkatan ketinggian turus biojisim. Secara keseluruhannya , biojisim dari alga marin tempatan, Sargassum sp. berpotensi sebagai bahan penjerap biologi bagi logam berat, Cu, Zn, Cd dan Pb.*

LIST OF CONTENTS

CHAPTER 3: MATERIALS AND METHODS

CHAPTER 4: HEAVY METAL REMOVAL – BATCH EXPERIMENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

~	about
±	plus/minus
°C	degree Celsius
%	percent
⇌	reversible
=	equal to
C_o	initial concentration
AAS	atomic absorption spectroscopy
cm	centimeter
e.g	example
FTIR	fourier transform infrared spectroscopy
g	gram
h	hour
M	molar
mg	miligram
mg/g	miligram per gram
mg/L	miligram per liter
min	minute
mL	mililiter
mL/min	mililiter per min
mm	milimeter
mmol/g	milimol per gram
mol/L	mol per liter
ppm	parts per million
rpm	round per minute
s	second
sp.	species
t	time
µg	microgram
µg/g	microgram per gram
µg/mL	microgram per mililiter

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1. Heavy Metals Pollution

Heavy metals are generally defined as metallic elements with a specific gravity greater than five gcm^{-3} and atomic number greater than 20 (Mason, 1996). Examples include copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd), nickel (Ni), chromium (Cr), arsenic (As) and mercury (Hg).

Heavy metals can exist in the environment as a result of natural biogeochemical processes as well as due to anthropogenic activities (Laws, 1993). The types and concentrations of heavy metals discharged anthropogenically, however, are dependent on the type of source (Table 1.1). The natural geochemical cycle of heavy metals can be greatly modified by such anthropogenic activities, and the resultant presence of above normal concentration of heavy metals in the environment can cause adverse effects on animals, plants and humans. This condition is generally termed as heavy metal pollution (Novotny, 1995).

The presence of heavy metals can lead to undesirable effects on water quality and impede a variety of potential water uses. Unlike toxic organics, which in many cases can be degraded, heavy metals that are released into the environment tend to persist indefinitely, accumulating in living tissues upward the food chain (Laws, 1981). These toxicants, for example, can be picked up by fish or shellfish and concentrated until the organisms are no longer fit for human consumption.

Table 1.1: Heavy metal discharges from various industries

Type of industry	Heavy Metal	Heavy Metal Concentration (mg/L)	References
Automotive machining industry	Pb Zn	23 24	Thomas, 1995
Boatyard	As Cd Cr Cu Ni Pb Zn	0.07 0.004 0.16 190.00 0.09 3.40 6.90	Thomas, 1995
Food industry	Cd Cr Cu Zn	0.006 0.150 0.29 1.08	Scragg, 1999
Integrated circuit manufacturing	Cu	0.23	Eckenfelder, 2000
Meat industry	Cd Cr Cu Zn	0.01 0.15 0.09 0.43	Scragg, 1999
Plating	Cr Cu Zn	41.6 11.4 18.4	Eckenfelder, 2000
Petroleum refinery	Cu Cr Zn	0.5 2.2 0.7	Eckenfelder, 2000
Sugar manufacturing	Pb Cd	0.1 0.1	Silvalingam *et al.*, 1978
Textiles	Cd Cr Cu Zn	0.03 0.80 0.03 0.47	Scragg, 1999

Majority of heavy metals are toxic to humans and the effects range from hypertension to carcinogenic (Table 1.2). Two well known examples of the consequences of heavy metal pollution are Minamata and Itai-itai diseases. In 1953, a large number of inhabitants near Minamata, Japan was found to be suffering from nervous disorders such as speech disturbances, delirium and difficulties in walking. Subsequently this was associated with consumption of

seafood contaminated with mercury (Mason, 1996). The illness was termed as Minamata disease.

Meanwhile, in 1955, residence in Jintsu River Valley, Japan were found to be suffering from a disease which was called Itai-itai or ouch-ouch, characterized by severe back and joints pains and a decalcification of the bones, leading sometimes to multiple fractures. This problem was associated with the consumption of rice containing high concentration of cadmium (Friberg & Elinder, 1985). Apparently, the high Cd was due to nearby mining activities (Mason, 1996).

The above examples, although far from conclusive, nevertheless serve to illustrate the point that heavy metals pollution can be a serious problem on a local and global scale. In economic term, when a certain area is contaminated by heavy metals, a massive cleanup is required and the cost can run into literally billions of dollars (Laws, 1981). In addition, it will take a very long time for the degraded environment to be restored to it's original condition.

Table 1.2: Effects of heavy metals

Heavy metal	Adverse Effects / Symptoms
Cu	Various acute and chronic disorders such as haemochromatosis and gastrointestinal catarrh.
Zn	Damage to upper alimentary tract, nausea, emesis, pneumonitis, fever, diarrhea.
Pb	Diseases such as anaemia, encephalopathy, hepatitis and nephritic syndrome; Long term – plumbism, brain and kidney damage and birth defects.
Cd	Acute and chronic disorders such as 'itai-itai' disease, renal damage, emphysema, hypertension and testicular atrophy.
Cr	Corrosive to tissue, develop nose ulcers and maybe lost sense of smell; Long term – skin sensitization, kidney and liver damage, convulsions and cramps.
Hg	Corrosive to intestinal tract, damage to kidney and liver, loss of fertility, interfere with the development of reproductive, endocrine, immune and nervous systems both male and female, Minamata disease.

Source: Manahan (1996)

1.2. Controls of Heavy Metal Discharges

Due to the potentially adverse impacts of heavy metals to the environment, many countries have stringent environmental regulations with respect to wastewater discharges. Typically, these regulations specified that wastewaters need to be treated effectively prior to discharge to remove pollutants such as heavy metals. In Malaysia, wastewater discharges from industries, including metal-based industries, are required to comply with the limits set by the Environmental Quality Act 1974, specified under Sewage and Industrial Effluents Regulations, 1978. The discharge standards are shown in Table 1.3. In general, the more toxic is the heavy metal, the lower is the discharge limit, while the limits for Standard A is more stringent compared with Standard B.

Conventional treatment technologies for removal of heavy metals from wastewaters include flocculation (Johnson *et al.*, 2008), coagulation (Johnson *et al.*, 2008), crystallization (Minato *et al.*, 2001), chemical precipitation (López *et al.*, 2004), chemical oxidation or reduction (Sundstrom *et al.*, 1996), electrochemical treatment (Kurniawan *et al.*, 2006), ion exchange (Kurniawan *et al.*, 2006), membrane separation (Kurniawan *et al.*, 2006), biological methods (Mantis *et al.*, 2005) and adsorption (Volesky, 2001). Some of these methods have drawbacks in terms of efficiency, operational cost, selectivity and by-products (Wong & Tam, 1998; Wase & Forster, 1997). For example, chemical treatment methods can prove costly to the users as the active agent cannot be recovered for reuse in successive treatment cycles (Kurniawan *et al.*, 2006). Also, the end products are metal-bearing sludges which need further disposal. Application of biological methods involving live organisms is difficult for industries because of some special precautions on conditions such as temperature, nutrients and light.

Table 1.3: Discharged standards for industrial effluent in Malaysia according to Environmental Quality Act 1974 (Sewage and Industrial Effluents Regulation 1978)

Parameter	Industrial Effluent (mg/L)	
	Standard A	Standard B
As	0.05	0.10
Cd	0.01	0.02
CN	0.05	0.10.
Cr (VI)	0.05	0.05
Cu	0.20	1.00
Fe	1.00	5.00
Hg	0.005	0.05
Mn	0.20	1.00
Ni	0.20	1.00
Pb	0.10	0.50
Sn	0.20	1.00
Zn	1.00	1.00

Adsorption is by far the most versatile and widely used technique for the removal of toxic pollutants including heavy metals from aqueous solutions (Selatnia *et al.*, 2004; Gupta *et al.*, 2000; Vegliò *et al.*, 1997). Generally, this technique involves the interaction between an adsorbent with the heavy metal ion in solution. Until recently, the adsorbents used for this purpose are inorganic materials such as activated carbon (Chen *et al.*, 2003) and zeolite (Hui *et al.*, 2005).

1.3. Biosorption

1.3.1. Definition

A recent development in adsorption technology involves the use of biological materials or biomass as adsorbent to accumulate adsorbates (such as heavy metals) from aqueous solutions or wastewaters. This adsorption method is termed as biosorption while the adsorbent is known as biosorbent (Nuhoglu *et al.*, 2002; Volesky & Holan, 1995).