BIOSORPTION OF COPPER(II) AND CHROMIUM(VI) ONTO ACTIVATED SLUDGE : ISOTHERMS AND KINETIC MODELS

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BIOJERAPAN KUPRUM(II) DAN KROMIUM(VI) PADA ENAPAN TERAKTIF : MODEL ISOTERMA DAN KINETIK

Abstrak

Objektif kajian ini adalah untuk: (i) menilai kecekapan enapan teraktif terkultur makmal dalam penyingkiran Cu(II) dan Cr(VI) daripada larutan akueus secara berasingan dan gabungan, (ii) mengenalpasti model penjerapan keseimbangan yang sesuai bagi sistem logam tunggal dan gabungan dengan menggunakan enapan teraktif terkultur makmal dan (iii) mengenalpasti model penjerapan kinetik bagi sistem logam tunggal dengan menggunakan enapan teraktif terkultur makmal. Enapan teraktif yang digunakan dalam kajian ini dikulturkan dalam tiga buah reaktor kelompok berturutan (SBR) berskala makmal serbasama yang dioperasikan dengan mod PENGISIAN, TINDAK BALAS, PEMENDAPAN, PENGELUARAN dan REHAT dalam nisbah 2:12: 2.5: 1.5: 6 untuk tempoh 24 jam per kitaran. Enapan berusia 20-, 30- dan 40-hari disediakan dengan membazir satu amaun tetap campuran reaktor daripada reaktor berkenaan sebelum berakhirnya mod TINDAK BALAS dalam setiap kitaran. Enapan disediakan dalam keadaan yang hidup dan kering. Ciri-ciri enapan teraktif kering ditentukan dengan spektrofotometri FT-IR, penentuan kandungan kation utama dan pentitratan potensiometri. Kajian keseimbangan biojerapan untuk sistem logam tunggal bagi Cu(II) dan Cr(VI) dijalankan dalam kelompok. Masa keseimbangan bagi Cu(II) dan Cr(VI) masing-masing adalah 4 dan 24 jam. Data keseimbangan biojerapan disesuaikan dengan model Langmuir, Freundlich dan Redlich-Peterson. Model Langmuir dan Freundlich dalam bentuk linear dan bukan linear digunakan dalam menyesuaikan data keseimbangan manakala hanya bentuk bukan linear bagi model Redlich-Peterson digunakan. Keputusan menunjukkan bahawa model Langmuir dan Freundlich dalam bentuk bukan linear adalah lebih baik untuk disesuaikan dengan data eksperimen Cu(II) dan Cr(VI) berbanding dengan bentuk linear. Model Langmuir dan Redlich-Peterson dalam bentuk bukan linear didapati lebih baik daripada model

Freundlich dalam menyesuaikan data keseimbangan Cu(II) manakala ketiga-tiga model memberi kesesuaian yang baik untuk Cr(VI). Dalam biojerapan Cu(II), enapan kering yang berusia 20-, 30- dan 40-hari memaparkan kapasiti penjerapan terendah pada pH 2 tetapi tertinggi pada pH 4. Bagi enapan hidup, tiada corak jelas bagi kapasiti penjerapan diperhatikan berhubung dengan pH dan usia enapan. Dalam biojerapan Cr(VI), kapasiti penjerapan tertinggi bagi enapan kering berusia 20- dan 40-hari adalah pada pH 2 dalam julat pH 2 – 6. Kajian keseimbangan biojerapan dalam sistem logam gabungan dijalankan pada pH 2 dan 4. Pada pH 2, kapasiti penjerapan maksimum untuk Cr(VI) didapati berkurang secara mendadak daripada 15 ke 1.7 mg/g dalam kehadiran Cu(II). Ini menunjukkan bahawa Cu(II) mempunyai kesan antagonistik terhadap biojerapan Cr(VI) pada enapan. Pada pH 4, kapasiti penjerapan maksimum untuk Cu(II) didapati bertambah dari lebih kurang 9 kepada 12 mg/g dalam kehadiran Cr(VI) dan ini menunjukkan kesan sinergistik terhadap biojerapan Cu(II) pada enapan. Lima model kinetik, iaitu model pseudo-tertib pertama, pseudo-tertib kedua, tindak balas berbalik tertib-kedua, tindak balas tak berbalik tertib-kedua dan eksponensial berganda, digunakan untuk memuat dengan data kinetik biojerapan dalam sistem logam tunggal. Bagi Cu(II), kesemua model dapat menyesuaikan data kinetik dengan baik kecuali model tindak balas berbalik tertib-kedua. Bagi data kinetik biojerapan Cr(VI), kesesuaian baik diperhatikan untuk kesemua model kecuali model pseudo-tertib kedua dalam bentuk linear dan model tindak balas berbalik tertib-kedua.

BIOSORPTION OF COPPER(II) AND CHROMIUM(VI) ONTO ACTIVATED SLUDGE : ISOTHERMS AND KINETIC MODELS

Abstract

The objectives of this research are: (i) to evaluate the efficiency of laboratory-prepared sludge for the removal of Cu(II) and Cr(VI) individually and in combination from aqueous solutions, (ii) to ascertain appropriate adsorption equilibrium models for both single and binary metal systems using the laboratory-prepared sludge and (iii) to ascertain appropriate adsorption kinetic models for the single metal system using the laboratory-prepared sludge. The sludge used in this study was cultivated in three identical laboratory-scale sequencing batch reactors (SBR) operated with FILL, REACT, SETTLE, DRAW and IDLE periods in a ratio of 2: 12: 2.5: 1.5: 6 for a cycle time of 24 h. Sludges of 20-, 30- and 40-day sludge ages were prepared by wasting a fixed amount of mixed liquor from the respective reactor just before the end of the REACT period during every cycle. The sludge was prepared in the live and dried forms. The characteristics of dried sludges were determined by the FT-IR spectrophotometry, determination of major cation content and potentiometric titration. Biosorption equilibrium studies for the single metal systems of Cu(II) and Cr(VI) were carried out in batches. The equilibrium times for Cu(II) and Cr(VI) were found to be 4 and 24 h, respectively. The equilibrium biosorption data were fitted to the Langmuir, Freundlich and Redlich-Peterson models. The Langmuir and Freundlich models in the linearized and non-linear forms were used to fit the equilibrium data whereas only the non-linear form for the Redlich-Peterson model was used. The results show that the non-linear forms for the Langmuir and Freundlich models were better fitted to the experimental data for Cu(II) and Cr(VI) than the linearized forms. Among the non-linear forms of the models, the Langmuir and Redlich-Peterson models were better than the Freundlich model in fitting the adsorption equilibrium data for Cu(II) whereas all the three models provided good fit for Cr(VI). In the Cu(II) biosorption, dried sludges of all the sludge

ages exhibited the lowest adsorption capacity at pH 2 but the highest at pH 4. For live sludges, no pronounced trend for the adsorption capacity was observed with respect to pH and sludge age. In the Cr(VI) biosorption, the highest adsorption capacities of 20- and 40-day dried sludges were at pH 2 in the pH range of 2 - 6. The biosorption equilibrium studies for binary metal system were conducted at pH 2 and 4. At pH 2, the maximum adsorption capacity for Cr(VI) was found to decrease drastically from 15 to 1.7 mg/g without and with the presence of Cu(II). This showed that Cu(II) had an antagonistic effect on the biosorption of Cr(VI) onto the sludge. At pH 4, the maximum adsorption capacity for Cu(II) was found to increase from around 9 to 12 mg/g without and with the presence of Cr(VI) indicating a synergistic effect of Cr(VI) on the biosorption of Cu(II) onto the sludge. Five kinetic models, namely pseudo-first-order, pseudo-second-order, second-order reversible reaction, second-order irreversible reaction and double-exponential models, were applied to the biosorption kinetic data in the single metal systems. In the case of Cu(II), all the models fitted the kinetic data very well except for the second-order reversible model. For the kinetic data of biosorption of Cr(VI), the best fit was obtained with all the models except the linearized form of the pseudo-second-order and second-order reversible reaction models.

1.0   Introduction

The discharge of industrial wastewater containing toxic heavy metals to the environment is becoming a serious environmental issue. Metals are mostly originated from industries such as metal finishing, chemical, electronic and electrical, printing and packaging. In order to control and prevent pollution, as well as to protect and enhance the quality of the environment, environmental legislation has been enacted in most countries. In Malaysia, the Environmental Quality Act was promulgated in 1974 and the Department of Environment is empowered to enforce the Act.

As heavy metals pose serious environmental problem and are dangerous to human health, it is very important to treat the metal-contaminated wastewaters before being released to the environment. Among all heavy metals, ingestion of copper, chromium and zinc beyond permissible quantities causes various chronic disorders in human beings. In this research, copper and chromium were selected because of their widespread use in industries.

1.1   Heavy metals

Heavy metals refer to metallic elements that have specific gravities greater than 4.0 and are toxic or poisonous at low concentrations. Examples of heavy metals include chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), copper (Cu), zinc (Zn), molybdenum (Mo), silver (Ag), mercury (Hg), cadmium (Cd), nickel (Ni), tin (Sn), lead (Pb), antimony (Sb), bismuth (Bi), and selenium (Se). Heavy metals are natural components from the earth's crust. They cannot be destroyed or degraded. In very small amounts, many of these heavy metals are essential for normal development of biological cycle. However most of these heavy metals become toxic at high concentrations due to their ability to accumulate in living tissues. Eventually, the heavy metals threaten humans as they become pre-concentrated throughout the food chain.

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1.2   Sources of heavy metals (Copper and Chromium)

Copper(II) and chromium(VI) ions are serious environmental pollutants, frequently encountered together in industrial wastewaters, including those from mining, metal finishing, plating, electroplating, metal processing, dyeing and petroleum industries. Copper and chromium were chosen for biosorption studies with regard to their wide use in industry and potential pollution impact. The worst polluter is the metal finishing, plating and metal processing industries. According to the Environment Quality Act 1974, the permitted concentrations for copper(II) and chromium(VI) discharged in effluents are 1.0 and 0.05 mg/L, respectively.

1.2.1   Copper

Copper usually occurs in nature as oxides and sulphides. In acidic environments, free aqueous Cu^{2+} dominates. At pH 6 – 8, the predominant species are Cu^{2+}, $Cu(OH)_2$, $CuHCO_3^+$, $CuCO_3$, and $CuOH^+$. The major species are $Cu(OH)_4^{2-}$ and $Cu(OH)_3^-$ at pH more than 10 (Bodek *et al.*, 1998). Copper is an essential substance to human life. Copper is found in a variety of enzymes and is used for biological electron transport. Like all heavy metals, it is potentially toxic, especially at high concentrations. Thirty grams of copper sulfate is potentially lethal in humans. In high doses, it can cause anemia, liver and kidney damage, and stomach and intestinal irritation. Wilson's disease, a disease that causes the body to retain copper can lead to brain and liver damage if untreated. Inhalation of copper produces symptoms similar to those of silicosis and allergic contact dermatitis. Copper normally occurs in drinking water from copper pipes, as well as from additives designed to control algal growth. The suggested safe level of copper in drinking water for humans varies depending on the source, but tends to be pegged at 1.3 mg/L according to the US Environmental Protection Agency. Too much copper in water has also been found to damage marine life. The observed effect of these higher concentrations on fish and other creatures is damage to gills, liver, kidneys, and the nervous system. Common oxidation states of

copper include the less stable copper(I) state, Cu^+, and the more stable copper(II) state, Cu^{2+}, which forms blue or blue-green salts and solutions. Under unusual conditions, a +3 state and even an extremely rare +4 state can be obtained.

1.2.2 Chromium

The most common oxidation states of chromium are +2, +3, and +6, with +3 being the most stable whereas +1, +4 and +5 are rare. Chromium compounds of oxidation state +6 are powerful oxidants. Chromium(0) is unstable in oxygen, immediately producing a thin oxide layer that is impermeable to oxygen and protects the metal below. Chromium hexavalent (VI) compounds, are used as pigments for photography, and in pyrotechnics, dyes, paints, inks, and plastics. They can also be used for stainless steel production, textile dyes, wood preservation, leather tanning, and as anti-corrosion coatings.

Trivalent chromium occurs naturally in many fresh vegetables, fruits, meat, grains, and yeast, and is often added to vitamins as a dietary supplement. Trivalent chromium, Cr(III), is required in trace amounts for sugar metabolism in humans, and its deficiency can cause chromium deficiency. In contrast, hexavalent chromium is very toxic. Potassium dichromate is a powerful oxidizing agent and is the preferred compound for cleaning laboratory glassware of any possible organics. It is used as a saturated solution in concentrated sulphuric acid for washing the apparatus. Chrome green is the green oxide of chromium, Cr_2O_3, used in enamel painting, and glass staining. Chrome yellow is a brilliant yellow pigment, $PbCrO_4$, used by painters. Chromic acid has the hypothetical structure H_2CrO_4. Neither chromic nor dichromic acid is found in nature, but their anions are found in a variety of compounds. Chromium trioxide, CrO_3, the acid anhydride of chromic acid, is sold industrially as "chromic acid". Chromium is present in the electroplating wastewater as Cr(VI) in the form of oxyanion, such as chromates (CrO_4^{2-}), dichromates ($Cr_2O_7^{2-}$) and bichromates

($HCrO_4^-$). Hexavalent chromium exists as different form depending on the pH. The species of H_2CrO_4 predominates at pH less than 1, $HCrO_4^-$ at pH between 1 and 6, and CrO_4^{2-} at pH above 6. The dichromate ion, $Cr_2O_7^{2-}$, exists when the concentration of chromium exceeds approximately 1 g/L (Dionex,1996).

1.3   Conventional metal-removal technologies

In recent years, the removal of heavy metals ions from wastewaters has received a great deal of attention. There are several methods currently available for the removal of heavy metals from industrial wastewaters. The main methods are chemical precipitation, ion-exchange, membrane technologies, chemical reduction, electrolytic processes and adsorption. In conventional practice, chemical precipitation is the most commonly employed technology for metals removal (Vazquez *et al.*, 2002). However, many of these approaches can be less cost effective or difficult for practical use. These processes have significant disadvantages including incomplete metal removal at low concentrations in vast wastewater quantities.

Chemical precipitation is a widely used, proven process for the removal of metals and other inorganics, suspended solids, fats, oils, greases and some other organic substances (including organophosphates) from wastewater. Precipitation involves the alteration of the ionic equilibrium of a dissolved metallic compound to produce an insoluble precipitate. The process typically uses an alkaline reagent to cause the solubility of the metal ions to decrease, and thus precipitate out of solution. The chemicals most frequently used for precipitation of metals are hydroxides, sulfides, and carbonates. Majority of present technology is based on hydroxide precipitation. In certain cases where heavy metals are complexed, or at concentration below the level of minimum hydroxide solubility, sulfide precipitation is a viable alternative. Carbonate precipitation is used where it provides superior precipitation

properties or lower effluent concentrations. The disadvantage of precipitation is the production of sludge which constitutes a solid waste disposal problem.

Ion exchange is a versatile separation process used to remove metal contaminants from aqueous wastewater and to recycle or discharge the treated solution. It involves the use of an ion selective resin to remove ionic contaminants such as metals from the solution. Three basic types of resins, namely, cation exchange resins, anion exchange resins, and metal selective chelating resins are employed. The major attraction of ion exchange is the broad range of resins manufactured to treat specific wastewaters. The ion exchange resin works selectively to remove only the toxic compound while allowing the non-toxic dissolved ionic solid to remain in solution. Ion exchange can provide an effective pollution control in a wide range of applications such as water purification and chemical recovery. However, a high capital expenditure is usually required in order to purchase and operate such a system. Furthermore, the economics of this method depend very strongly on the energy price and the amount of electricity consumed per treated volume of metal solution.

Membrane technologies such as reverse osmosis and electrodialysis are used commercially to recover dissolved metals from aqueous wastes generated through electroplating or metal etching processes. The technology is applicable to specific wastewaters, provided pretreatment measures can be used to remove suspended and dissolved solids and ensure acceptable membrane lifetimes. Current membrane processes tend to be hindered by the problems of limited flow-rates, instability of the membranes in salt and acid conditions and fouling by inorganic and organic species.

Chemical reduction as a waste treatment process is an established and well developed technology. The reduction of hexavalent chromium's oxidation state to decrease toxicity and encourage precipitation is presently used as a treatment

technology in numerous electroplating facilities. Major advantages of using chemical reduction in the case of reducing hexalent chromium include operation at ambient conditions, automatic controls, high reliability, and modular process equipment. Hexavalent chromium can be reduced to trivalent chromium, which can then be removed by precipitation. The pH of the aqueous solution is reduced to 2 with hydrochloric or sulfuric acid. Then the reducing agents such as sulfur dioxide and sodium metabisulfite are added. The pH is increased to 8.5 by addition of lime and the trivalent chromium is precipitated. An alternative reducing agent applicable to most heavy metals is sodium borohydride. The disadvantage of this process is the utilization of chemicals throughout the reduction process.

Electrolytic process is used to remove dissolved metals from rinse waters generated by metal plating and etching processes. In this case, an electrolytic cell is attached to the rinse bath following the plating or etching tank, the rinse solution is circulated through the electrolytic cell. As the solution passes through the cell, dissolved metals ions are reduced and deposited on the cathode in elemental form. There are a number of different electrolytic cell designs. The use of one design over another depends upon the application. Noble metals such as gold and silver are easy to remove electrolytically using flat plate electrode, but metals such as copper, tin, lead and cadmium are more difficult to remove and sometimes may require the use of the more complex electrolytic cell designs.

Adsorption was first observed by Lowitz in 1785 and applied as a process for the removal of colour from sugar during refining. The first granular activated carbon units were used in the treatment of water supplies in Hamm, Germany in 1929 and at Bay City, Michigan in 1930 (Montgomery, 1985). Adsorption on activated carbon is a recognized method for the removal of heavy metals from wastewater. Activated carbon adsorption involves the separation of a substance from one phase, typically an

aqueous solution, and the concentration of the substance at the surface of an activated carbon adsorbate. Adsorption is a relatively simple method for the removal of heavy metals compared to other conventional methods. Important adsorbents in industrial use are activated carbon, silica gel and alumina. Although promising results have been reported, the high cost of the adsorbents, which increases the cost of the wastewater treatment limit their use.

1.4   Biological technologies (biosorption and bioaccumulation)

Searching for a low cost and easily available adsorbent has led to the selection of materials from agricultural and biological origin, along with industrial by-products, as adsorbents. Biological treatment using either living or dead microorganisms or plants, offers unique capabilities to concentrate and reduce the levels of heavy metals to environmentally acceptable limits in a economically and environmentally friendly manner (Volesky, 2001).

From the terminological point of view, the term bioaccumulation is usually used for metal uptake by living cells and the term biosorption for passive sequestering by dead cells (Volesky, 1990). Biosorption and bioaccumulation belong to the group of biological methods suitable for heavy metal removal from wastewater. These methods have many advantages over the conventional methods in that they are highly selective, more efficient, easy to operate and cost effective for the treatment of large volume of wastewaters containing low level of heavy metals. The use of dead biomass eliminates the problem of toxicity and no activation or chemical modifications of the sorbent are necessary.

Biosorption or bioadsorption is in fact a passive immobilization of metals by biomass. A variety of microbial and other biomass types has been shown to have good biosorption potential and several have been proposed as the basis for treatment for

metal-bearing industrial wastewaters. The microorganism's cell wall consists mainly of polysaccharides, lipids and proteins, which have many binding possibilities for metals.

1.4.1 Biosorbent

There is a large volume of literature relating to the performance of different biosorbents for the removal of different heavy metals (Bailey *et al.* 1999). Cost is a very important factor when considering materials for use as biosorbents. A material can be deemed as low cost if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry (Bailey *et al.* 1999).

Agricultural wastes have been applied as biosorbents for Cu(II) and Cr(VI) remediation from wastewaters. The most commonly-used agricultural wastes or by products include sawdust (Hamadi *et al.*, 2001), sugar beet pulp (Pehlivan *et al.*, 2006), shea butter seed husks (Eromosele *et al.*, 1996), rice hull (Tang *et al.*, 2003), papaya wood (Saeed *et al.*, 2005) and coconut shell (Babel and Kurniawan, 2004).

Besides agricultural waste, removal of Cu(II) and Cr(VI) using industrial waste or by products has been explored. The most important of these adsorbents are used tyres (Hamadi *et al.*,2001), activated sludge (Aksu *et al.*, 2002, Hammaini *et al.*, 2002, Wang *et al.*, 2005, Gulnaz *et al.*, 2005, Hawari and Mulligan, 2006), lignin (Mohan *et al.*, 2006) and fly ash (Pehlivan *et al.*, 2006).

For simplicity, biomass-derived metal sorbents have been subdivided into 5 categories: (a) algae and seaweed, (b) fungi and yeast, (c) bacteria, (d) plants and (e) wood, grasses, compost, peat moss (Mohan and Pittman Jr., 2006). These biomasses produced encouraging results in removing heavy metals from dilute aqueous solutions.

(a) Algae and seaweed used for Cu(II) and Cr(VI) removal include *Chlorella kessleri* (Kaduková and Virčíková, 2004), *Caulerpa lentillifera* (Apiratikul and Pavasant, 2006), *Chlamydomonas reinhardtii* (Arıca *et al.*, 2005), *F. vesiculosus* (Cochrane *et al.*, 2006), *C. vulgaris* (Acikel and Aksu, 1999), *Sargassum sp.* (Valdman *et al.*, 2001) and *Ecklonia maxima*, *Lessonia flavicans* and *Durvillea potatorum* (Aderhold *et al.*, 1996).

(b) Fungi and yeast

Various types of fungal biomass and yeast have been used for the removal of Cu(II) and Cr(VI) from wastewater. These include *Rhizopus arrhizus* (Sağ and Kutsal, 1996, Prakasham *et al.*, 1999) and waste beer yeast (Han *et al.*, 2006).

(c) Bacteria

Biosorption of Cu(II) and Cr(VI) using bacteria gave promising results. *Sphaerotilus natans* (Esposito *et al.*, 2001), *Nocardia sp.* (Sadowski, 2001), *Arthrobacter sp.* (Pagnanelli *et al.*, 2000), *Bacillus sp.* (Nourbakhsh *et al.*, 2002), *Ochrobactrum anthropi* (Ozdemir *et al.*,2003), *Bacillus thuringiensis* (Sahin and Öztürk, 2005) and *Aeromonas caviae* (Loukidou *et al.*, 2004) have been used for Cu(II) and Cr(VI) remediation.

(d) Plants

Cu(II) and Cr(VI) remediation were studied using various plants, including *Thuja orientalis* (Nuhoglu and Oguz, 2003), olive pomace (Pagnanelli *et al.*, 2005), *Pinus sylvestris* (Ucun *et al.*, 2002) and *Tectona grandis* l.f. (King *et al.*, 2006).

(e) Wood, grasses, compost, peat moss

The ability of wood to remove Cu(II) and Cr(VI) from wastewater was investigated by Saeed *et al.* (2005). Utilization of peat moss for treating Cu(II) and Cr(VI) contaminated

wastewater was carried out by Ho and Mckay (2000), Ma and Tobin (2003), Ma and Tobin (2004) and Cochrane *et al.* (2006).

1.4.2 Removal of metals by biosorption

The literature reviewed below presents some of the common heavy metals such as Cu(II), Cr(VI), Cd(II), Ni(II) and Pb(II) studied by researchers. The literature review was divided into two parts, namely single metal and binary metal systems.

1.4.2.1 Single metal system

The biosorption of Cr(VI) in aqueous solution onto native, heat and acid-treated microalgae *Chlamydomonas reinhardtii* was investigated by Arıca *et al.* (2005). The Langmuir and Freundlich isotherm models were found to describe well the experimental data. The kinetics of Cr(VI) biosorption on the biomass was determined with the first and second-order equation. The experimental data were better fitted with the second-order equation than the first-order equation.

Biosorption of Cr(VI) was studied by Prakasham *et al.* (1999) using free and immobilized *Rhizopus arrhizus* in stirred tank and fluidized bed reactor at pH 2. The immobilized biomass exhibited similar adsorption capacity as free biomass as evaluated using the Freundlich adsorption isotherm. The studies with fluidized bed reactor revealed higher efficiency in Cr(VI) removal over stirred tank reactor.

Vijayaraghavan *et al.* (2005) reported Ni(II) biosorption onto *Sargassum wightii*, a brown marine algae, in batch experiments. The equilibrium data obtained at pH 3.0 to 4.5 have been analyzed using five two-parameter models (Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Flory-Huggins) and five three-parameter models (Redlich-Peterson, Sips, Khan, Radke-Prausnitz and Toth). From the results obtained, the Toth equation provided the best model for nickel biosorption data at all pH

conditions. Besides, the three-parameter models better described the nickel biosorption data compared to two-parameter models.

Cochrane *et al.* (2006) compared three biosorbents, crab carapace, the macroalgae *Fucus vesiculosus* and peat with two commercial materials, an activated carbon and an ion-exchange resin for the removal of Cu(II) from aqueous media. Kinetic models of Lagergren first-order, pseudo-second-order and intraparticular diffusion were used to model the data. The kinetic process for all materials was found to follow the pseudo-second-order rate model. Ion exchange was found to be the main mechanism occurring in the biosorption of Cu(II) using crab carapace, *Fucus vesiculosus* and peat. Langmuir and Freundlich isotherms were used to describe the adsorption equilibrium data. It was found that Langmuir and Freundlich isotherm models could not be fitted to the experimental data for peat and activated carbon. Based on the results from the study, it was suggested that both crab carapace and *Fucus vesiculosus* were effective and efficient biosorbent materials for the removal of copper from aqueous solution and may be considered as viable alternatives to activated carbon and ion-exchange resin.

Esposito *et al.* (2001) utilized *Sphaerotilus natans* for the biosorption of Cu(II) and Cd(II), respectively, from aqueous solution. Equilibrium biosorption studies of Cu(II) and Cd(II) were carried out to investigate the effects of pH and biomass concentration. Equilibrium modelling was performed for both metals by using the Langmuir, Freundlich and Redlich-Peterson adsorption models. The Langmuir model was found to be the most suitable model to fit the data for both metals.

Sahin and Öztürk (2005) reported batch adsorption of aqueous Cr(VI) using dried vegetative cell and spore-crystal mixture of *Bacillus thuringiensis*. Cr(VI) ions uptake of *Bacillus thuringiensis* spore-crystal mixture exhibited better performance

than dried vegetative cell of *Bacillus thuringiensis*. The Scatchard, linearized form of the Langmuir equation, were used to obtain more compact information about the interaction between Cr(VI) ions and biosorbents. The plot results are further studied using Langmuir and Freundlich models. The adsorption data provided an excellent fit to both the Langmuir and Freundlich isotherms.

Biosorption of Cr(VI) from aqueous solutions on *Aeromonas caviae* particles was investigated in a well-stirred batch reactor by Loukidou *et al.* (2004). Equilibrium and kinetic experiments were performed at various initial bulk concentrations, biomass loads, temperatures and ionic background. The adsorption equilibrium data fitted the Langmuir model a little better than the Freundlich model. Several chemical reaction kinetic models included Ritchie second-order equation and pseudo-second-order were used to identify a suitable kinetic equation. Predictions based on the pseudo-second-order rate expression were found in satisfactory accordance with experimental data.

Cone biomass of *Thuja orientalis* was assessed for its capability for Cu(II) removal from wastewater with respect to pH, contact time, temperature, agitation speed at several initial metal ion and biosorbent concentrations (Nuhoglu and Oguz, 2003). The adsorption constants were defined according to the Freundlich, Langmuir and BET isotherm models. The experimental data were fitted well to the Langmuir adsorption model.

The applicability of cone biomass of *Pinus sylvestris* in Cr(VI) removal from aqueous solution was reported by Ucun *et al.* (2002). Decreasing pH from 7.0 to 1.0 increased the removal extent of Cr(VI) and Freundlich isotherm was used to calculate the adsorption constants.

Ünlü and Ersoz (2006) studied the adsorption of Cu(II), Pb(II) and Cd (II) metal ions onto sporopollenin. Adsorption on sporopollenin can be expressed better with the Freundlich adsorption isotherm rather than the Langmuir and D-R isotherms. Experimental data were also evaluated using the pseudo-first, pseudo-second and intraparticle diffusion kinetic models. Adsorption processes for Cu(II), Pb(II) and Cd (II) ions were found to follow the pseudo-second-order kinetic model. Intraparticle diffusion was found to take part in adsorption processes but it could not be accepted as the primary rate-determining step. Adsorption of heavy metal ions onto sporopollenin was found to occur with an ion-exchange process and chelating effect of the functional groups on sporopollenin.

Studies on a batch adsorption system using *Tectona grandis* l.f. as the biosorbent to remove Cu(II) from aqueous solution were performed under various conditions such as different initial concentrations, pH, adsorbent dosage and adsorbent particle size (King *et al.*, 2006). The experimental equilibrium data were fitted with the Langmuir and Freundlich models. The best model to the experimental equilibrium data was the Langmuir model. The optimum pH value was found to be 5.5. The pseudo-first and pseudo-second order kinetic models were used to describe the kinetic data. The kinetics of the adsorption of Cu(II) on *Tectona grandis* l.f. was found to be better described with the pseudo-second-order model.

Adsorbent materials derived through pyrolysis and activation from waste carbonaceous materials such as used tyres and sawdust were reported to have comparable performance to commercial activated carbon in the removal of Cr(VI) from aqueous solution (Hamadi *et al.*, 2001). The results indicated that the optimum pH for the removal of all types of carbon was around 2. The batch adsorption kinetics have been tested for a first-order reversible reaction, pseudo-first-order and pseudo-second-order reaction. The pseudo-second-order reaction model provides the best correlation

of the data. The equilibrium data for adsorption of Cr(VI) onto the carbon followed the Langmuir model. The negative values of the free energy change (ΔG^0) at different temperatures indicate the endothermic nature of Cr(VI) adsorption on the carbons.

The use of non-living anaerobic biomass treated with Ca ions appeared to be a promising biosorbent to remove Pb(II), Cd(II), Cu(II) and Ni(II) from aqueous solution (Hawari and Mulligan, 2006). The cation exchange capacity of treated biomass was found to be comparable to the metal binding capacities of commercial ion exchange resin. The initial pH value of the solution affected metal adsorption. The pH effects were not significant over the pH range of 4.0 to 5.5 but the uptake capacity of biomass decreased at lower pH values. The data pertaining to the adsorption dependence upon metal concentration fitted to Langmuir isotherm.

The equilibrium and kinetic characteristics of Cu(II) adsorption on partially deacetylated prawn shell were studied in batch stirred-tank experiments (Chu, 2002). The extent of Cu(II) removal increased with an increase in pH. Both the Langmuir model with pH-dependent parameters and the extended Langmuir-Freundlich model with pH-independent parameters account very well for the equilibrium data. A diffusion-based model and two surface reaction rate models, a second-order reversible reaction model and a second-order irreversible reaction model were used to describe the transient behaviour of the batch contactor. Modelling studies using two different second- order surface reaction models demonstrated that transient profiles obtained experimentally for a range of initial metal concentrations and adsorbent dosage were in good agreement with calculated curves of both models provided their rate constants were properly correlated with the two system variables. In contrast, deviation exists between experimental data and theoretical curves calculated from a diffusion-based model.

The biosorption of Cu(II) and Pb(II) from aqueous solutions by dried activated sludge was investigated with respect to initial pH, initial metal ion concentration and temperature (Wang *et al.*, 2005). The results showed that both the heavy metals uptake processes obeyed the pseudo-second-order kinetics. The equilibrium data fitted well to both Langmuir and Freundlich adsorption models. The main mechanism of Cu(II) and Pb(II) biosorption on dried activated sludge was binding of heavy metals with the amide I group.

The kinetics of adsorption of Pb(II), Cu(II) and Ni(II) onto sphagnum moss peat was evaluated as a function of initial metal concentrations and peat doses using pseudo-second-order rate equation (Ho and Mckay, 2000). The biosorption of three divalent metals onto sphagnum moss peat was described by pseudo-second-order based on the assumption that the rate limiting step was chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate. The rate constant, equilibrium adsorption capacity and the initial adsorption rate were calculated and an empirical model was derived for predicting the adsorption capacity of metal ions adsorbed.

Sadowski (2001) assessed the effect of biosorption of Pb(II), Cu(II) and Cd(II) on the zeta potential and flocculation of *Nocardia* sp. Biosorption of these metals was due to the net negative charge of the biomass surface and the degree of electronegativity of the metal ions. The electrostatic interaction of metal ions with the negatively charged functional groups on the bacteria surface was proposed as the primary mechanism of biosorption. The electrokinetic data showed that the isoelectric point of *Nocardia* cells was around pH 3.5. An increase of the metal ion concentration led to a decrease in the negative value of zeta potential of the bacteria cell. Usage of the combination of oppositely charged flocculant and surfactant was found to be suitable for the separation of bacteria cells after the biosorption.

The biosorption of Cu(II) ions from aqueous solution by dried activated sludge was investigated in batch systems with respect to pH, initial metal concentration and particle size by Gulnaz *et al.* (2005). The optimum pH and temperature for Cu(II) biosorption were 4.0 and 20 $^{\circ}$C, respectively. Langmuir and Freundlich isotherms were fitted very well with studied temperature and concentration ranges. The biosorption of Cu(II) on dried activated sludge was determined as an exothermic reaction. The pseudo-first-order, pseudo-second- order and intraparticle diffusion model were applied to analyze the biosorption data. The pseudo-second-order was found to be the most appropriate model to describe the biosorption system. The FT-IR spectrum showed that the different functional groups of dried activated sludge were responsible in binding metal ions or protons in aqueous solution.

Ho *et al.* (2004) assessed the kinetics and equilibrium of Pb(II) adsorption onto tree fern with respect to initial concentration and temperature. Three equilibrium models, namely the Langmuir, Freundlich and Redlich-Peterson isotherms were used to analyze the adsorption data. The Langmuir and Redlich-Peterson isotherms were found to have higher correlation coefficients than that of Freundlich isotherm. The pseudo-first-order, pseudo-second-order and the chemical phenomenon model were applied to fit the kinetic data. Adsorption of Pb(II) fitted the pseudo-second-order best. The results on the effect of temperature suggested the adsorption rate-controlling step was likely chemical in nature for the adsorption of Pb(II) on tree fern.

The ability of bacteria *Arthrobacter sp.* to remove Cu(II), Cd(II) and Fe(II) was evaluated and the chemical modeling of experimental data was applied to interpret the mechanism of biosorption (Pagnanelli *et al.*, 2000). The potentiometric titration of an aqueous cellular suspension showed that the biomass cell wall had two weakly acidic sites. Adsorption isotherms obtained from the subsequent additions method, SAM, were found to be pH dependent. A chemical model was developed based on a

possible set of reactions between ions in solution and biomass. Copper biosorption between pH 3-5 was mainly due to two mechanisms, namely ion exchange and complexation while for pH above 5, the suggested mechanism involved was superficial microprecipitation.

A dead exopolysaccharide producing bacterium, *Ochrobactrum anthropi* was found to be capable of removing Cr(VI), Cu(II) and Cd(II) from single metal ion solution (Ozdemir *et al.*, 2003). Experiments were performed as a function of pH, initial concentration and biosorption time. The optimum pH values for Cr(VI), Cu(II) and Cd(II) were 2.0, 3.0 and 8.0, respectively. Biosorption data fitted both the Freundlich and Langmuir isotherms.

Papaya wood was evaluated as a new biosorbent for Cu(II), Cd(II) and Zn(II) removal from their aqueous solutions as a function of pH, contact time, amount of biosorbent and initial metal ion concentration (Saeed *et al.*, 2005). The affinity of papaya wood to adsorb metals was in the order of Cu(II)>Cd(II)>Zn(II). The biosorption data fit perfectly to the Langmuir isotherm. The biosorption kinetics obeyed the pseudo-second-order rather than pseudo-first-order models. Based on the desorption results, it was concluded that desorption process of all the three metals based on the treatment of papaya wood with 0.1 N HCl was almost 100 % complete.

The sugar beet pulp (SBP) and fly ash (FA), an industrial by-product and solid waste of sugar industry were utilized as potential low cost sorbents for the removal of Cu(II) and Zn(II) ions from aqueous solution (Pehlivan *et al.*, 2006). Parameters such as initial pH, adsorbent dose, initial metal ion concentration, and contact time on adsorption of Cu(II) and Zn(II) onto the SBP and FA were studied. Adsorption of metal was pH dependent. The maximum uptake of Cu(II) and Zn(II) occurred at pH 5.5 and 6.0, respectively, for SBP and at pH 5.0 and 4.0, respectively, for FA. The adsorption

data for SBP fitted very well to the Freundlich model and those for the FA fitted to the Langmuir model for Zn(II) and Freundlich model for Cu(II). The adsorption data for FA in the adsorption of Zn(II) suggested that the monolayer adsorption occurred mainly due to ion exchange. The presence of low concentration of Na and Cl ions did not reveal any significant effect on the adsorption of both metals by SBP and FA.

The literature review above indicated that there were many studies on the biosorption of copper(II) and chromium(IV) as single metal using various kind of biosorbents. However, the presence of only one kind of heavy metal ion is a rare situation either in nature or in wastewaters. The following review presents the results from those researchers who studied the biosorption of two metal ions simultaneously onto biosorbents in binary metal system. In comparison, relatively fewer studies were conducted on the biosorption of binary system consisting of two metal species of opposing charges.

1.4.2.2 Binary metal system

Sağ and Kutsal (1996) studied the biosorption of Cu(II) and Cr(VI) from binary metal mixtures onto *Rhizopus arrhizus*, a filamentous fungus, as a function of metal ion concentration, pH and temperature. The optimal pH for Cu(II) and Cr(VI) biosorption was 4.0 and 2.0, respectively. In the Cu(II) and Cr(VI) binary metal system, the combined effects of these two metals were found to be antagonistic but the total interactive effects of Cu(II) and Cr(VI) ions on *Rhizopus arrhizus* were found to be synergistic.

Acikel and Aksu (1999) investigated the simultaneous biosorption of Cu(II) and Cr(VI) onto an algae, *Chlorella vulgaris,* from binary metal mixtures in a single-staged batch reactor. The pH values of 2.0 and 4.0 were chosen as the optimum biosorption

pH for Cr(VI) and Cu(II). The adsorption phenomenon was expressed by the competitive, multi-component Freundlich adsorption isotherm.

Tang *et al.* (2003) reported the adsorption characteristics of Cu(II) and Cr(VI) by ethylenediamine-modified rice hull from single and binary metal ion solutions. Optimum adsorption pH values of Cu(II) and Cr(VI) in single metal ion solutions were 5.5 and 2.0, respectively. Simultaneous removal of Cu(II) and Cr(VI) occurred at pH greater than 3.0. The adsorption kinetics of both metals from single and binary metal system were studied as a function of metal concentration, agitation rate and particle size. Adsorption of Cr(VI) was more rapid than Cu(II). Kinetics of adsorption were fitted to the pseudo-first-order and pseudo-second-order models. It was found that application of the pseudo-second-order-model provided better correlation of the experimental data than the pseudo-first-order model, implying that the rate-limiting step may be chemisorption. Equilibrium adsorption data fitted the Langmuir isotherm. Ethylenediamine-modified rice hull possessed higher adsorption capacity for both metals compared with natural rice hull in single and binary metal system. Synergistic effect was observed in binary metal system.

Waste beer yeast, a by-product of brewing industry, was found to be a low cost and promising adsorbent for adsorbing Cu(II) and Pb(II) from wastewater (Han *et al.*, 2006). Biosorption of Cu(II) and Pb(II) ions was investigated in batches and the equilibrium data was fitted well to both the Langmuir and Freundlich model isotherms. Competitive biosorption of two metal ions was investigated in terms of adsorption quantity. The competitive results showed that the adsorptive quantity for one metal was significantly decreased in the presence of the other metal, but the total capacity for binding heavy metals changed little. The binding capacity for Pb(II) was more than that for Cu(II). It was referred that ion exchange was probably one of the main mechanisms during the adsorptive process.

By-product lignin from paper production was used for the biosorption of Cu(II) and Cd(II) from aqueous solution in single, binary and multi-component systems with respect to pH, temperature, lignin particle size and solid to liquid ratio (Mohan *et al.*, 2006). The adsorption data fitted the Langmuir isotherm better than the Freundlich isotherm. Cu(II) and Cd(II) adsorption data were best described by a pseudo-second-order rather than pseudo-first-order kinetic model. Adsorption occurred through a particle diffusion mechanism at 10 and 25 $^{\circ}$C while at 40 $^{\circ}$C it occurred through a film diffusion mechanism. The results showed that the adsorption capacity of black liquor lignin was higher than many other adsorbents or carbons or biosorbents utilized for the removal of Cu(II) and Cd(II) from wastewater in single and multi-component systems.

Ma and Tobin (2003) investigated the biosorption of Cr(III), Cu(II) and Cd(II) from binary metal solutions onto peat at pH 4. The order of maximum uptake was found to be Cr(III) > Cu(II) > Cd(II). The presence of co-ions had inhibited the uptake of individual metals by up to 70 %. As the solution pH was largely unchanged during biosorption, speciation effects were unlikely to have a major influence on metal uptake. Three models, Model A, B and C were chosen to model the experimental metal uptake data. Model B which involved valency considerations was found to be unsuitable. In contrast, Model A, which assumed negligible H^+ ion uptake and neglected valence effects on uptake and Model C, which included binding and competition effects of H^+ ions but neglected metal valence influences, were found to exhibit good fit to the experimental data. Using Model A and the corresponding best-fit parameters, three-dimensional biosorption surfaces were generated using the MATLAB software.

Apiratikul and Pavasant (2006) studied the binary adsorption of Cu(II), Cd(II) and Pb(II) by dried green macroalga, *Caulerpa lentillifera*. The studying of binary component biosorption model using three concepts consisted of competitive, uncompetitive, and partial competitive adsorption isotherm models. The partial

competitive binary isotherm model was proven to be effective in describing the experimental data. Antagonistic competitive effect was found to occur for the adsorption in binary systems where the adsorption capacity of primary metal ion decreased in the presence of the secondary metal ion. Pb(II) was found to be the most favorable metal adsorbed by *Caulerpa lentillifera,* followed by Cu(II) and Cd(II). The partial competitive binary isotherm could also be used to predict the effect of pH on the adsorption of these metal ions. Reduction in the adsorption capacity and adsorption affinity was observed with a decrease in pH. The carboxyl, hydroxyl, sulfonate, amine and amide functional groups were proposed to be responsible for the adsorption of these metals.

The competitive biosorption of Cd(II) and Ni(II) onto dried *Chlorella vulgaris*, a green alga from binary metal mixture was studied and compared with single metal ion in a batch stirred system (Aksu and Dönmez, 2006). The dried biomass was selective for mixed cation components and it exhibited higher adsorption capacity for Cd(II) than for Ni(II). The effects of single and binary metal ion concentrations on the biosorption capacity of biomass were investigated at an initial pH 4.0. The biosorption data in binary systems showed that the Ni(II) biosorption was strongly repressed by increasing Cd(II) concentration in solution. The Langmuir and Freundlich adsorption models were found suitable for describing the biosorption equilibria of cadmium(II) and nickel(II) ions in both single and binary metal systems.

The biosorption of Cr(VI), Ni(II) and Cr(VI)-Ni(II) binary mixtures on the dried activated sludge was investigated in a batch system by Aksu *et al.* (2002). The individual Langmuir and Freundlich adsorption isotherms for Cr(VI) and Ni(II) ions were obtained at pH 1.0 and 4.5, respectively. Although dried activated sludge exhibited higher adsorption capacity for Cr(VI) and Ni(II) individually but the equilibrium uptake of Cr(VI) and Ni(II) in the binary mixture were found to be decreasing due to the

antagonistic interaction occurred between the metals. Adsorption isotherms were developed for the single and binary metal systems at pH 1.0 and 4.5 and expressed by the mono- and multi-component Langmuir and Freundlich adsorption models. The results indicated that the mono-component equilibrium data fitted very well to both the mono-component Langmuir and Freundlich models for both the metals and the pH studied. For the case of multi-component system, multi-component Freundlich model agreed well with the experimental data in the studied initial mixture concentration range at both the studied pH values.

1.5   Equilibrium and kinetic models of biosorption

1.5.1   Sorption equilibrium models

Modelling the equilibrium data allows comparison of different biosorbents under different operating conditions. Equilibrium data, also known as adsorption isotherms, are basic requirements for the design of adsorption systems and provide information on the capacity of the adsorbent or the amount required to remove a unit mass of pollutant under the system conditions such as initial pH of metal solution, initial metal ion concentrations and amount of biosorbent. There are many equilibrium models in use but the most common models are the Langmuir, Freundlich and Redlich-Peterson models. These three equilibrium models were used to analyze the equilibrium data of Cu(II) and Cr(VI) in the single metal system for this study. In the binary metal system, the extended Langmuir model and the non-competitive Langmuir model were used to evaluate the biosorption data.

1.5.1.1 Langmuir model

The Langmuir adsorption isotherm (Langmuir, 1916) is valid for monolayer coverage of the adsorption surface. This model assumes that adsorption occurs at specific homogeneous adsorption sites within the adsorbent and intermolecular forces decrease rapidly with the distance from the adsorption surface. The Langmuir

adsorption model further bases on the assumption that all the adsorption sites are energetically identical and adsorption occurs on a structurally homogeneous adsorbent. The well-known expression of the Langmuir model is given by:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad \text{(non-linear form)} \tag{1.1}$$

or in its linearized form:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \tag{1.2}$$

where q_e (mg/g) and C_e (mg/L) are the amount of adsorbed metal per unit weight of biomass and unadsorbed metal concentration in solution at equilibrium, respectively. The quantity q_m (mg/g) is the maximum adsorption capacity and K_L is a constant related to the affinity of the binding sites (L/mg). The parameters q_m and K_L can be determined from the C_e/q_e versus C_e plot based on Eq. (1.2).

1.5.1.2 Freundlich model

The Freundlich isotherm was originally empirical in nature, but was later interpreted as adsorption to heterogeneous surfaces or surfaces supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation. The Freundlich model is formulated as (Freundlich, 1906):

$$q_e = K_F C_e^{1/n} \quad \text{(non-linear form)} \tag{1.3}$$

which can be linearized in the logarithmic form as shown below:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \tag{1.4}$$

Here, C_e and q_e have the same meaning as noted above whereas n (dimensionless) and K_F (L/g) are the Freundlich constants denoting the relative adsorption capacity and the intensity of adsorption, respectively. According to Eq. (1.4), the plot of the ln q_e versus ln C_e gives a straight line and K_F and n values can be calculated from the intercept and the slope of this straight line, respectively.

1.5.1.3 Redlich-Peterson model

The Redlich-Peterson isotherm (Redlich and Peterson, 1959), which contains three parameter incorporating the features of the Langmuir and the Freundlich isotherms, can be expressed as:

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad \text{(non-linear form)} \tag{1.5}$$

where C_e and q_e have the same meaning as in the Langmuir isotherm, A is the Redlich-Peterson model isotherm constant, B the Redlich-Peterson model constant and g the Redlich-Peterson model exponent which lies between 0 and 1. All of them can be evaluated from the linear plot represented by Eq. (1.6) using a trial-and-error optimization method.

$$\ln\left(A\frac{C_e}{q_e} - 1\right) = g\ln(C_e) + \ln(B) \tag{1.6}$$

1.5.1.4 Extended Langmuir equation for binary system

The extended Langmuir equation (Chong and Volesky, 1995) was used to evaluate the adsorption data in a binary metal system. This equation consisted of three parameters generated using the MATLAB software. The equation was derived based on the binding of metals onto the binding sites of adsorbent at equilibrium.