

OPTIMIZATION OF BIOSORPTION PROCESS USING *CUCUMIS MELO* RIND
FOR THE REMOVAL OF FE, MN AND PB IONS FROM GROUNDWATER

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ABSTRACT

Biosorption can be an effective technique for the treatment of metal-bearing groundwater. Several fruits and agricultural by-products demonstrated the ability to remove the heavy metals and thereby reduce the water contaminants. In the present study, the potential use of biosorbent material obtained from *Cucumis melo* rind for the removal of Pb, Fe and Mn ions from groundwater was investigated according to four types of parameters namely pH, biosorbent dosage, initial metal concentration and contact time. Characterization of biosorbent was done by the means of SEM-EDX, XRF and FTIR analysis to observe for the surface morphology, elemental composition and functional groups available on the biosorbent. Sorption was most efficient at pH 7 for Fe(II) and pH 6.5 for both Mn(II) and Pb(II) using 0.05g/100ml biosorbent dosage at contact time of 45 minutes. The biosorption of all metals increased with increasing biosorbent dosage. FTIR study revealed the presence of functional groups on the surface of biosorbent facilitates the biosorption of the metal ions. The Langmuir, Freundlich and BET isotherm models were used to predict the behavior metal binding while Langergren Pseudo-first and Pseudo-second order were used to study the kinetics aspects. The equilibrium data for all metals were best fit to the Langmuir adsorption isotherm with maximum adsorption capacity of 5.3505 mg/g, 2.7525 mg/g and 0.0830 mg/g respectively for Fe(II), Mn(II) and Pb(II). The result indicates that the Pseudo-second order model best describes the kinetics data. The *Cucumis melo* rind successfully removes up to 90.73%, 91.47% and 90.94% respectively to Fe, Mn and Pb in the groundwater samples which reduce the metals level below the WHO recommended limits of heavy metal for drinking water.

ABSTRAK

Bioresapan boleh menjadi teknik yang berkesan untuk merawat air bawah tanah yang tercemar dengan logam. Beberapa jenis bahan buangan buah-buahan dan pertanian menunjukkan keupayaan untuk menyingkir logam berat dan dengan itu mengurangkan bahan cemar air. Dalam kajian ini, potensi penggunaan bioperesap yang diperolehi daripada kulit *Cucumis melo* untuk penyingkiran ion-ion Pb, Fe dan Mn dari air bawah tanah telah disiasat mengikut empat jenis parameter iaitu pH, dos bioperesap, kepekatan logam awal dan masa sentuhan. Pencirian bioperesap dilakukan dengan kaedah SEM - EDX, XRF dan analisis FTIR untuk memerhatikan morfologi permukaan, komposisi unsur dan kumpulan berfungsi yang boleh didapati pada bioperesap tersebut. Penyerapan adalah paling berkesan pada pH 7 untuk Fe(II) dan pH 6.5 untuk kedua-dua Mn(II) dan Pb(II) dengan menggunakan dos 0.05g/100ml bioperesap pada masa sentuhan 45 minit. Kajian FTIR mendedahkan kehadiran kumpulan berfungsi pada permukaan bioperesap memudahkan bioserapan ion logam. Model isoterma penjerapan seperti Langmuir, Freundlich dan model isoterma BET telah digunakan untuk meramalkan pengikatan logam manakala Pseudo- pertama Langergren dan Pseudo- kedua telah digunakan untuk mengkaji aspek-aspek kinetik logam. Data keseimbangan untuk semua logam itu didapati lebih bersesuaian dengan isoterma penjerapan Langmuir dengan kapasiti maksimum penjerapan 5.3505 mg/g, 2.7525 mg/g dan 0.0830 mg/g masing-masing untuk Fe(II), Mn(II) dan Pb(II). Hasil kajian menunjukkan bahawa model Pseudo- kedua adalah yang terbaik untuk menerangkan data kinetik. Kulit *Cucumis melo* telah berjaya menyingkirkan sehingga 90.73%, 91.47% dan 90.94% masing-masing untuk Fe, Mn dan Pb dalam sampel air bawah tanah dan mengurangkan kandungan logam di bawah paras yang dicadangkan oleh WHO untuk air minuman.

CONTENTS

	TITLE	
	TITLE	i
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	CONTENTS	vii
	LIST OF TABLES	xi
	LIST OF FIGURES	xii
	LIST OF ABBREVIATIONS	xiv
CHAPTER 1	INTRODUCTION	1
	1.1 Introduction	1
	1.2 Problem Statement	2
	1.3 Objectives of study	4
	1.4 Scopes of study	4
CHAPTER 2	LITERATURE REVIEW	5
	2.1 Groundwater	5
	2.2 Metals contamination in groundwater	5
	2.3 Malaysia National Drinking Water Quality Standards	6
	2.4 Health effect of Iron (Fe) to human	7
	2.5 Health effect of Manganese (Mn) to human	8
	2.6 Health effect of Lead (Pb) to human	9

2.7	Common techniques of heavy metal removal for contaminated waters	9
2.7.1	Chemical precipitation	10
2.7.2	Membrane separation	10
2.7.3	Chemical oxidation and reduction	10
2.7.4	Ion-exchange	11
2.7.5	Electrodialysis	11
2.8	Biosorption	12
2.8.1	Mechanisms of biosorption	12
2.8.1.1	Transport across cell membrane	13
2.8.1.2	Physical adsorption	13
2.8.1.3	Ion-exchange	14
2.8.1.4	Precipitation	14
2.8.1.5	Complexation	14
2.9	Differences between bioaccumulation and biosorption	14
2.10	Biosorbent	15
2.11	Advantages and disadvantages of biosorption using living and non-living biomass	16
2.12	Fruit wastes and agricultural by-products as biosorbent	16
2.13	<i>Cucumis melo</i> rind biomass	18
2.14	Pretreatment of biosorbent	19
2.15	Factors affecting biosorption	19
2.15.1	pH	19
2.15.2	Temperature	20
2.15.3	Biosorbent dosage	20
2.15.4	Particle size	20
2.15.5	Agitation rate	21
2.16	Sorption isotherm studies	21
2.16.1	Langmuir Isotherm	21
2.16.2	Freundlich Isotherm	22
2.16.3	BET Isotherm	23
2.17	Kinetics of biosorption	23



2.17.1	Pseudo-first order equation	24
2.17.2	Pseudo-second order equation	24
2.18	Instrumental tools and techniques used in biosorption	25
2.19	Application of biosorption to real industrial effluent	26
2.20	Regeneration of biosorbent	27
CHAPTER 3	METHODOLOGY	29
3.1	Framework of study	29
3.2	Materials and methods	30
3.2.1	Biosorbent	30
3.2.2	Chemicals	30
3.2.3	Apparatus	30
3.2.4	Equipments	31
3.3	Preparation of metal solutions	31
3.4	Preparation of <i>Cucumis melo</i> rind	32
3.5	Characterization of <i>Cucumis melo</i> rind	33
3.6	Groundwater sampling	35
3.7	Batch adsorption studies on synthetic groundwater solutions	36
3.7.1	Effect of biosorbent dosage on Fe(II), Mn(II) and Pb(II) removal	37
3.7.2	Effect of pH on Fe(II), Mn(II) and Pb(II) removal	37
3.7.3	Effect of initial metal concentrations on Fe(II), Mn(II) and Pb(II) removal	37
3.7.4	Effect of contact time on Fe(II), Mn(II) and Pb(II) removal	38
3.8	Adsorption Isotherm Study	39
3.9	Kinetics Study	39
3.10	Removal of Pb, Fe and Mn from actual groundwater	39
3.11	Statistical analysis	40

CHAPTER 4	RESULTS AND DISCUSSION	41
4.1	Characterization of biosorbent	41
4.1.1	SEM-EDX analysis	41
4.1.2	FTIR analysis	48
4.1.3	X-Ray Fluorescent Analysis on <i>Cucumis melo</i> rind	51
4.2	Batch adsorption studies	53
4.2.1	Effect of biosorbent dosage on Fe(II), Mn(II) and Pb(II) removal	53
4.2.2	Effect of pH on Fe(II), Mn(II) and Pb(II) removal	55
4.2.3	Effect of contact time on Fe(II), Mn(II) and Pb(II) removal	58
4.2.4	Effect of initial metal ion concentrations on Fe(II), Mn(II) and Pb(II) removal	60
4.2.5	Removal of Fe(II), Mn(II) and Pb(II) under optimum conditions	61
4.3	Biosorption Isotherm Study	62
4.4	Biosorption Kinetics Study	68
4.5	Biosorption studies on Fe, Mn and Pb ions removal by <i>Cucumis melo</i> rind using actual groundwater	71
CHAPTER 5	CONCLUSIONS AND RECOMMENDATIONS	75
5.1	Conclusions	75
5.2	Recommendations	76
	REFERENCES	77
	APPENDICES	87



LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Malaysia: National Drinking Water Standards	6
2.2	Comparison of several fruit waste biosorbents	18
2.3	Biological based sorbent particles (biosorbents) developed for metal bearing water treatment	27
3.1	List of apparatus to be used in the experiment	30
3.2	List of equipments to be used in the experiment	31
3.3	Working conditions used for batch adsorption studies for synthetic groundwater solution	36
3.4	Working conditions used for batch adsorption studies for actual groundwater samples	40
4.1	The FTIR spectral characteristics of <i>Cucumis melo</i> rind	50
4.2	The XRF analysis of elemental composition of untreated and Acid-treated <i>Cucumis melo</i> rind	52
4.3	The XRF analysis of elemental composition of watermelon rind before and after Zn biosorption	53
4.4	Percentage of removal and uptake capacity of all parameters at optimum conditions	62
4.5	Isotherms parameters of biosorption of Fe(II), Mn(II) and Pb(II) onto <i>Cucumis melo</i> rind	68
4.6	Kinetics parameters of biosorption of Fe(II), Mn(II) and Pb(II) onto <i>Cucumis melo</i> rind	71
4.7	Initial metal concentration of groundwater samples	72

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
2.1	Biosorption mechanism	13
3.1	Flow chart of experimental works	29
3.2	<i>Cucumis melo</i> rinds	32
3.3	Oven-dried <i>Cucumis melo</i> rind	32
3.4	Pulverized <i>Cucumis melo</i> rind	33
3.5	SEM-EDX	33
3.6	XRF	34
3.7	Manual Hydraulic Press	34
3.8	FTIR	34
3.9	Maps to RECESS, UTHM, Batu Pahat, Johor	35
3.10	Sampling site at RECESS, UTHM	36
3.11	Orbital shaker	38
3.12	Glass filtration unit and vacuum pump	38
4.1	SEM micrograph of untreated <i>Cucumis melo</i> rind	42
4.2	SEM micrograph of acid-treated <i>Cucumis melo</i> rind	42
4.3	SEM micrographs of <i>Cucumis melo</i> rind	43
4.4	EDX spectrum of un-loaded biosorbent	44
4.5	EDX spectrum of Fe-loaded biosorbent	45
4.6	EDX spectrum of Mn-loaded biosorbent	46
4.7	EDX spectrum of Pb-loaded biosorbent	47
4.8	FTIR spectra of <i>Cucumis melo</i> rind	49
4.9	Effect of biosorbent dosage on the biosorption of Fe(III)	54
4.10	Effect of biosorbent dosage on the biosorption of Mn(II)	55
4.11	Effect of biosorbent dosage on the biosorption of Pb(II)	55

4.12	Effect of pH on the bisorption of Fe(III)	57
4.13	Effect of pH on the bisorption of Mn(II)	57
4.14	Effect of pH on the bisorption of Pb(II)	57
4.15	Effect of contact time on the bisorption of Fe(III)	59
4.16	Effect of contact time on the bisorption of Mn(II)	59
4.17	Effect of contact time on the bisorption of Pb(II)	59
4.18	Effect of initial metal concentrations on the bisorption of Fe(III)	60
4.19	Effect of initial metal concentrations on the bisorption of Mn(II)	61
4.20	Effect of initial metal concentrations on the bisorption of Pb(II)	61
4.21	Langmuir isotherm plots	64
4.22	Freundlich isotherm plots	65
4.23	BET isotherm plots	66
4.24	Pseudo-first order plots	69
4.25	Pseudo-second order plots	70
4.26	Removal of Fe, Mn and Pb ions under optimum condition of Fe ion	73
4.27	Removal of Fe, Mn and Pb ions under optimum condition of Mn and Pb ion	73



LIST OF ABBREVIATIONS

°C	Degree Celcius
AAS	Atomic Absorption Spectrophotometer
Ca	Calcium
CaCO ₃	Calcium Carbonate
Cd	Cadmium
Cr	Chromium
Cu	Copper
DNA	Deoxyribonucleic Acid
EDX	Electron Dispersive X-Ray Spectrometry
FeCl ₃	Ferric Chloride
Fe	Ferum
Fe(II)	Ferum (II)
FTIR	Fourier Transform Infrared Spectrometer
g	Gram
mg/L	Milligram per liter
mg/g	Milligram per gram
MnSO ₄	Manganese sulphate
Mn	Manganese
Mn(II)	Manganese (II)
NADH	Nucleotinamide Adenine Dinucleotide
Pb	Plumbum
Pb(II)	Plumbum (II)
RECESS	Research Centre for Soft Soil
SEM	Scanning Electron Microscopy
XRF	X-Ray Fluorescence Spectrophotometer
Zn	Zinc

CHAPTER 1

INTRODUCTION

1.1 Introduction

Industrialization is a vital necessity for the development of the nation's socio-economic and its political standing in the international community. While development are aiming to improve human life, uncontrolled consumption of natural resources both in developed and developing countries have unintentionally directed to environmental pollution, incurable diseases and social conflicts [1].

The deterioration of groundwater quality caused by the introduction of pollutions is becoming a problem of industrial cities across the world. Cases of contamination of groundwater and drinking water were reported as not uncommon in several states in the USA where a large percentage of the population relies on groundwater sources [2]. While in Italy, more than 85% of the drinking water is extracted from the groundwater [3]. A study conducted in the Vercelli province in North Italy showed that expanded use of fertilizers and pesticides in the farm fields has increasingly contaminating the groundwater.

While in Malaysia, the rapid industrialization in the last decade has affected the quality of natural resource such as groundwater. The contamination of groundwater by heavy metals originating either from natural soil sources or from anthropogenic sources driven threats to public health. Though, purification of contaminated groundwater is utmost important since billions of people over the world use it for drinking purpose.

Iron, manganese and lead occur in the earth's crust and may get solubilised in groundwater through natural processes and pH changes. Decreasing pH promoting solubility of many minerals including lead, which occur in trace amount. The augmented concentrations of these trace elements can detrimentally affect

groundwater quality and potentially exceeding drinking water standards [4]. In another condition, water leaching through soil and rock can dissolve minerals containing iron and manganese [5]. When exposed to the air, dissolved iron and manganese contains in the groundwater turn into insoluble and producing brown-red colour water [6]. The change of physical characteristic like colour will reduce the quality of water especially for human consumption. Therefore, it is necessary to alleviate these metals from groundwater before their discharge into receiving bodies for public use.

Several technologies exist for the remediation of heavy metals-contaminated groundwater ranging from physico-chemical, chemical and biological treatments. Physico-chemical treatments like activated carbon and membrane separation, although demonstrated high efficiency in metal removal, these methods facing problems of filter clogging and high maintenance cost. Chemical treatment such as chemical oxidation and reduction is difficult to handle and producing toxic intermediate in aquifer. As for biological treatments, this method provides a numbers of advantages over other methods such as low cost, minimization of chemical sludge production, high efficiency, regeneration of biosorbents and possibility of metal recovery [7]. Due to these reasons, recently many studies have shown the potential of exploiting low-cost biological material in a metal removal process called biosorption [8].

Biosorption is a passive process of metal uptake and sequestering by chemical sites that naturally present and functional even when the biomass is dead [9]. Process of biosorption can be described as biological ion exchange with binding groups such as carboxyl, sulfonate, phosphoryl, amido, amino and imidazole [10]. Agricultural materials contain proteins, polysaccharides and lignin which are associated with functional groups responsible for metal adsorption [11]. Agricultural by-product being economic and eco-friendly due to their unique chemical composition, availability in large quantity, renewable, low cost and highly efficient for metal removal. Hence, those facts make them a good choice of metal sorbent.

1.2 Problem statement

Groundwater pollution for the past decade has not been identified as major environmental issue in Malaysia. This is true since not many cases of groundwater-

human health incidents have been reported. However, the utilization of groundwater as clean water supply for domestic use as well as agricultural and industrial use is still high especially in the areas which are lacking in clean water supply from the dams such as Kelantan, Perlis, Terengganu, Pahang, Kedah, Sarawak and Sabah [12].

Conversely, fast-growing industrial activities have caused toxic metals contamination in the groundwater. Heavy metals such as iron, manganese and lead that leach through rocks and soils from various sources into groundwater are non-biodegradable and cause adverse effects not only to human, but also animals and plants [13][14]. The presence of these metals in groundwater above a certain level turns the water unusable mainly for esthetic considerations such as discolouration of food and beverages, metallic taste, odor, turbidity, staining of laundry and plumbing fixtures [15]. Apart from that, exposure to high concentration of metal contaminants has been associated with toxicity to affect human organ systems, causing liver damage, gastrointestinal pain as well as reducing immune function [16]. In this way, remediation of metal contaminated groundwater is necessary for providing a good quality of water supply for the community.

A number of technologies to remove metals in polluted groundwater have been developed including chemical precipitation, coagulation, flocculation, membrane separation, reverse osmosis and oxidation. Major drawbacks of these methods are toxic sludge generation, handling and disposal problems, high cost, technical constraints and incomplete metal removal [17] [18]. Hence, in considering techno-economic constraints, the biosorption method will be employed in this study to remove metal toxicants in groundwater.

Successful metal biosorption has been reported by variety of low-cost agricultural waste. Though, to the best of our knowledge there is no literature describe the potential of *Cucumis melo* rind to remove heavy metals in groundwater. The *Cucumis melo* belongs to the family of Cucurbitaceae and is one of the most important fruit crops grown in many tropical countries. The pulp of the fruit is very refreshing and sweet in taste with a pleasant aroma, the intensity of which varies depending upon the variety [19]. A great variation exist in the fruit characteristics in term of their size, shape, colour of fruit and rind firmness [20]. *Cucumis melo* rind is the non-profitable part of the fruit, which is a by-product of fruit juice industries and fruit stalls. Therefore, it is totally inexpensive and available in abundant.

1.3 Objectives of study

This study embarks on the following objectives:

- a) To characterize the surface morphology and chemical composition of *Cucumis melo* rind as biosorbent before and after biosorption process
- b) To determine optimize conditions namely biosorbent dosage, pH, contact time and initial metal concentration by *Cucumis melo* rind as biosorbent
- c) To determine the adsorption isotherm and kinetics for Fe(II), Mn(II) and Pb(II) removal by *Cucumis melo* rind
- d) To determine the maximum percentage of removal for Fe, Mn and Pb in RECESS groundwater under optimized conditions

1.4 Scopes of study

This study consists of field activities and comprehensive batch experimental work. This study investigates the biosorption abilities of *Cucumis melo* rind for the removal of Fe, Mn and Pb from groundwater. Optimum conditions of the biosorbent to remove metals in synthetic metal solutions were determined by varying four types of parameters namely biosorbent dosage, pH, initial metal concentration and contact time. Isotherm and kinetics studies were conducted and the experimental data were fitted to isotherm and kinetics models. The Fe, Mn and Pb removal efficiency of *Cucumis melo* rind were also tested using groundwater samples collected from monitoring well at RECESS UTHM in Parit Raja, Johor.

CHAPTER 2

LITERATURE REVIEW

2.1 Groundwater

Aquifers have the capabilities of both storing and transmitting groundwater. Groundwater plays an important role in the formation and alteration of soils through salinization. Another feature of groundwater that makes it valuable as a resource is its physical chemical quality. Natural groundwater has few suspended solids, small concentration of bacteria and viruses, and usually minimal amount of dissolved mineral salts. These characteristics promote groundwater as an ideal source of water to support human life [21].

However, the connection between groundwater pathways in the hydrologic cycle to the land surface provides the chance for humans to devalue the resource by pollution. Therefore, the issues of groundwater pollution and how to treat the groundwater provide an important reason to study groundwater.

2.2 Metals contamination in groundwater

Heavy metals can be defined as those elements having a density > 5 g/cc in elemental form. These metals comprise 38 elements, but in usual terminology, heavy metals refer to twelve metals most commonly used and discharged as wastes by industry namely cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), tin (Sn), and zinc (Zn). Sources of metals include domestic and industrial effluents, the atmosphere, runoff and lithosphere [22]. Moreover, groundwater can get contaminated with metals from landfill leachate, sewage, leachate from mine tailings, deepwell disposal

of liquid wastes, seepage from industrial waste lagoons or from industrial spills and leaks [23].

Metals that pass through the municipal waste facilities will return to the environment and cannot be biodegraded. Thus, the metals can absorb onto the soil, runoff into river and lakes or leach into the groundwater, which an important source of drinking water [24]. Exposure to the metals through consumption of drinking water, the food chain or high ambient air concentrations near emission sources can lead to toxicant accumulation in animals, plants and humans. In natural environment, organisms living in chronically polluted sites are exposed to low concentrations of metals for long period. The storage of metals by cellular detoxifying mechanisms makes them available for assimilation by the biota and biomagnification along the food chain, with the potential for producing adverse effects throughout the environment [25].

2.3 Malaysian National Drinking Water Quality Standards (Benchmark for Groundwater)

The quality of groundwater is often described by the minerals composition, color, taste and odor. Fe and Mn are usually present in the groundwater as divalent ions, are considered as contaminants due to their organoleptic properties [26]. Other contaminants in groundwater also include ammonium, arsenic and phosphates. The groundwater quality status are usually determined using the National Guidelines for Raw Drinking Water Quality from the Ministry of Health as the benchmark (refer to Table 2.1).

Table 2.1: Malaysia: National Guidelines for Raw Drinking Water Quality [27]

Parameters	Mandatory Standards
Turbidity (NTU)	5
Colour (TCU)	15
pH	6.5 - 8.5
Iron (Fe)	0.3
Aluminium (Al)	0.2
Mercury (Hg)	0.001

Table 2.1 (continued)

Cadmium (Cd)	0.005
Selenium (Se)	0.01
Arsenic (As)	0.05
Cyanide (Cn)	0.1
Lead (Pb)	0.05
Chromium (Cr)	0.05
Silver (Ag)	0.05
Copper (Cu)	1
Manganese (Mn)	0.1
Magnesium (Mg)	150
Zinc (Zn)	5
Sodium (Na)	200
Sulphate (SO ₄)	400
Phosphate (PO ₄)	-
Mineral oil	0.3
Phenol	0.002
Chloroform	0.03
Biocides (total)	0.1
Pesticides aldrin	0.00003

2.4 Health effect of Fe to human

Fe is fourth most abundant metals in the earth's crust and usually occurs along with manganese [28]. It is considered as one of the trace elements due to its essentiality and very limited quantity to human. Trace elements belong to the category of micronutrients, which are needed by the human body in very small quantities (generally less than 100 mg/day), as opposed to elements considered macronutrients, such as sodium, calcium, magnesium, potassium, chlorine and others which are required in larger quantities [29]. Fe is essential components of biological structures, but at the same time they can be toxic at concentrations exceed those necessary for the cell biological functions. According to Baynes & Bothwell [30], recommended daily intakes of dietary iron for normal infants are 1 mg iron per kg per day while for children, male and female adolescents, 10, 12 and 15 mg per day respectively. As well as for women during reproductive years, 15 mg per day but adult men and postmenopausal women require only 10 mg per day.

Fe can be found in four classes of proteins consist of Fe-heme proteins (e.g. hemoglobin (2/3 body iron), myoglobin, catalase, cytochromes); Fe–sulfur enzymes (e.g. aconitase, fumarate reductase); proteins for Fe storage and transport (transferrin, lactoferrin, ferritin, hemosiderin), and other Fe-containing or Fe-activated enzymes (e.g. NADH dehydrogenase, succinate dehydrogenase, alcohol dehydrogenase, cyclooxygenases) which mostly function in oxygen transport by the blood and production of energy currency of the body [31].

Although Fe plays a critical metabolism function for human, its presence in groundwater above a certain level make the water unusable mainly for aesthetic considerations such as discoloration, metallic taste, odor, turbidity, staining of laundry and plumbing fixtures. Besides, iron oxides, which are formed in reservoirs upon aerial oxidation of dissolved iron promotes growth of micro-organism in water [32].

2.5 Health effect of Mn to human

Mn is another trace element which is ubiquitous in the environment. Stumm and Morgan [33] stated that dissolved Mn concentrations in anaerobic groundwaters can reach several mgL^{-1} , however usual Mn concentrations fall in the range between 0.1 and 1 mg L^{-1} . On exposure to oxygen, manganese can form products of Mn dioxides or manganese oxyhydroxides which are insoluble, thus resulting undesirable dark black colour in groundwater intended for drinking water [34].

Like Fe, Mn also a nutrient and toxicant, depending on their concentration. Manganese is important element in metabolism of amino acid, lipid and carbohydrate. Mn is also acting a crucial function for normal bone structure and the formation of mucopolysaccharides. Moreover, Mn is found in various enzymes such as mitochondrial Mn superoxide dismutase, glutamine synthetase, arginase, and activates several hydrolases, transferases and carboxylases. Mn is transported in the body by transferrin and by macroglobulins and albumin [35].

Despite of the importance of this trace element to human body metabolism, several studies in different environmental settings have reported significant associations between exposure to Mn in groundwater-sourced drinking water supplies and adverse human health effects. Occupational exposures to Mn produce a clinical syndrome of memory loss, behavioral/mood changes and, in its final stages, a

Parkinsonian-like motor dysfunction [36]. In rural areas of Bangladesh, most people rely on groundwater as the only source of fresh drinking water. Nevertheless, Mn and arsenic contains in the groundwater have been recognized as threats to rural public health [37]. Khan et. al [38] reported that Mn-bearing drinking water potentially threatening children's health due to its associations with a wide range of outcomes including cognitive, behavioral and neuropsychological effects. While In mammalian cells, Mn causes DNA damage and chromosome aberrations [39].

2.6 Health effect of Pb to human

Pb is a group IV A metal with many properties in common with the alkaline earth elements. It is a globally well distributed environmental and industrial pollutant that has been detected in almost all phases of environmental and biological systems. Pb were mined to be used in storage batteries (1 220 000 metric tons). Other uses were in water pipes, house paint, textiles, matches, as well as gasoline additive [40].

Once ingested through the gastrointestinal track, Pb accumulates in vital organs and bones, and finally causes a number of diseases. Lead is known to induce a broad range of physiological, biochemical, and behavioral dysfunctions in laboratory animals and humans [41], including male and female reproductive system [42] [43], haemopoietic system [44], sensory nervous system [45], endocrine system [46] and excretory system [47].

2.7 Common techniques of metal removal for contaminated waters

Several techniques have been employed for the treatment of metals contaminated waters. Among the most commonly applied techniques are chemical precipitation, chemical oxidation and reduction, ion-exchange, filtration, electrochemical treatment, reverse osmosis, evaporative recovery and solvent extraction [48]. These classical techniques give rise to several problems such as generation of toxic sludge which requires extreme caution in the method of disposal [49]. Another example is activated carbon techniques which have been recognized as effective commercial adsorbents for treating metal contaminated waters however it is highly expensive but low efficiency have limited their commercial use in actual industrial scenarios [50]. Some of the conventional methods are briefly described with their disadvantages.

2.7.1 Chemical precipitation

This method is effective and the most widely used method in the industry due to its relatively simple to operate [51]. Precipitation of metals is accomplished by the addition of coagulants such as alum, lime, iron salts and other organic polymers. In a study of hydroxide precipitation using $\text{Ca}(\text{OH})_2$ and NaOH on the removal of $\text{Cu}(\text{II})$ and $\text{Cr}(\text{VI})$ ions from wastewater, it was observed that the concentration of chromate was reduced from 30 mg/l to 0.01 mg/l [52]. Results revealed from another study of chemical precipitation by lime to treat synthetic wastewater containing Zn, Cd, Mn and Mg found that the treated wastewater successfully meet the wastewater standards of the Ministry of Industry with further decreases when coagulant was added [53]. While the main disadvantages over this method is production of large amount of sludge containing toxic compound during the treatment process [54]. In addition, this method become less effective and more expensive when adsorbates concentration in aqueous solution is lower than 50 mg/L [50].

2.7.2 Membrane separation

Through this method, the adsorbates are separated by a semi-permeable membrane at a pressure greater than osmotic pressure caused by dissolved solids in wastewater. This is one of the techniques which able to remove wide range of dissolved species from the water [55]. Cu^{2+} and Ni^{2+} ions were successfully removed by membrane separation technologies and the removal efficiency of the two ions were reported to increase up to 99% by using Na_2EDTA [56]. However, this method prone to serious problem regarding membrane clogging and reduction of permeability which resulting to bypass of groundwater flow [54].

2.7.3 Chemical oxidation and reductions

In this technique, chemicals are used to decrease the toxicity or mobility of metal contaminants by converting the metals to inactive states by the means of oxidation, reduction or neutralization reaction. On the other hand, for example dithionate was found to be difficult to handle and generating hazardous toxic gases [17].

2.7.4 Ion-exchange

Ion exchange process have been widely implemented to remove heavy metals from wastewaters due to their advantages such as high treatment capacity, high removal efficiency and fast kinetics [57]. In this process, metal ions from dilute solutions are exchanged with ions driven by electrostatic forces on the exchange resin. The metal uptake by ion-exchange resins may be affected by certain parameters such as pH, temperature, initial metal concentration, contact time and also ionic charge [58]. The investigation of the removal of Ce^{4+} , Fe^{3+} and Pb^{2+} from aqueous solutions by cation exchange resins purolite C100 was found that the metal ions adsorption were influenced by ionic charge with the metal ions adsorption sequence can be arrange as $Ce^{4+} > Fe^{3+} > Pb^{2+}$ [59]. A research conducted using clinoptilolite-Fe system to simultaneously remove Cu, Mn and Zn from drinking water revealed that the system has very large metal adsorption capacity and all the treated water samples were suitable for human consumption and agricultural use [60]. The disadvantages of this method include less cost effective and only partially remove the adsorbates [17].

2.7.5 Electrodialysis

In this method, the ionic compounds are separated through semi-permeable membranes. Application of an electrical potential between the two electrodes causes the movement of cations and anions towards respective electrodes. Due to alternate spacing of cation and anion permeable membranes, cells of concentrated and diluted salts are formed. This process was proved to be effective in the removal of Cu and Fe from solutions in copper electrowinning operations [61]. Another study conducted to investigate the effect of operating parameters on Pb^{2+} separation from wastewater using electrodialysis showed that increasing voltage and temperature improved cell performance. But the separation percentage decreased with increasing flow rate. At concentrations over than 500 mg/l, dependence of separation percentage on concentration was diminished [62]. Additionally, this process leading to the formation of metal hydroxides which tend to clog the membrane thus require expensive maintenance cost [54].

2.8 Biosorption

Biosorption is emerging as a sustainable effective technology that utilizes inactive and dead biomass for the recovery of heavy metals from aqueous solutions [63]. Many conventional method such as chemical precipitation, chemical redox, ion exchange, reverse osmosis, membrane separation, evaporation, activated carbon and adsorption have used to remove heavy metals from aqueous solution [64]. Each of this method posses its own merits and demerits. Chemical precipitation for example, produces large amounts of sludge to be treated with great difficulties while ion exchange, membrane separation and activated carbon adsorption processes are extremely expensive [65] As an alternative to conventional method, biosorption has proved to be a promising alternative for cleaning up plant effluent and industrial wastewater as it is economical, eco-friendly, highly selective, efficient and easy to operate [66]. The biosorption process involves a solid phase (sorberent or biosorberent) and a liquid phase (solvent; normally water) which contains dissolved species to be sorbered (sorberate; metal ion). Due to higher affinity of the sorberent for the sorberate, the latter is attracted and bound with different mechanisms [67].

2.8.1 Mechanism of biosorption

The understanding about the mechanisms of biosorptive removal of metal ions by biosorberent is crucial for the development of biosorption system. The mechanism of biosorption can be classified according to two conditions: i) the dependence on the cell's metabolism and ii) the location where the metal removed from solution is found. Figure 2.1 shows schematically the variability of mechanisms of biosorption [68].

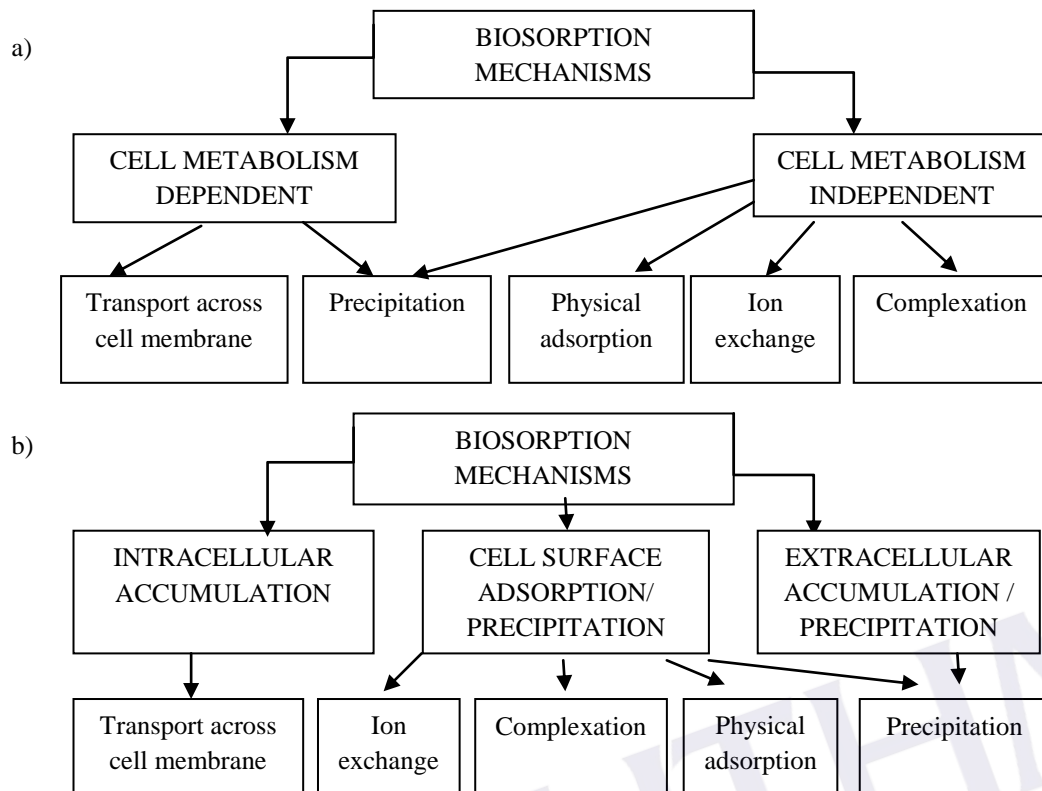


Figure 2.1: Biosorption mechanism (a) Classified according to the dependence on the cells' metabolism. (b) Classified according to the location where the metal removed is found [68].

2.8.1.1 Transport across the cell membrane

The movement of metals across the cell membrane resulting in intracellular accumulation, which is dependent on the cells metabolism activity. Hence, this kind of mechanism may take place only in living cells. This case of biosorption depends on the time required for the reaction taken by microorganism in responding to the presence of a toxic metal [68].

2.8.1.2 Physical adsorption

This mechanism is based on the psychochemical interaction between the metal and functional group exhibited on the cell surface. Usually, it is associated with the existence of Van der Waals' interaction [68].

2.8.1.3 Ion-exchange

The mechanism of ion exchange involve the replacement of protons, alkali, alkali earth or other cations present on the surface of biomass by the heavy metal ions in the solutions. Evidence presented by numerous researchers on biosorption studies proven that this replacement phenomenon is taking place [69] [70] [71] [72].

2.8.1.4 Precipitation

Precipitation may be either cellular metabolism dependent or independent. The removal of metal from solution by microorganisms is often associated with their active defense system which secreting compound which favour the precipitation process [68]. Research on the removal of Mn(II) and Zn(II) from aqueous solutions by crab shell particles found that calcium carbonate (CaCO_3) that constituting the crab shell favors micro-precipitation of metal ions which dissociated to Ca^{2+} and CO_3^{2-} [73].

2.8.1.5 Complexation

The removal of metal sorbate from solution may also happen through complex formation on the cell surface after the interaction between sorbate species and active groups [68]. This mechanism was found to be the mechanism responsible for the uptake of Cr(III) by microalgal isolate, *Chlorella miniata* [74]. Mn(II) biosorption by green tomato husk modified by formaldehyde was proposed to take place not only through ion-exchange mechanism, but also involve complex metal formation between the metal ion and the organic functional group of the modified tomato husk [75].

2.9 Difference between bioaccumulation and biosorption

Biosorption and bioaccumulation are mainly used for the removal of metal cations from the aqueous solutions. Biosorption is metabolically passive process which is performed by material of biological origin, non-living biomass while bioaccumulation is metabolically active and is performed by living cells. Biosorption

can be described as biological ion exchange with binding groups exhibited on the surface of the cell wall.

Conversely in bioaccumulation, it is defined as intracellular accumulation of sorbate. It occurs in two stages. The first stage is identical to biosorption process where the process of ion-exchange takes place. In subsequent stage, the pollutants will be transported into the cell via the process of active transport which finally the pollutant becomes concentrated inside the cell. Thus, in order for bioaccumulation process to take place, the organism must be cultivated in the presence of pollutants which are to be removed. Bioaccumulation offers more binding sites to the pollutants, either on the cell surface or inside the cell, eventually lowering residual concentration of sorbate in the solution. Nonetheless, this process posing the danger of cellular intoxication due to intracellular sorbate accumulation, where such danger is not exists in biosorption [10].

2.10 Biosorbent

A successful removal of metal ions by the means of biosorption process requires preparation of good biosorbent. The process begins with selection of biomass to be used as the sorbent species. Some biosorbents were modified and immobilized to increase metal uptake capacity [76][77]. In recent times, studies of biosorption have emerged to employ eco-friendly, effective and low-cost material biosorbents. These biosorbents come from diverse origin. Successful metal biosorption has been reported by a variety of biological materials including fungi [78], algae [79], bacteria [80] and yeast [81]. Uptake of Cd, Pb, Co and Cu by mycelia and sporocarps of an edible mushroom, *Volvariella volvacea* was reported by Purkayastha & Mitra [82]. Also, seaweeds which comes from group of marine benthic algae, offers several advantages for biosorption due to their large surface area as studied by Romera et al [63]. Large quantity of fungal biomass which is available from the antibiotic and food industries provide efficient and economical advantages for the removal of toxic metals because of their high percentage of cell wall material which shows excellent metal binding properties. Fast growing microbial such as bacteria was proven by Ilhan et al. [83] to be a good biomass for biosorption. The research reported that *Staphylococcus saprophyticus* is highly capable for the removal of Cr, Pb and Cu ions from industrial wastewater. Some studies exploit the advantage of using living

biomass, while another studies employing non-living biomass to remove metal toxicants.

2.11 Advantages and disadvantages of biosorption using living and non-living biomass

Pollutants like metals can be removed by living and non-living biomass. However, feasibility studies for large scale applications have proven that biosorptive process using non-living biomass are more applicable than bioaccumulation process using living biomass since the latter require nutrient supply and complicated bioreactor systems [49]. Besides, it is difficult to maintain a healthy microbial population due to toxicity of pollutant being extracted, and other stressing environmental factors such as temperature and pH of the solution being treated. Moreover, it is necessary to supply nutrients such as molasses and sucrose as energy source to the growing cells. In addition, recovery of valuable metals may also limited in living cells since the metal may be bound intracellularly. Due to these reasons, attention has been focused on the use of non-living biomass as potential biosorbent [84]. However, in biosorption using living cells, it is possible to reach lower residual concentration of sorbate because the cells offer more binding sites both on the surface and inside the cells, thus additional amount of sorbate can be bound to the sites depending on the equilibrium biosorption dependence [10].

Non-living biomass has several advantages because it shows metabolism-independent metal transport into the cell which it is not pH and temperature sensitive. In addition, non-living biomass is not affected by the toxicity of the metal ions. Moreover, this type of biomass can be subjected to different chemical and physical treatment techniques to enhance their performance. Chemical treatment techniques such as acid or base pre-treatment have usually shown an increase in biosorption performances of plant biomass due to re-organization of cell wall structure [85].

2.12 Fruit wastes and agricultural by-products as biosorbent

Another type of biomass which large attention has been paid as metal biosorbents is fruit waste and agricultural by-products. These include coconut shell [86], durian

rind [87], banana peel [88], mango peel [89], mangosteen shell [90], pomegranate peel [84], mandarin peel [91], papaya wood [92], yellow passion-fruit shell [93], grape waste [94], orange peel [95] and coconut coir [96]. Table 2.2 shows the summary of some fruit wastes that had been used to different kind of target metal. It was demonstrated that each fruit waste require different optimum pH, contact time and yields different metal uptake capacity.

Fruit wastes are cheap, unlimited, easily disposed by incineration, and even reusable after being rejuvenated. A study have reported successful desorption and rejuvenation of metal-loaded papaya wood using 0.1 HCl [92]. The rejuvenated papaya wood retained its efficiency to biosorb copper and cadmium after five repeated cycles of sorption-desorption. Optimum biosorption for all three metals was reached at pH 5 during contact time of 60 minutes with relative order of metal sorption affinity of Cu(II) > Cd(II) > Zn(II). Sorption of Cr(III) and Pb(II) from aqueous solution by yellow passion fruit shell (YPFS) was studied by Jacques [93]. The study presented that YPFS have higher adsorption capacities when compared with several different adsorbent of 151.6 mg⁻¹ and 85.1 mg⁻¹ respectively for Pb(II) and Cr(III).

In another study of the removal of Cr(VI) from aqueous solution by cross-linked grape waste gel was reported by Chand [94]. Effect of process parameters (pH and contact time) was studied and sorption was most efficient at pH 1 during contact time of 60 minutes. The metal adsorption on the gel was highly pH dependent and the adsorption capacity was found to increase with increasing solute concentration.

Adsorption behavior of Cd²⁺ and Pb²⁺ on mango peel waste (MPW) was studied by Iqbal [89]. The adsorption of the metals was dependent on such experimental conditions like pH, sorbate-sorbent concentrations and contact time. Maximum adsorption for both Cd²⁺ and Pb²⁺ by MPW was reported at pH 5. The result showed 99% of both metals were removed in 60 minutes contact time. Experimental and reaction kinetics were expressed by Langmuir adsorption isotherm and pseudo-second order kinetics model.

The potential to remove Pb²⁺ from aqueous solution by honey dew waste was reported by Akar [97]. The biosorption was rapid in the initial stage of the process and increased with an increase in contact time up to 80 minutes at pH 5.5. The temperature positively affecting the biosorption efficiency of biosorbent for metal

ion where the biosorption capacity increased from $52.09 \pm 1.47 \text{ mg}^{-1}$ to $75.88 \pm 0.75 \text{ mg}^{-1}$ where the temperature was raised from 20°C to 40°C .

Table 2.2: Comparison of several fruit waste biosorbent

Biosorbent	Target Heavy Metal	Parameter
Mangosteen shell [90]	Pb(II) Cd(II)	pH-2.5; contact time-30 min; uptake- 3.6 mg/g pH-4; contact time-30 min; uptake 3.15 mg/g
Banana peel [88]	As(III)	pH-7; contact time-90 min; uptake 0.843 mg/g
Dragon fruit skin [98]	Mn(II)	pH-3; contact time-60 min; uptake 15.47 mg/g
Passion fruit skin [99]	Pb(II)	pH-4; contact time-170 min; uptake 204 mg/g
Pomelo peel [100]	Cd(II)	pH-5; contact time-20 min; uptake 21.83mg/g
Pomegranate peel [84]	Pb(II)	pH-4.5; contact time-240 min; uptake 111.52 mg/g
Maize stalk [101]	Zn(II) Cd(II) Mn(II)	pH-7.6; contact time-90 min; uptake 30.3 mg/g pH-6; contact time-90 min; uptake 18.05 mg/g pH-5; contact time-90 min; uptake 16.61 mg/g

2.13 *Cucumis melo* rind biomass

Cucumis melo (honeydew melon) is among major fruits that are grown worldwide. The demand for fresh honeydew is increasing for its excellent flavor, attractive fragrance, beautiful colour, delicious taste and health giving properties.

Cucumis melo rind is a by-product of the fruit juice industry and local fruit stalls. Therefore, it is inexpensive biosorbent material. The rind thickness is in between 0.4 - 0.6 cm during its maturity stage [102]. The rind colour progressively changes during fruit growth and developments. The colour change from dark-green to grayish-green before turns to greenish-yellow as the fruit approaches maturity. This change indicates the reduction of chlorophyll content. *Cucumis melo* rind is naturally enriched with pectin and α -cellulose to provide the function of rigidity and resistance to tearing [103]. Moreover, the rind contains non-essential amino acid citrulline [104]. Pectin, cellulose and amino acids containing abundant carboxyl, hydroxyl and amino groups which have significant capabilities of binding heavy metals from aqueous solution [105].

In the present study, it was found that there are 35.30% of silica constitutes in *Cucumis melo* rind. A biosorption study using watermelon (*Citrullus lunatus*) rind demonstrated that watermelon rind contains 75.20% of silica [106]. Other study reported that among the major components which contribute to high metal uptake is carbon and silica [107].

2.14 Pretreatment of biosorbent

Biosorbent are initially prepared by pretreatment process using several methods. Methods involved in pretreatment include alkalies, acids, detergent and heats used to enhance its metal affinity [54]. The increase in metal uptake capacity after pretreatment process were suggested due to the removal of surface impurities and rupture of cell membrane which exposing more available binding sites of the surface of the biosorbents [108].

The heat treatment could cause protein denaturation which disrupt the amino functional groups on the fungal surface [109]. In a study using autoclaved *Mucor rouxii* demonstrated that the biosorption capacity was decreased as compared to live fungus due to the loss of intracellular uptake [109].

The enhancement in Cd, Ni and Zn removal were observed using NaOH treated *Pencillium digitatum* [110]. Several studies showed that alkali pretreatment could release polymers such as polysaccharides that have high affinity towards certain metal ions [111].

While in the case of acid pretreatment, the adsorption capacity of *Aspergillus oryzae* mycelia was reported to be enhanced after biomass was acid-pretreated [112].

2.15 Factors affecting biosorption

The research on the efficiency of metal removal by selected biosorbent is essential to prepare for the industrial application of biosorption, as it gives the information about the equilibrium of the process which is mandatory in order to design the biosorption system. Since biosorption is determined by equilibrium, it is largely influence by several factors such as pH, particle size, temperature, biosorbent dosage and agitation rate.

2.15.1 pH

pH is one of the most crucial environmental variable governing the biosorption of the metal ions by biosorbent. It is not only influencing the functional groups but also the solution chemistry of the heavy metals [113]. At low pH, carboxyl and sulfate groups for example, will be protonated due to their acidic property, thereby become less

attracted for metal binding. Binding of many metals increase as the ph increase due to the basis of decrease in competition between protons and metal cation for the same functional groups [114] [115].

2.15.2 Temperature

Temperature is an important parameter in adsorption reaction. Based on the adsorption theory, adsorption decreases with increases in temperature and molecules adsorbed earlier on a surface tend to desorb from the surface at elevated temperature [116]. However, many studies proven that temperature seems not affecting biosorption process in the range of 20°C – 35°C [117]. At high temperature, the tendency of metal ions to escape from the biomass surface to the solution phase is increased, which causing in a decrease in adsorption [79].

2.15.3 Biosorbent dosage

Apart from pH and temperature, process of biosorption also influenced by the concentration of biomass in the solution. High dosage of biosorbent was suggested leads to interference between the binding sites. Decrease of biomass concentration in the suspension at a particular metal concentration enhances the metal-biosorbent ratio, thus increases metal uptake per gram of biosorbent, as long as the biosorbent is not saturated [118]. Azizul-Rahman [106] reported that the removal of Pb(II) by watermelon rind reached up to 77.00% by increasing amount of the sorbent from 0.01g to 0.02g and than stayed constant up to 0.04g of sorbent dosage. Similar type of result was noted by a biosorption study using pomegranate waste [84].

2.15.4 Particle size

The ion exchange capacities are dependent on the surface activity, particularly the specific surface area available for solute-surface interaction. Studies validated that ion-exchange capacity increase with increasing surface area of biosorbent [90] [119].

2.15.5 Agitation rate

The percentage of metal uptake increase with the increase in agitation speed due to the change in the boundary layer resistance of the sorption system. The boundary layer resistance will be affected by the rate of adsorption. Increasing the agitation rate will reduce this resistance and mobility of the system thus forcing the attraction of sorbate towards the sorbent [120].

2.16 Sorption isotherm studies

Sorption isotherms are fundamental requirement in designing a sorption system. This requirement is very important in explaining how metal ions interact with the biosorbent [121]. The equilibrium of the biosorption process is often described by fitting the experimental data with models that are commonly used for the representation of the isotherm adsorption equilibrium [122]. There are two widely accepted and easily linearized equilibrium adsorption isotherms namely Langmuir and Freundlich isotherm [54].

2.16.1 Langmuir isotherm

This model describes quantitatively about the formation of a monolayer adsorbate on the surface of the adsorbent and no further adsorption takes place after the sorption site was occupied. The Langmuir adsorption isotherm is the most widely used isotherm for the biosorption of pollutants from a liquid solution based on the following hypotheses [123]: (a) Monolayer adsorption. (b) Adsorption takes place at specific homogeneous sites on the adsorbent. (c) Once a pollutant occupies a site; no further adsorption can take place in that site. (d) Adsorption energy is constant and does not depend on the degree of occupation of an adsorbent's active centres. (e) The strength of the intermolecular attractive forces is believed to fall off rapidly with distance. (f) The adsorbent has a finite capacity for the pollutant. (g) All sites are identical and energetically equivalent. (h) The adsorbent is structurally homogeneous. (i) There is no interaction between molecules adsorbed on neighbouring sites.

Langmuir isotherm assumes monolayer biosorption [124], and is presented by the following equation:

$$\frac{1}{q_e} = \left(\frac{1}{q_{\max}} \right) + \left(\frac{1}{q_{\max} b} \right) \left(\frac{1}{C_e} \right) \quad (2.1)$$

Where:

q_e = equilibrium metal concentration on the biosorbent (mg/g)

C_e = equilibrium metal concentration on the solution (mg/L)

q_{\max} = maximum monolayer biosorption capacity of the biosorbent (mg/g)

b = Langmuir biosorption constant (L/mg)

Langmuir constant, q_{\max} is often used to compare the performance of the biosorbent. Thus for a good biosorbent, a high q_{\max} and a steep initial isotherm slope, b , are usually desirable [123].

2.16.2 Freundlich isotherm

Freundlich isotherm is an empirical equation based on the assumption of heterogeneous surfaces as well as multilayer sorption and also being the binding sites are not equivalent. Freundlich isotherm implies that adsorption energy exponentially decreases on the finishing point of adsorptional centres of an adsorbent. The Freundlich constants are empirical constants depends on many environmental factors. The value of $1/n$ ranges between 0 and 1 indicates the degree of non-linearity between solution concentration and adsorption. If the value of $1/n$ is equal to 1, the adsorption is linear [123].

It is expressed by the equation [125]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2.2)$$

Where:

q_e = uptake of metal per unit weight of biosorbents (mg/g)

C_e = equilibrium concentration of metal ions in solution (mg/L)

K_F = Freundlich constant denoting adsorption capacity (mg/g)

n = empirical constant, indicating of adsorption intensity (L/mg)

2.16.3 BET isotherm

Brunauer–Emmett–Teller (BET) theory is a popular method to interpret nitrogen adsorption isotherms for determining the specific surface area. This isotherm model assumes that adsorbent surfaces are perfectly flat and that gas molecules can adsorb on this surface or pile on top of another molecule that is already adsorbed. BET isotherm is identical to Langmuir in all respects, except that BET allow several molecules to adsorb on top of each other in each adsorption site. According to Volesky [122], a further assumption of the BET model is that a given layer need not complete formation prior to initiation of subsequent layers; the equilibrium condition will therefore involve several types of surfaces in the sense of number of layers of molecules on each surface site.

The equation describes as follow [126]:

$$\frac{C_e}{(C_i - C_e)q_m} = \frac{1}{K_B \cdot q_m} + \left[\frac{K_B - 1}{K_B \cdot q_m} \right] \left[\frac{C_e}{C_i} \right] \quad (2.3)$$

Where:

C_i = equilibrium concentration of metal ions in solution (mg/L)

C_e = final concentration of metal ions in solution at equilibrium (mg/L)

K_B = BET constant denoting energy interaction with the surface (mg/g)

q_m = equilibrium metal concentration on the biosorbent (mg/g)

2.17 Kinetics of biosorption

Kinetics models are used to investigate the mechanism of biosorption and potential rate controlling step such as mass transport and chemical reaction processes [86]. The kinetics models of pseudo first order and pseudo second order equation can be applied to biosorption data to analyze the biosorption kinetics. A good correlation of the kinetic data explains the biosorption mechanism of the metal ion in solid phase [69].

2.17.1 Lagergren Pseudo-first-order equation

As early as 1898, Lagergren described the liquid–solid phase adsorption systems, which consist of the adsorption of oxalic acid and malonic acid onto charcoal. Lagergren’s first-order rate equation is the earliest known equation that describing the adsorption rate based on the adsorption capacity. In order to differentiate kinetics equations based on concentrations of solution from adsorption capacities of solids, Lagergren’s first-order rate equation has been named as Pseudo-first order equation [127].

Lagergren’s kinetics equation has been most widely adopted for the adsorption of an adsorbate from an aqueous solution. Vast majority of the solutes in the adsorption systems from the articles studied were aqueous phase pollutants such as metal ions, and contaminating organic compounds. Some of the adsorbents were activated carbon, materials of biological organic compounds, agricultural by-products such as banana pith, palm-fruit bunch, coir pith, coconut husk and orange peel [128].

Linearized form of pseudo-first-order equation [129]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2.4)$$

Where:

q_t (mg/g) = the amounts of the metal ions biosorbed at equilibrium (mg/g)

q_e (mg/L) = amounts of the metal ions biosorbed at time, t (min)

k_1 = rate constant of the equation (min^{-1})

2.17.2 Pseudo-second-order equation

Pseudo-second order expression for solid-liquid sorption systems was developed in 1995 by Ho [130]. This equation demonstrates how the rate depended on the sorption equilibrium capacity but not the concentration of the sorbate. The pseudo-second order equation has the following advantages: (a) it does not have the problem of assigning an effective sorption capacity; (b) the sorption capacity, rate constant of pseudo-second order and the initial sorption rate all can be determined from the equation without knowing any parameter beforehand. If the equilibrium sorption

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