Chapter 8
Cheap Materials to Clean Heavy Metal Polluted Waters

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Abstract The rapid growth of the human population and industrialization in the world has increased the environmental problems such as water, air and land pollution. Heavy metals can be considered as one of the most problematic pollutants. This chapter reviews developments and technical applicability of treatments methods for the removal of heavy metals. We focus on the use of low-cost materials to remove heavy metals. Isotherm equilibrium models and kinetics are discussed. Designing adsorption columns under continuous flow conditions are evaluated.

Keywords Water pollution • Heavy metal • As • Ni • Pb • Membrane filtration • Ion exchange • Fly ash • Rice husk • Wheat straw • Chitosan • Algae • Bacteria

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8.1 Heavy Metals

In recent years, water pollution by heavy metals poses one of the most serious environmental problems and of the most difficult to solve. Activities such as extensive use of fertilizers, municipal waste to land, electroplating, energy and fuel production, and wastewater from manufacturing industries including textile industry are among the major contributions to the contamination of environment by heavy metals. These metallic agents, once concentrated in the biosphere, generally persist and are not broken down. It is reported that cadmium, lead, cobalt, copper, mercury, chromium, nickel, selenium and zinc are the most important metals related to chain food contamination (McLaughlin et al. 1999). These metals are carcinogenic to human beings if consumed in higher quantity. Therefore, heavy metal pollution poses a great potential threat to the environment and human health.

Heavy metals may be defined as the elements having atomic weights between 63.5 and 200.6 and have a minimum specific gravity of 5 (Srivastava and Majumder 2008). Specific gravity is dimensionless property of matter and its value is obtained by dividing the density of that substance with the density of water. In addition, other experimental conditions, such as temperature, for determining the two densities must be the same. Heavy metals are "trace elements" with individual concentrations that do not exceed 1,000 mg/kg (0.1 %) of earth's crust. They are classified as essential, beneficial, or detrimental. For instances, iron, zinc, copper, chromium, iodine, cobalt, molybdenum, and selenium are recognised as essential for human health, of course with specific recommended daily allowances (RDA) or reference dose (RfD) set by respective authorities. On the other hand, some heavy metals are regarded as purely toxic metals such as cadmium, lead, nickel and mercury, which do not provide any essential or potentially beneficial health effect at any level of exposure (Nordberg et al. 2002). As arsenic, nickel and lead are metals of widespread use and frequently found in industrial wastewater, these metals were discussed in the following section.

8.1.1 Arsenic

Arsenic (As) is a metalloid belonging to group 15 of the periodic table with atomic number of 33 and atomic weight of 74.92. It is found naturally in the environment with estimated crustal abundance of 1.8 mg/kg and estimated oceanic abundance of 3–3.7 mg/L. The common oxidation states for arsenic are 5, 3 and −3, which appear widely in a variety of minerals. Realgar (As_4S_4) and orpiment (As_2S_3) are the two common arsenic sulfides. Arsenic also occurs as arsenide and sulfaresenides of heavy metals such as iron, copper, lead, silver, and gold (Yan Chu 1994). Loellingite ($FeAs_2$), safforlite (CoAs), niccolite (NiAs), arsenopyrite (FeAsS) and enargite (Cu_3AsS_4) are some of the examples of minerals containing arsenide and sulfaresenides. Arsenic can also be found in oxidised form such as in the mineral arsenolite (As_2O_3) (Greenwood 1989)

As a result of its toxicity, arsenic compounds are used mainly in wood preservation and insecticides. It is also employed in the making of special glass and semi-conductors, gallium arsenide (GaAs). GaAs is a semiconductor used in laser diodes and light emitting diodes (LEDs). While arsine gas (AsH_3) has become an important dopant gas in the microchip industry under strict guidelines. The widely used of arsenic in aforementioned activities, mining as well as erosion and weathering of rocks have contributed significantly to the content of this element in the environment.

Ingestion and inhalation of arsenic and its compounds cause various health effects. Arsenic interferes with enzyme action, DNA transcription, and metabolism. It causes chronic weakness, general debility and lassitude, loss of appetite and energy and sometimes a degree of dementia (Hindmarsh and McCurdy 1986; Yamanaka et al. 1996). Uptake of significant amounts of inorganic arsenic is associated with cancer development, especially development of lung, liver and lymphatic cancer. Prolong exposure to arsenic compounds will also cause dermatological effect such as hyperpigmentation and hypopigmentation, progressing to palmar/plantar hyperkeratosis and cause skin cancer eventually (Hindmarsh and McCurdy 1986). In addition, a very high exposure to inorganic arsenic contributes to infertility and miscarriages in women and most importantly to note that the lethal dose of arsenic is reported as 100 mg (Lenntech 2012a).

8.1.2 Nickel

Nickel (Ni) is a silvery white, hard, malleable and ferromagnetic metallic element belonging to group 10 of the periodic table with atomic number of 28 and atomic weight of 58.69. Nickel is a fairly good heat and electric conductor. It is a commonly found constituent in most meteorites with iron meteorites (siderites). Besides, nickel is also found sparingly in nature, usually combined with arsenic or iron and sulfur such as niccolite (NiAs) and pentlandite (NiS·2FeS). The estimated crustal abundance of Ni is 8.4×10^1 mg/kg and its estimated oceanic abundance is 5.6×10^{-4} mg/L.

Nickel is corrosion resistant and used primarily for making of stainless steel and many other corrosion resistant alloys. Typical composition of stainless steel is 8 % nickel, 18 % chromium and the remaining is iron. In fact, approximately 65 % of the nickel consumed in the western world is used to make stainless steel (Lenntech 2012b) .Other uses of nickel are in coinage, electroplating and battery production, foundry products as well as catalyst for hydrogenation process.

Nickel is exposed to human beings through inhalation, ingestion and skin contact. Workers in the industries related to nickel applications are the main group to suffer of nickel poisoning via inhalation of nickel-containing aerosols, dusts, fumes, and mists, especially those involved in production, processing, and use of nickel. Smokers are also at high risk to nickel inhalation as cigarettes, on average, contain 1–3 μg nickel (ATSDR 1993; Von Burg 1997) and mainstream smoke from one cigarette contains 0–0.51 μg nickel (Smith et al. 1997). Out of the total inhalation of nickel, about 20–35 % is deposited in the lungs causing lungs inflammation. On the other hand, nickel is also exposed to human population through ingestion of food and drinking water. Drinking water is the main contribution to nickel ingestion with 27 % nickel in drinking water is absorbed in humans compare to food which is approximately 1 %. This is because more soluble nickel compounds have higher absorption efficiencies.

Absorbed nickel is unable to be metabolised by human body. It is eliminated via urine with the elimination half-time of 28 days for the oral route. In fact, serum and urine nickel levels are the most useful monitoring of nickel exposure. According to the Agency for Toxic Substances and Disease Registry (ATSDR) of United States, the reference values for nickel in healthy adults are 0.2 μg/L in serum and 1–3 μg/L in urine (ATSDR 2005). For dermal contact of nickel, it causes dermatitis which is the most adverse health effect associated with nickel exposure. The common dermal contact of nickel is via nickel alloy and nickel-plated products such as stainless steel, coin and jewelry.

8.1.3 Lead

Lead (Pb) is a soft, malleable, ductile and dense metal. It has bluish-gray colour and belongs to group 14 with atomic number 82 and atomic weight of 207.2.

Though lead do not occur abundantly in nature but it is readily accessible in the earth's crust as the mineral galena (PbS), anglesite ($PbSO_4$) and cerussite ($PbCO_3$). The estimated crustal abundance is 1.4×10^1 mg/kg and the estimated oceanic abundance is 3×10^{-5} mg/L.

Lead is corrosion resistant, thus historically it was used in plumbing. Nowadays it is used to line tanks that store corrosive materials such as sulfuric acid (H_2SO_4) and as covering for cables. Lead's high density makes it useful as a shield against X-ray and gamma-ray radiation and is used in X-ray machines as well as in the glass of computer and television screens, where it shields the viewer from radiation (Lenntech 2012c). The other major use of lead is in lead-acid batteries manufacturing and formation of lead alloys. For instances, solder, an alloy constituted of half lead and half tin, is a material with a relatively low melting point that is used to join electrical components, pipes and other metallic items.

Like arsenic, lead is toxic in nature. Lead poisoning in human population is due to inhalation, ingestion and dermal contact to lead compounds. The emission of lead particulate in the air is primarily due to anthropogenic activities including automobiles using leaded gasoline. Lead is also found in soil due to adsorption at mineral interfaces, weathering and chipping of lead-based paint from buildings, bridges and other structures. Lead can also leach into drinking water from the leaded pipes in water distribution systems (Madden et al. 2002).

It is reported that children are more vulnerable to the effects of lead than adults. Children have higher gastrointestinal absorption of lead (40–50 %) compare to adults (3–10 %) (ATSDR 2007). A study on the lead content was conducted in Saratov, a town in Russia which its environment is exposed to lead discharge due to automobiles and operations of battery and lead glass factories. Blood lead and environmental samples from 579 children and their homes for soil, water, dust and paint are collected for lead content analysis. The study included the first pediatric blood lead screening among Russian children and the result shows that nearly one-fourth of the children had blood lead levels above the United State level of concern, 10 μg/dL (Rubin et al. 1997). Absorbed and retained of high dose of lead in children will disturb their neurological development. A well-developed literature argues that these neurological impacts reduce cognitive ability and lead to behavioral problems and learning disabilities later in life. Exposure to lead also increases the risk of kidney failure, disruption of central nervous system, brain damage and even death in cases of extremely high exposure (Jones 2012).

8.2 Heavy Metal Removal: Conventional and Emerging Methods

Extensive research and financial resources have been spent on the treatment of heavy metals pollution especially in industrial wastewater which is contaminated by heavy metals. These technologies include conventional physico-chemical methods and biological treatments, where the latter have gradually getting momentum because they are more eco-friendly and cost-effective compare to the conventional techniques. The physical-chemical methods include chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation-flocculation and electrochemical methods. Biological treatments involve the use of plants and microbes in any of the above said methods.

8.2.1 Chemical Precipitation

Chemical precipitation is the most common and effective method used in the industry for treatment of wastewater because it is relatively easy and inexpensive to operate (Ku and Jung 2001). This technique is employed in almost 75 % of electroplating facilities to treat wastewater (Karthikeyan et al. 1996). Generally, the metals are precipitated as insoluble hydroxides, carbonates, or sulfides and separated from water by sedimentation and filtration (Table 8.1).

Hydroxide Precipitation

Of all the chemical treatments, hydroxide precipitation is the most preferable and being extensively used method in the industry, particularly where complex chemical compounds are not involved and economic recovery is not a consideration. Lime, $Ca(OH)_2$ and caustic soda, NaOH are the preferred choice of bases used to precipitate heavy metals as their respective hydroxides. There are numerous factors govern the efficiency of metal hydroxides precipitation. For instances, the pH of the metals solution, the electrolyte composition of the effluent, the presence of soluble and/or insoluble products following reaction with complexing agents, ionic strength, electrical potential, temperature, and the time of reaction (Lin et al. 2005).

Dean et al. (1972) have found that there is almost complete precipitation and removal of metals such as cobalt, copper, iron, manganese, nickel, and zinc as the hydroxide with no special modification. However addition of soda ash (for lead) or sodium sulfide (for cadmium and mercury) is required to complete the precipitation of cadmium, lead and mercury. Chen et al. (2009) also reported that fly ash is used to enhance lime precipitation of metals. The fly ash-lime-carbonation treatment increased the particle size of the precipitate and significantly improved the efficiency of heavy metal removal. As a result, the removal efficiency of chromium, copper, lead and zinc in effluents had achieved 99 % removal. For strong acidic wastes, limestone ($CaCO_3$) is used as part of the neutralisation together with lime since limestone is less expensive and it reduces the operational cost significantly. However, limestone must be evaluated carefully for each acid waste since its efficiency depends upon particle coating and size, and pH limitation of calcium carbonate (Dean et al. 1972).

Table 8.1 Removal of heavy metals using chemical precipitation

Cation (heavy metal)	Anion (precipitant)	Optimum pH	Contact time (h)	Initial metal concentration (mg/L)	Removal efficiency (%)	Reference
Cu^{2+}, Cr^{4+}	$Ca(OH)_2$, NaOH, Na_2CO_3	12.0, 8.7	2	48.51, 30	98.6, 99.97	Mirbagheri and Hosseini (2005)
Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}	$Ca(OH)_2$, NaOH	8.1–8.3	24	0.1–29.7	50–100	Meunier et al. (2006)
Soil, fly ash and sewage leachates (Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe, Mg^{2+}, Mn, Ni^{2+}, Pb^{2+}, Zn^{2+}, P, S)	NaOH, $Ca(OH)_2$, NaOH/Na_2S, NaOH/Na_2CO_3, NaOH/Na_2HPO_4	5.0 7.5 7.5 8.0	0.3	0.13–719[a] 1.38–11,100[b] 0.23–827[c]	0.0–100[a] 23.9–100[b] 3.5–100[c]	Djedidi et al. (2009)
Ni^{2+}, Co^{2+}, Cu^{2+}	Na_2S	5.81–11.6	0.5–2	50–2,051	66.9–99.9	Lewis and van Hille (2006)
Zn^{2+}	Na_2S	6.5	NA	7,500	99.9 (<0.01 mg/L)	Veeken et al. (2003)
Acid mine drainage (Fe^{2+}, Mn^{2+})	1,3-benzenediamidoethanethiolate	4.5	20	194 4.65	99.9 (<0.009 ppm), 97.3	Matlock et al. (2002)

NA not available

[a] Refers to the soil leachates

[b] Refers to the fly ash leachates

[c] Refers to the sewage sludge leachates

Another important parameter for precipitation of heavy metals is the adjustment of optimum pH. Heavy metals, like chromium, copper, lead, manganese and zinc do not precipitate at pH below 7.0, thus allow their separation from ferric ion (Fe^{3+}) and aluminium ion (Al^{3+}), which precipitate at pH below 6.5 (Djedidi et al. 2009). The investigation from Mirbagheri and Hosseini (2005) agreed well with Djedidi et al. (2009). In their study of Cu(II) and Cr(IV) removal from wastewater using $Ca(OH)_2$ and NaOH, the Cr(VI) which was converted to Cr(III) using ferrous sulfate showed the maximum precipitation at pH 8.7 with the addition of $Ca(OH)_2$. At this pH value, the concentration of chromate was successfully reduced from 30 to 0.01 mg/L. While the maximum precipitation of copper occurred at pH 12.0 for both $Ca(OH)_2$ and NaOH and the concentration of copper was successfully reduced from 48.51 to 0.694 mg/L.

Although hydroxide precipitation is reported as the most widely used method for heavy metals removal in industry effluent, it also has some limitations. Hydroxide precipitation requires a large amount of chemicals to reduce metals to an acceptable level prior discharge especially if the effluents have high acidity where large amounts of lime are required for neutralisation. In this case, excessive secondary sludge, such as gypsum ($CaSO_4 \cdot 2H_2O$) are produced that require further treatment. These secondary precipitates not only increase the costs of sludge handling but also give long-term environmental impacts (Kurniawan et al. 2006). Secondly, some metal hydroxides are amphoteric, and the mixed metals create a problem using hydroxide precipitation since the ideal pH for one metal may change another metal back into solution. On top of these, some complexing agents present in the wastewater will inhibit the efficacy of metal hydroxide precipitation (Fu and Wang 2011).

Sulfide Precipitation

Sulfide precipitation is another effective method used for removal of heavy metals from wastewater. It has several advantages over hydroxide precipitation. For instances, sulfide precipitates are not amphoteric, hence, the sulfide precipitation process can achieve a high degree of metal removal over a broad pH range compared with hydroxide precipitation. Moreover, the solubilities of the metal sulfide precipitates are intensely lower than hydroxide precipitates. Metal sulfide sludges also exhibit better thickening and dewatering characteristics than the corresponding metal hydroxide sludges, thus reducing the amount and cost of sludges handling (Fu and Wang 2011). The sulfide precipitation process can be employed using various sulfide sources, such as solid FeS, CaS, aqueous Na_2S, NaHS, NH_4S or gaseous H_2S. Some researchers use the degeneration reaction of sodium thiosulfate ($Na_2S_2O_3$) as a source of sulfide for metal precipitation (Lewis 2010).

In fact, metal sulfide precipitation is preferable than hydroxide precipitation in hydrometallurgical processes in recent decades (Bhattacharyya et al. 1979; Lewis and van Hille 2006). The reasons that support its preferential use are based on the high degree of metal removal at relatively low pH values; the low solubility of sulfide precipitates; favourable dewatering characteristics and the stability of the metal sulfides formed. In the batch study of metal recovery conducted by Lewis and van Hille (2006), the maximum metal removal achieved for nickel and cobalt are 99.8 % and 99.9 %, respectively, when the metal: sodium sulfide molar ratio was 1:1. However, when excess sulfide is used, it compromises metal removal efficiency due to the formation of aqueous polysulfide species that will re-dissolve in the solution. The reaction is described as following equation:

$$MS_{(s)} + HS^{-}{}_{(aq)} \rightarrow MS(HS)^{-}{}_{(aq)} \tag{8.1}$$

whereby MS: solid metal sulfide

HS^{-}: aqueous sulfide

$MS(HS^{-})$: aqueous polysulphide complex

Hence, sulfide precipitation is not used as widely as it could due to this limitation. Moreover, it is rather difficult to control the dosing of sulfide due to the very low solubility of the metal sulfides and thus the sensitivity of the process to the dose. The colloidal precipitates that formed during metal sulfide precipitation also tend to cause some separation problems in either settling or filtration processes (Veeken et al. 2003).

In order to overcome the disadvantages between hydroxide and sulfide precipitation, nowadays, the combination of these two methods in treatment of heavy metals is being considered (Marchioretto et al. 2005; Djedidi et al. 2009). The set up for this treatment is usually a two-stage processes in which hydroxide precipitation is followed by sulfide precipitation. Djedidi et al. (2009) has reported that the combination of NaOH and Na_2S led to better removal of Pb^{2+}, Zn^{2+}, Cu^{2+} and Mn^{2+} ions in soil, fly ash and sewage sludge leachates than with $NaOH/Na_2CO_3$ or $NaOH/Na_2HPO_4$. The metal sulfide precipitations occurred at pH 7.5 with percentage removal of almost 100 %. This combination technique has reduced the reagents consumption.

Chemical Precipitation Combined with Other Methods

There are also reports on the combination of chemical precipitation with other methods in the treatment of heavy metals. González-Muñoz et al. (2006) have studied precipitation of metals using sulfides followed by nanofiltration as a second step in order to optimise the reuse of water and the recovery of heavy metal ions (Zn, Se, As, Cd and Pb). This study showed a promising outcome whereby the heavy metals are being successfully precipitated and the resultant solution after these processes can be directly reused in the plant. Ghosh et al. (2011) investigated a stepwise combination of electro-Fenton process and chemical precipitation to treat rayon industry wastewater contains chemical oxygen demand (COD) and Zn^{2+}. The two-step treatment processes refer to electro-Fenton treatment for COD reduction, followed by removal of zinc by addition of lime, CaO. From the results obtained with industrial wastewater having a COD of 2,400 mg/L and 32 mg/L

Zn^{2+}, approximately 88 % COD was reduced by the electro-Fenton method but this step does not have any appreciable effect on zinc removal. Thus, CaO is added to precipitate zinc as zinc hydroxide, $Zn(OH)_2$ with removal efficiency of 99–99.3 % in the range of pH 9–10. Another study in combination of chemical precipitation and electrocoagulation to remove Cu^{2+} from lithium bromide refrigerant was conducted by Cheng (2006). Cu^{2+} removal from lithium bromide refrigerant was successfully achieved by pretreatment with $Ba(OH)_2$ solution followed by electrocoagulation using carbon steel plates as electrodes. Up to 98.5 % of Cu^{2+} in the contaminated refrigerant could be removed by this combined treatment.

8.2.2 Ion Exchange

Ion exchange is the process through which an ion is removed out of an aqueous solution and is replaced by another ionic species. It has been continuously used in the treatment of heavy metals due to several advantages, such as high treatment capacity, high selectivity for certain heavy metal ions and most significantly, fast kinetics and most importantly it reduces the major problem faces in chemical precipitation – handling and disposal of large amount of sediments and sludge (Lacour et al. 2001; Abo-Farha et al. 2009, Al-Enezi et al. 2004). Dąbrowski et al. (2004) concluded that industrial wastewaters containing 0.1 g/L of Cu^{2+}, Cd^{2+} or Hg^{2+} compounds give 10-, 9- and 5-times larger amounts of sediments, respectively, and 6 kg of sediments are obtained from one kilogram of chromates.

Strongly acidic resins with sulfonic acid groups ($-SO_3H$) and weakly acid resins with carboxylic acid groups ($-COOH$) are the most common cation exchangers. Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations in the wastewater (Lacour et al. 2001; Fu and Wang 2011). The degree of exchange that occurs depends on the size and ionic charge of the metal cations, initial metal concentration, nature (both physical and chemical) of the ion exchange substance, pH and temperature (Lee et al. 2006a; Al-Enezi et al. 2004). Since resins have different swelling characteristics, the total exchange capacity on a volumetric basis ranged from 1.0 to 4.0 meq/mL. Abo-Farha et al. (2009) studied the adsorption behaviour of cation exchange resin purolite C100 with respect to Ce^{4+}, Fe^{3+} and Pb^{2+} from aqueous system. Purolite C100 is a polymer of polystyrene-divinyl benzene, with sulfonic acid groups as the functional groups. They found that the metal ions adsorption sequence can be given as $Ce^{4+} > Fe^{3+} > Pb^{2+}$. Another batch study conducted by Lacour et al. (2001) shows the potential usage of cation-exchange-textiles (CET) – a special class of grafted textiles carrying different functional groups namely carboxylate($R - COO^-$,Na^+), sulfonate ($R–SO_3{}^-$,Na^+) or phosphate ($R–O–PO_3{}^{2-}$, $2Na^+$) in removing Cu^{2+} and Cd^{2+} from the solution. The report reveals the adsorption behaviour of the CET towards Cu^{2+} and Cd^{2+} is influenced by parameters such as the counter-ion and functional group nature, the metal concentration and the presence of different competitors in the solution.

Besides synthetic resins, natural zeolites also show effective removing efficiency towards heavy metal from aqueous solutions under different experimental condition (Inglezakis and Grigoropoulou 2004; Petrus and Warchoł 2005; Barreira et al. 2009). Clinoptilolite is one of the most frequently studied natural zeolites that have received extensive attention due to its selectivity for heavy metals. (Inglezakis and Grigoropoulou 2004) reported that the uptake of Pb^{2+}, Cu^{2+}, Fe^{3+} and Cr^{3+} in aqueous solutions using natural clinoptilolite is influenced by different parameters following this order: metal cations concentration > volumetric flow rate > particle size > modification of the material. In fact, modification of the natural sample by NaCl has led to an increase of removal efficiency by 32–100 %. The study also focused on the fixed bed reactors design rather that batch systems because kinetics in beds is influenced by the whole equilibrium curve and diffusion rates in the material. This indicates the effect of operating conditions carry out in fixed beds is more representative than that obtained in batch systems. Warchoł and Petrus (2006) supported the column study of clinoptilolite by investigating heavy metals removal, ion-exchange equilibrium and column dynamics through mathematical modeling. In fact, the possibility of replacing expensive synthetic ion-exchangers by natural zeolites – low cost sorbents with abundant availability has added value to the application of this method in wastewater treatment.

8.2.3 Membrane Filtration

The ultimate objective of most of the traditional methods in heavy metals treatments is not the recovery of the metal but rather its elimination. However, recovery of heavy metals shows greater benefits. It allows re-use of the metals and thus provides further economic and environmental benefits by reducing the disposal costs and raw material requirements. In this case, membrane processes exert as an alternative for heavy metal recovery, as they can achieve high permeate fluxes and high rejection coefficients with low energy costs and under mild conditions. (Landaburu-Aguirre et al. 2006). Other advantages of this technique including fewer chemicals are used in the process, which helps to minimise the negative impacts of those chemicals on the whole process; produce more reliable performance; simple operation and convenience since it occupies less floor space in comparison to the conventional treatment systems (Paul Chen et al. 2006). Besides, there are many studies show that membrane processes can be easily combined with other separation processes for better removal efficiency (Blöcher et al. 2003; Mimoune and Amrani 2007; Rivas and Palencia 2011).

Membrane separation system consists of a membrane that can separate materials depending on their physical and chemical properties when a driving force, either a gradient of chemical potential (concentration or pressure gradient) or electrical potential, is applied across the membrane. A good membrane must have a narrow range of pore sizes, a high porosity, and a thin layer of material (Paul Chen et al. 2006). The membrane processes used for wastewater treatment containing

Table 8.2 Pore size of the membrane processes

Membrane process	Pore size
Microfiltration	0.1–10 μm (>100 nm)
Ultrafiltration	0.005–0.2 μm (5–200 nm)
Nanofiltration	0.001–0.01 μm (<10 nm)

heavy metals including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and electrodialysis (ED) depending on the size of the particle that can be retained (Table 8.2). The membrane techniques that are often used for heavy metals removal are UF, NF, RO and ED.

Ultrafiltration

Ultrafiltration (UF) is a membrane technique used to separate heavy metals, organic pollutants or inorganic pollutants from aqueous solution. UF membranes are capable of retaining species in the range of 300–500,000 Da of molecular weight, with pore sizes ranging from 0.005 to 0.2 μm (5–200 nm) (Paul Chen et al. 2006). Since the pore sizes of UF membranes are larger than dissolved metal ions in the form of hydrated ions or as low molecular weight complexes, these ions would pass easily through UF membranes. Hence, two important techniques – micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) are proposed for effectively use in removal of metal ions (Table 8.3).

The combination of surfactants and membranes in separation of dilute polluted water has led to the development of MEUF. It is considered an economical alternative available to the conventional membrane separation process, because it reduces the requirement of higher pressure and high membrane costs. In this process, surfactants are added into the aqueous stream at levels equal to or higher than their critical micelle concentrations (CMCs). At this particular surfactant concentration, surfactant monomers will assemble and form aggregates called micelles. The anionic micelles, which are negatively charged, can bind to metal cations, which are positively charged. This micelle solution is then filtered through an ultrafiltration membrane whose pore size is smaller than the micelle size to reject the micelles. The metal cations that adsorbed onto the micelles can thus be removed from the polluted water (Mungray et al. 2012).

MEUF can be used to remove different heavy metals from wastewater containing single metal, mixture of metals or feed mixtures containing metals and organic material (Juang et al. 2003; Häyrynen et al. 2012; Rahmanian et al. 2012). As the binding of metal cations to oppositely charged micelle surface is primarily electrostatic in nature, it is expected that the ions with the same charge are removed with a nearly equal rejection in MEUF. Juang et al. (2003) reported that the rejection of Sr^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+} and Zn^{2+} are 99.1, 78.6, 80.6, 82.1 and 83.7 % respectively. The comparatively high rejection of Sr^{2+} by the GE membrane in this system promotes the application of MEUF for selective separation of Sr^{2+} from low-level waste effluents. Increases of surfactant (sodium dodecyl sulfate) to

Table 8.3 Heavy metal removal by micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF)

UF type	Membrane material	Surfactant/complexing agent	Heavy metal	Initial concentration	Optimum pH	Removal efficiency (%)	Reference
MEUF	Polyamide, polyethersulfone	Sodium dodecyl sulfate	Cs^{+}, Sr^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cr^{3+}	50 mg/L	3–12	40.0, 99.1, 78.6, 80.6, 82.1, 83.7, 86.7	Juang et al. (2003)
MEUF	Ceramic	Dodecylbenzenesulfonic acid, dodecylamine	Pb^{2+}, AsO_4^{-}	4.4–7.6 mg/L	7.47	>99.0, 19.0	Ferella et al. (2007)
MEUF	Regenerated cellulose acetate	Sodium dodecyl sulfate	Pb^{2+}	50–150	7.84	99.5	Rahmanian et al. (2012)
MEUF	Polyethersulfone	Sodium dodecyl sulfate	Cd^{2+}, Cu^{2+}	0.37, 0.41	2.7	85, 81	Häyrynen et al. (2012)
PEUF	Ceramic	Chitosan	Cd^{2+}	10 mg/L	7.5	98.5	Llorens et al. (2004)
PEUF	Polysulfone	Chitosan, polyethyleneimine, pectin	Cr^{3+}, Cr^{4+}	10 ppm	7–9	>99, <50	Aroua et al. (2007)
PEUF	Poly(vinyl alcohol)	Poly(ethyleneimine)	Pb^{2+}, Cd^{2+}, Cu^{2+}	100 ppm	5.0	96.0, 99.5, 99.0	Bessbousse et al. (2008)
PEUF	Polyethersulfone	Carboxy methyl cellulose	Cu^{2+}, Cr^{3+}, Ni^{2+}	10 mg/L	7.0	97.6, 99.5, 99.1	Barakat and Schmidt (2010)

metal ratio increase the rejection because the sizes of micelles are relatively larger at higher concentration of surfactant compare to the UF membrane. However the metal rejection shows a decrease of 3–6 % at pH lower than 3 due to competition of H^+ trapped on micelle surface with metal ions. A combination process of micellar enhanced ultrafiltration and activated carbon fibre (ACF) shows nearly complete rejection of copper from the solution. The coupling of MEUF with ACF has the potential to overcome the problems caused by excessive surfactant concentration since activated carbon has proved to be a good adsorbent for surfactants that contained in the permeate (Bade and Lee 2007).

In PEUF, water soluble polymer is used to bind with metal ions to form macromolecular complexes which have a larger molecular weight and size than the membrane. As a result, these macromolecular complexes will be retained and removed while the non-complexed ions will pass through the membrane. So far, polymers with carboxylic or amine groups have been extensively studied for this purpose. PEUF process is more economically competitive because the non-protonated form of the polymers that bind to the metal ions, will release the metal ions when an acid is added. This has led to the regeneration and reuse of the polymer. Hence, pH plays an important role in the binding and removal of metal species from the solution. Llorens et al. (2004) and Aroua et al. (2007) had conducted studies on the removal of cadmium and chromium from aqueous solution using PEUF. For both of the studies, high rejections were obtained at pH 7 or higher and decrease when pH is lowered for all types of the polymers tested namely chitosan, polyethyleneimine and pectin.

Reverse Osmosis

Reverse osmosis (RO) is one of the techniques able to remove a wide range of dissolved species from water. It is not only able to remove suspended solid $> 1\ \mu m$ (conventional filtration), but also dissolved solids, bacteria, viruses, and other germs contained in the water. In the application of RO, when the waste stream flows past the membrane, the solvent (e.g., water) is driven through the membrane (operation pressure ranges from 10 to 70 bars) while the remaining solutes (e.g., organic or inorganic components) do not pass through, and become increasingly concentrated on the feed side of the membrane. The general use of RO is desalination of seawater for its conversion into potable water. It is reported that more than 20 % of the world's desalination process is using this technique (Shahalam et al. 2002). The RO membranes have pore size ranging from approximate 0.5–1.5 nm (5–15 Å). The extremely small size of RO pores allows only the smallest organic molecules and unchanged solutes to pass through the semipermeable membrane along with the solvent (Paul Chen et al. 2006). Nowadays, many studies have been going on to utilise RO process in wastewater treatment.

A study by Ozaki et al. (2002) shows that it is successful to remove Ni^{2+}, Cu^{2+} and Cr^{6+} ions from industrial wastewater using RO membrane separation at lower pressures (350–450 kPa). The rejections 99.03 % of Ni^{2+}, 98.75 % of Cu^{2+} and 99.37 % of Cr^{6+} were achieved at pH 7. Metal rejections are higher at high pH values (7–9) due to the formation of insoluble complexes with OH^{-} ions, causing the solute changed to a larger molecule and precipitate onto the membrane surface. They also found that presence of co-ions such as calcium and magnesium in the industrial wastewater decreases the rejection. Meanwhile, a pilot-scale combination of membrane bioreactor (MBR) with RO separation is conducted by Dialynas and Diamadopoulos (2009). The combination technique shows high heavy metal removals, whereby Pb and Ni were removed completely, while Cr and Cu were removed by 89 % and 49 %, respectively. However, the performance of RO and its life-time are highly sensitive to wastewater properties. The accumulation of particulate and colloidal matters at the feed side of the membrane surface caused membrane fouling and permeate flux decline (Lee et al. 2006b).

Nanofiltration

Nanofiltration (NF) is the intermediate process between UF and RO and used to separate different fluids or ions. It has larger membrane pore structure, 0.001–0.01 μm (1–10 nm) as compared to the RO membranes, which allows more salt passage through the membrane. The advantages of NF compared to RO processes including operation at lower pressure (7–14 bar) but able to produce high recoveries, thereby conserving total water usage due to a lower concentrate stream flow rate (Paul Chen et al. 2006). Ortega et al. (2008) studied the removal of various metal ions from an acidic leachate solution by two different nanofiltration membranes (Desal5 DK and NF-270). The results show good metal ion rejection (62–100 %) where divalent ions were better rejected than monovalent ions. In recent years, Murthy and Chaudhari (2008) have conducted numerous studies on the removal of heavy metal ions from aqueous solution using NF membrane. They found that Ni^{2+} can be removed by a thin-film composite polyamide NF membrane. Rejection of nickel ions increases with increase in feed pressure and decreases with increase in feed concentration at constant feed flow rate. The maximum rejection of the metal is found to be 98 % and 92 % for an initial feed concentration of 5 and 250 ppm, respectively (Murthy and Chaudhari 2008). At the same year, Bouranene et al. (2008) also proved that Co^{2+} and Pb^{2+} ions can be removed by polyamide NF membrane. The rejection rate of 97 % and 81 % were observed for cobalt and lead, respectively, at constant permeate flux of $122 \pm 2\ Lh^{-1}\ m^{-2}$ and ion concentration of 1,600 mgL^{-1} in mixed-salt solution. In the following year, Murthy and Chaudhari (2009) continue to investigate removal efficiency of cadmium and nickel in a binary system. The maximum observed solute rejection of nickel and cadmium ions are 98.94 % and 82.69 %, respectively, for an initial feed concentration of 5 ppm.

Electrodialysis

Electrodialysis (ED), which requires electrical energy as a driving force, allows transportation of ions through ion permeable membranes from one solution to another due to the potential gradient that created. Since ED membranes have the ability to selectively transport ions having positive or negative charge and reject ions of the opposite charge, the removal or separation of ions/electrolytes can be achieved by this technique. Cifuentes et al. (2009) reported on the effectiveness of ED in separating Cu^{2+} and Fe^{2+} ions and subsequently water recovery in industrial copper electrowinning operations. Approximately 96.6 % of Cu and 99.5 % of Fe were separated from the working solution which constituted of initial concentration of 9 g/L and 5 g/L of Cu^{2+} and Fe^{2+}, respectively. Removal rates for Cu^{2+} and Fe^{2+} from the working solution increased linearly with cell current density and electrolyte agitation. Removal of Cr^{3+} from the tanning process in the leather industry is crucial due to the environmental issue and also to its industry. It is because presence of chromium ion has a negative effect on the quality of the tanned leather. Lambert et al. (2006) had proposed a two-step Cr(III) separation–concentration process. In the first step, a cation-exchange membrane, Nafion®117, modified by electrodeposition of polyethylenimine was used to separate successfully Cr(III) from NaCl solutions. In the second step, conventional electrodialysis with three different membranes permits to increase the concentration of Cr(III) in the solutions produced in the separation stage.

8.2.4 Adsorption

Adsorption is known as an efficient, convenient and economic method for wastewater treatment. The flexibility in design and operation, high removal efficiency and the possibility for most of the adsorbents to be regenerated and reuse by suitable desorption process have made adsorption process gaining its popularity (Krishnani et al. 2008; Elouear et al. 2008; Afkhami et al. 2010; Salehi et al. 2012). Adsorption is a mass transfer process whereby a substance is transferred from a gas or liquid phase to the surface of a solid and bound by physical and/or chemical and/or electrostatic interactions. Physical adsorption is caused by the van der Waals forces whereas chemical adsorption involved the electronic interactions between specific surface sites and solute molecules. This kind of electrostatic interaction is generally referred to coulombic attractive forces between ions and charged functional groups. The three steps involved in the adsorption process are: (i) the transport of the solute from the bulk solution to the sorbent surface; (ii) adsorption on the particle surface; and (iii) transport within the sorbent particle.

Activated carbon (AC) is being recognised as one of the most popular adsorbents used in the removal of heavy metal contaminants. AC has been used efficiently in both batch and column studies due to its large micropore and mesopore volumes. This kind of structure also resulted in a high surface area. However, the drawback of

AC is it remains as an expensive material because of depleting source of commercial coal-based AC. Higher cost is accounted for higher quality of activated carbon. Another limitation of AC adsorption in heavy metal removal is its high affinity towards organic molecules. As a result, these kinds of high molecular weight organic compounds will block the heavy metal ions from reaching the adsorbents bed.

The problems revealed by AC adsorption have led to the production of alternative adsorbents to replace the costly AC. Attention has been focused on various adsorbents that have metal-binding capacities, especially if it is a source that is readily abundant. Besides this, utilization of inexpensive sources is also being viewed as attractive alternatives. For this, many researchers have shown interest to convert carbonaceous materials into AC for heavy metals remediation. Momčilović et al. (2011) prepared activated carbon from the cones of the European Black pine to remove lead (II) ions from aqueous solutions. The maximum adsorption capacity of 27.53 mg/g is observed and the optimum adsorbent dosage was established to be 2.0 mg/l. Namasivayam et al. (2007) had converted jatropha husk, an agricultural solid waste, generated from bio-diesel industries, to jatropha husk activated carbon. This material is an effective adsorbent for the removal of toxic ions, dyes and organics. Besides AC, other adsorbents that are used for adsorption of heavy metal ions include natural minerals, modified biopolymers as well as low cost materials, which are derived from agricultural waste and industrial by products. Among these compounds, adsorbent from low cost materials have gained considerable attention because of their low cost and local availability, which will be elaborated further in next chapter.

8.2.5 Biological Treatment

The method of biological treatment was introduced in the early years of the twentieth century. It involved confining naturally occurring bacteria at very much higher concentrations in tanks. These bacteria, together with some protozoa and other microbes, are collectively referred to as activated sludge. The initial objective of biological treatment is to remove small organic carbon molecules by the bacteria. As a result, the bacteria grow, and the wastewater is cleansed. Lately, this method is applied in the removal of heavy metals from wastewater where biosorption phenomenon itself plays an important role. Biosorption is a metabolism-independent binding of heavy metals to living cells, non-living biomass, or microbial extracellular polymers (Volesky and Holan 1995).

Lipczynska-Kochany and Kochany (2009) have investigated the influence of humic substances (humate, HS) on the biological treatment of wastewater containing heavy metals (Cr, Cu, Fe, Mn, Ni, and Zn). Humic substances (HS) are naturally occurring compounds resulting from microbial and chemical transformation of organic debris. The removal of ammonia and metals was 99 % and over 90 %, respectively. Chipasa (2003) studied the accumulation and removal of heavy metals (Cd, Cu, Pb and Zn) through a biological wastewater treatment system. The results revealed that the removal of heavy metals from wastewater is influenced by their initial contents in the influent. The reduction in heavy metal contents was reported to follow this sequence: Cd < Pb < Cu < Zn. Biological wastewater treatment is a complex process depending not only on many biological and physicochemical conditions but also on process operating conditions and design. Consequently, all these are also influential variables in controlling the removal efficiency of heavy metals.

8.3 Utilization of Low-Cost Adsorbents in Heavy Metals Removal

Heavy metals such as chromium, lead, copper, nickel, zinc and iron are not biodegradable and they are toxic to human health and environment. Due to their tendency to accumulate in organisms and cause various disorders and diseases, these heavy metals are recognized as an emergent class of human carcinogenic compounds. Besides, the presence of high concentration of these metals in the environment may lead to serious problems including water pollution and soil degradation. Obviously, an effective method in heavy metal removal is urgently needed to lessen the pollution loads before the discharge enters the surface water.

Techniques currently used for the removal of heavy metals from wastewaters are chemical precipitation, ion exchange, membrane filtration, electrolytic reduction, coagulation, solvent extraction and catalysis. Owing to the drawbacks found in these techniques: generation of residues, low efficiency, applicability to a wide range pollutants, need of pre-treatments and high cost, they may not be suitable solutions at industrial scale. Since the last decades, adsorption process has been viewed as a highly effective method for removal of various heavy metals due to ease of operation. In particular, high surface area materials like activated carbon, silica aerogel and other mesoporous materials have been proven for their excellent adsorption capability for heavy metals. Unfortunately, production of these adsorbents is usually costly, making them not attractive to be applied by small and medium scale industries. Thus, the use of low cost materials as adsorbent for metal ion removal from the wastewaters has been highlighted. In general, the low-cost adsorbent materials are referred to those available at free cost and exist abundantly in nature. They may also represent the unused resources after a manufacturing process with serious disposal problems. Apparently, utilization of naturally occurring material or locally available agricultural waste materials or industrial by-products as the adsorbents in removing heavy metals from wastewaters is not only cost effective in heavy metal removal, but it also contributes to a zero waste situation in the environment.

A numerous studies have been carried out to investigate as well as to further improve the usage of different low cost adsorbent materials for adsorption of individual or multiple heavy metals in an aqueous solution. These low cost adsorbents range from industrial by-products, agriculture waste to biosorbents, for example wood bark, sawdust, mangoesteen peel, durian husk, oil palm empty fruit bunch, tea leaves and exhausted coffee etc. In this section, some of the intensively studied low cost adsorbents such as fly ash, rice husk, wheat straw, chitin and chitosan composites as well as algae and bacteria were discussed in terms of their efficiency for heavy metals removal. Recent reported adsorption capacities of the selected adsorbents are presented in Tables 8.4, 8.5, 8.6, 8.7, 8.8, and 8.9 to give some idea of adsorbent effectiveness. It is interesting to note that the reported values are strongly dependent on the experimental condition. Therefore it is advisable for the reader to refer to the original work in order to have a better understanding on the specific conditions that have been imposed on the adsorption process.

8.3.1 Fly Ash

Fly ash is a waste material produced during the combustion of various materials, such as coal, plant biomass and municipal solid waste in the electrical generation process. This industrial by-product is usually grey in color, abrasive, mostly alkaline and refractory in nature. It contains mainly silica (SiO_2) of ~47 %, alumina (Al_2O_3) of ~25 %, iron oxide (Fe_2O_3) of ~16 %, and calcium oxide (CaO) of ~5 % with varying amounts of carbon, calcium, magnesium and sulphur. The variations that are commonly found in fly ash, either in terms of their chemical composition or physical properties is most likely due to different sources of coal as well as diversity in the design of coal-fired boilers. However, an empirical formula for fly ash based on the dominance of certain key elements has been proposed as below (Iyer and Scott 2001): $Si_{1.0}Al_{0.45}Ca_{0.51}Na_{0.047}Fe_{0.039}Mg_{0.020}K_{0.013}Ti_{0.011.}$

Depending on the ratio of calcium to silica and ratio of alumina to iron in the ash, fly ash can be classified into two types: Type C and Type F. The Type C fly ash is normally produced from the burning of low-rank coals, such as lignites or sub-bituminous coals. This fly ash has cementitious properties as it is self-hardening upon reacted with H_2O. Meanwhile, the Type F fly ash is generated from the burning of higher-rank coals like bituminous coals or anthracites. This type of fly ash is pozzolanic in nature where it is hardening when reacted with $Ca(OH)_2$ and H_2O.

In fact, the fly ash has been used effectively as raw material in cement and brick production, soil amendment and as filler in road works. Besides, the fly ash can be converted into zeolite, another versatile material which is widely used as catalyst and adsorbent due to its outstanding high surface area and porosity. However, all the fly ash produced from the power industry cannot be reused by these applications. Consequently, most of the fly ash generated is disposed of as landfill, a practice which is under examination for environmental concerns. Therefore, continuing research efforts have been made to explore other applications prior to discarding in order to lessen the environmental burden. Since fly ash is enriched with SiO_2 and contains a portion of unburned carbon, this material is potentially used as low cost adsorbent to remove various hazardous elements from wastewaters. A lot of

Table 8.4 Adsorption capacities of metals by fly ash[a]

Metals	Adsorbent	Adsorption capacity[b]	Temperature (°C)	References
As(III)	Fly ash coal-char	3.7–89.2	25	Pattanayak et al. (2000)
	Fly ash brown coal-char	25.1–32.1	25	Polowczyk et al. (2011)
As(V)	Fly ash	7.7–27.8	20	Diamadopoulos et al. (1993)
	Fly ash coal-char	0.02–34.5	25	Pattanayak et al. (2000)
Cd(II)	Fly ash	1.6–8.0	–	Ayala et al. (1998)
	Fly ash zeolite	95.6	20	Ayala et al. (1998)
	Fly ash	0.67–0.83	20	Bayat (2002a)
	Afsin-Elbistan fly ash	0.08–0.29	20	Bayat (2002b)
	Seyitomer fly ash	0.0077–0.22	20	Bayat (2002b)
	Fly ash	198.2	25	Apak et al. (1998)
	Fly ash-washed	195.2	25	Apak et al. (1998)
	Fly ash-acid	180.4	25	Apak et al. (1998)
	Bagasse fly ash	1.24–2.0	30–50	Gupta et al. (2003)
	Fly ash	0.05	25	Weng and Huang (1994)
	Coal Fly ash	18.98	25	Papandreou et al. (2007)
	Coal Fly ash pellets	18.92	–	Papandreou et al. (2007)
	Bagasse fly ash	6.19	–	Ho et al. (1989)
	Fly ash zeolite X	97.78	–	Apiratikul and Pavasant (2008b)
	NaOH activated fly ash	30.21	20–25	Visa et al. (2012)
Co(II)	Fly ash zeolite 4A	13.72	–	Hui et al. (2005)
Cr(III)	Fly ash	52.6–106.4	20–40	Cetin and Pehlivan (2007)
	Fly ash porous pellet	22.88	25	Papandreou et al. (2011)
	Bagasse fly ash	4.35	–	Gupta and Ali (2004)
	Fly ash zeolite 4A	41.61	–	Hui et al. (2005)
Cr(VI)	Fly ash + wollastonite	2.92	–	Panday et al. (1984)
	Fly ash + China clay	0.31	–	Panday et al. (1984)
	Fly ash-chitosan composite	33.27	15	Wen et al. (2011)
	Fly ash	1.38	30–60	Banerjee et al. (2004)
	Fe impregnated fly ash	1.82	30–60	Banerjee et al. (2004)
	Al impregnated fly ash	1.67	30–60	Banerjee et al. (2004)
	Afsin-Elbistan fly ash	0.55	20	Bayat (2002b)
	Seyitomer fly ash	0.82	20	Bayat (2002b)
	Bagasse fly ash	4.25–4.35	30–50	Gupta and Ali (2004)
	Fly ash	23.86	–	Bhattacharya et al. (2008)
Cs(I)	Fly ash zeolite	443.9	25	Mimura et al. (2001)
Cu(II)	Fly ash	0.1825	–	Salam et al. (2011)
	Fly ash	1.39	30	Panday et al. (1985)
	Fly ash + wollastonite	1.18	30	Panday et al. (1985)
	Fly ash	1.7–8.1	–	Ayala et al. (1998)
	Afsin-Elbistan fly ash	0.34–1.35	20	Bayat (2002c)
	Seyitomer fly ash	0.09–1.25	20	Bayat (2002c)
	Fly ash	207.3	25	Ricou et al. (1999)
	Fly ash-washed	205.8	25	Ricou et al. (1999)

(continued)

Table 8.4 (continued)

Metals	Adsorbent	Adsorption capacity^b	Temperature (°C)	References
	Fly ash-acid	198.5	25	Ricou et al. (1999)
	Fly ash	0.63–0.81	25	Lin and Chang (2001)
	Bagasse fly ash	2.26–2.36	30–50	Gupta and Ali (2000)
	Fly ash	0.76	32	Rao et al. (2003)
	Fly ash	7.5	–	Ricou et al. (1999)
	Coal Fly ash pellets	20.92	25	Papandreou et al. (2007)
	Fly ash zeolite 4A	50.45	–	Hui et al. (2005)
	Fly ash	7.0	–	Hossain et al. (2005)
	Coal fly ash (CFA)	178.5–249.1	30–60	Hsu et al. (2008)
	CFA-600	126.4–214.1	30–60	Hsu et al. (2008)
	CFA–NAOH	76.7–137.1	30–60	Hsu et al. (2008)
	Fly ash zeolite X	90.86	–	Apiratikul and Pavasant (2008b)
	Fly ash	7.0	–	Gupta (1998)
	Fly ash mixed willow saw dusk	7.7160 ppm/g	–	Lucaci et al. (2011)
	Fly ash mixed white poplar saw dusk	6.2305 ppm/g	–	Lucaci et al. (2011)
Hg(II)	Fly ash	2.82	30	Sen and De (1987)
	Fly ash	11.0	30–60	Banerjee et al. (2004)
	Fe impregnated fly ash	12.5	30–60	Banerjee et al. (2004)
	Al impregnated fly ash	13.4	30–60	Banerjee et al. (2004)
	Sulfo-calcic fly ash	5.0	30	Ricou et al. (1999)
	Silico-aluminous ashes	3.2	30	Ricou et al. (1999)
	Fly ash-C	0.63–0.73	5–21	Kapoor and Viraraghavan (1992)
Ni(II)	Fly ash	9.0–14.0	30–60	Banerjee et al. (2003)
	Fe impregnated fly ash	9.8–14.93	30–60	Banerjee et al. (2003)
	Al impregnated fly ash	10–15.75	30–60	Banerjee et al. (2003)
	Afsin-Elbistan fly ash	0.40–0.98	20	Bayat (2002c)
	Seyitomer fly ash	0.06–1.16	20	Bayat (2002c)
	Bagasse fly ash	1.12–1.70	30–50	Gupta et al. (2003)
	Fly ash	3.9	–	Ricou et al. (1999)
	Fly ash zeolite 4A	8.96	–	Hui et al. (2005)
	Afsin–Elbistan fly ash	0.98	–	Bayat (2002c)
	Seyitomer fly ash	1.16	–	Bayat (2002c)
	Bagasse fly ash	6.48	–	Ho et al. (1989)
	Fly ash	0.03	–	Rao et al. (2002)
Pb(II)	Fly ash zeolite	70.6	20	Gan (2000)
	Fly ash	444.7	25	Yadava et al. (1987)
	Fly ash-washed	483.4	25	Yadava et al. (1987)
	Fly ash-acid	437.0	25	Yadava et al. (1987)
	Fly ash	753	32	Yadava et al. (1987)
	Bagasse fly ash	285–566	30–50	Goswami and Das (2000)
	Fly ash	18.8	–	Diamadopoulos et al. (1993)

(continued)

Table 8.4 (continued)

Metals	Adsorbent	Adsorption capacity[b]	Temperature (°C)	References
	Fly ash zeolite X	420.61	–	Apiratikul and Pavasant (2008b)
	Fly ash porous pellet	45.54	25	Papandreou et al. (2011)
	NaOH activated fly ash	2,000.0	20–25	Visa et al. (2012)
Zn(II)	Fly ash	6.5–13.3	30–60	Banerjee et al. (2003)
	Fe impregnated fly ash	7.5–15.5	30–60	Banerjee et al. (2003)
	Al impregnated fly ash	7.0–15.4	30–60	Banerjee et al. (2003)
	NaOH activated fly ash	18.87	20–25	Visa et al. (2012)
	Fly ash	0.25–2.8	20	Bayat (2002a)
	Afsin-Elbistan fly ash	0.25–1.19	20	Bayat (2002c)
	Seyitomer fly ash	0.07–1.30	20	Bayat (2002c)
	Bagasse fly ash	2.34–2.54	30–50	Gupta and Ali (2000)
	Bagasse fly ash	13.21	30	Gupta and Sharma (2003)
	Fly ash	4.64	23	Weng and Huang (1990)
	Fly ash	0.27	25	Weng and Huang (1994)
	Fly ash	0.068–0.75	0–55	Weng and Huang (2004)
	Fly ash	3.4	–	Ricou et al. (1999)
	Fly ash porous pellet	17.66	25	Papandreou et al. (2011)
	Fly ash zeolite 4A	30.80	–	Hui et al. (2005)
	Bagasse fly ash	7.03	–	Hui et al. (1989)
	Fly ash	11.11	–	Gupta (1998)
	Rice husk ash	14.30	–	Bhattacharya et al. (2006)
	Fly ash	7.84	–	Gupta (1998)
	Fly ash	0.1806	–	Salam et al. (2011)

[a] These reported adsorption capacities are values obtained under specific conditions. Readers are encouraged to refer to the original articles for information on experimental conditions

[b] In the unit of (mg g^{-1}) unless specified

investigations have been reported on usage of fly ash in adsorption of individual pollutants in an aqueous solution or flue gas. Overall, the results obtained when using these particular fly ashes are encouraging for the removal of heavy metals and organics from industrial wastewater. Some of the researches showed that the unburned carbon in fly ash is partly activated during the combustion process, resulting in a relatively high surface area and good porosity (Wang and Li 2007; Lu et al. 2008). These characteristics of unburned carbon are similar to that of activated carbon, hence fly ash could be a potential adsorbent and substitute of commercial activated carbon. Recently, biomass fly ash has attracted attention to be used as adsorbent in wastewaters treatment (Pengthamkeerati et al. 2008). It could be a better adsorbent as compared to other fly ash due to its higher percentage of unburned carbon.

In real practical, the fly ash is always submitted to heating treatment and/or modification before being applied as adsorbent. Adsorption capacities of metals by different fly ashes are provided in Table 8.4.

Table 8.5 Adsorption capacities of metals by rice husk[a]

Metals	Adsorbent	Adsorption capacity[b]	Temperature (°C)	References
As(III)	Copolymer of iron and aluminum impregnated with active silica derived from rice husk ash	146	–	Abo-El-Enein et al. (2009)
As(V)	Rice husk	615.11	–	Roy et al. (1993)
	Quaternized rice husk	18.98	–	Lee et al. (1999)
Au(I)	Rice husk	64.10	40	Nakbanpote et al. 2002)
	Rice husk	50.50	30	Nakbanpote et al. (2002)
	Rice husk	39.84	20	Nakbanpote et al. (2002)
	Rice husk ash	21.2	–	Nakbanpote et al. (2000)
Cd(II)	Partial alkali digested and autoclaved rice husk	16.7	–	Krishnani et al. (2008)
Cd(II)	Phosphate-treated rice husk	103.09	20	Ajmal et al. (2003)
	Rice husk	73.96	–	Ye et al. (2010)
	Rice husk	21.36	–	Roy et al. (1993)
	Rice husk	4	–	Tarley et al. (2004)
	Rice husk	8.58 ± 0.19	–	Kumar and Bandyopadhyay (2006)
	Rice husk	0.16	–	Munaf and Zein (1997)
	Rice husk	0.32	–	Marshall et al. (1993)
	NaOH activated rice husk	125.94	–	Ye et al. (2010)
	NaOH activated rice husk	7	–	Tarley et al. (2004)
	NaOH activated rice husk	20.24 ± 0.44	–	Kumar and Bandyopadhyay (2006)
	$NaHCO_3$ activated rice husk	16.18 ± 0.35	–	Kumar and Bandyopadhyay (2006)
	Epichlorohydrin treated rice husk	11.12 ± 0.24	–	Kumar and Bandyopadhyay (2006)
	Rice husk ash	3.04	–	Srivastava et al. (2008)
	Polyacrylamide grafted rice husk	0.889	–	Sharma et al. (2009)
	HNO_3, K_2CO_3 treated rice husk	0.044 ± 0.1 mmol g^{-1}	30	Akhtar et al. (2010)
	Partial alkali digested and autoclaved rice husk	9.57	–	Krishnani et al. (2008)
Cr(III)	Rice husk	1.90	–	Marshall et al. (1993)
	Rice husk ash	240.22	–	Wang et al. (2008)
Cr(VI)	Rice husk	164.31	–	Roy et al. (1993)
	Rice husk	4.02	–	Munaf and Zein (1997)
	Rice husk ash	26.31	–	Bhattacharya et al. (2008)

(continued)

Table 8.5 (continued)

Metals	Adsorbent	Adsorption capacity^b	Temperature (°C)	References
	Rice husk-based activated carbon	14.2–31.5	–	Guo et al. (2002)
	Formaldehyde treated rice husk	10.4	–	Bansal et al. (2009)
	Pre-boiled rice husk	8.5	–	Bansal et al. (2009)
Cu(II)	Rice husk	1.21	–	Marshall et al. (1993)
	Rice husk	0.2	–	Srivastava et al. (2008)
	Rice husk	7.1	–	Nakbanpote et al. (2007)
	Rice husk ash	11.5191	–	Feroze et al. (2011)
	Raw rice hush	4.90	–	Luo et al. (2011)
	Expending rice husk	8.02	–	Luo et al. (2011)
	RH-cellulose	7.7	–	Nakbanpote et al. (2007)
	Rice husk heated to 300 °C (RHA300)	6.5	–	Nakbanpote et al. (2007)
	Rice husk heated to 500 °C (RHA500)	16.1	–	Nakbanpote et al. (2007)
	HNO_3, K_2CO_3 treated rice husk	0.036 ± 0.2 mmol g^{-1}	30	Akhtar et al. (2010)
	Microwave incinerated rice husk ash (800 °C)	3.497	–	Johan et al. (2011)
	Microwave incinerated rice husk ash (500 °C)	3.279	–	Johan et al. (2011)
	Partial alkali digested and autoclaved rice husk	10.9	–	Krishnani et al. (2008)
	Tartaric acid modified rice husk	29	27	Wong et al. (2003a)
	Tartaric acid modified rice husk	22	50	Wong et al. (2003a)
	Tartaric acid modified rice husk	18	70	Wong et al. (2003a)
	Tartaric acid modified rice husk	31.85	–	Wong et al. (2003b)
	Carbonized rice husk	42.1	15	Ye et al. (2012)
	Carbonized rice husk	45.5	25	Ye et al. (2012)
	Carbonized rice husk	55.2	35	Ye et al. (2012)
Fe(II)	Copolymer of iron and aluminum impregnated with active silica derived from rice husk ash	222	–	Abo-El-Enein et al. (2009)
Hg(II)	Rice husk ash	6.72	30	Feng et al. (2004)
	Rice husk ash	9.32	15	Feng et al. (2004)
	Rice husk ash	40.0–66.7	–	Tiwari et al. (1995)
	Polyaniline/rice husk ash nanocomposite	Not determined	–	Ghorbani et al. (2011)
	Partial alkali digested and autoclaved rice husk	36.1	–	Krishnani et al. (2008)
Mn	Copolymer of iron and aluminum impregnated with active silica derived from rice husk ash	158	–	Abo-El-Enein et al. (2009)
	Partial alkali digested and autoclaved rice husk	8.30	–	Krishnani et al. (2008)

(continued)

Table 8.5 (continued)

Metals	Adsorbent	Adsorption capacity[b]	Temperature (°C)	References
Ni(II)	Rice husk	0.23	–	Marshall et al. (1993)
	Rice husk ash	4.71	–	Srivastava et al. (2009)
	Microwave-irradiated rice husk (MIRH)	1.17	30	Pillai et al. (2009)
	Partial alkali digested and autoclaved rice husk	5.52	–	Krishnani et al. (2008)
Pb(II)	Rice husk ash	12.61	30	Feng et al. (2004)
	Rice husk ash	12.35	15	Feng et al. (2004)
	HNO_3, K_2CO_3 treated rice husk	0.058 ± 0.1 mmol g^{-1}	30	Akhtar et al. (2010)
	Rice husk ash	207.50	–	Wang et al. (2008)
	Rice husk ash	91.74	–	Naiya et al. (2009)
	Copolymer of iron and aluminum impregnated with active silica derived from rice husk ash	416	–	Abo-El-Enein et al. (2009)
	Tartaric acid modified rice husk	120.48	–	Wong et al. (2003b)
	Tartaric acid modified rice husk	108	27	Wong et al. (2003a)
	Tartaric acid modified rice husk	105	50	Wong et al. (2003a)
	Tartaric acid modified rice husk	96	70	Wong et al. (2003a)
	Partial alkali digested and autoclaved rice husk	58.1	–	Krishnani et al. (2008)
	Tartaric acid modified rice husk	21.55	–	Tarley et al. (2004)
	Rice husk	6.385	25	Surchi (2011)
	Rice husk	5.69	30	Zulkali et al. (2006)
	Rice husk	45	–	Tarley et al. (2004)
	Rice husk	11.40	–	Roy et al. (1993)
Zn(II)	HNO_3, K_2CO_3 treated rice husk	0.037 ± 0.2 mmol g^{-1}	30	Akhtar et al. (2010)
	Rice husk	30.80	50	Mishra et al. (1997)
	Rice husk	29.69	40	Mishra et al. (1997)
	Rice husk	28.25	30	Mishra et al. (1997)
	Rice husk	26.94	20	Mishra et al. (1997)
	Rice husk ash	14.30	–	Bhattacharya et al. (2006)
	Rice husk ash	7.7221	–	Feroze et al. (2011)
	Rice husk ash	5.88	–	Srivastava et al. (2008)
	Partial alkali digested and autoclaved rice husk	8.14	–	Krishnani et al. (2008)
	Rice husk	0.75	–	Marshall et al. (1993)
	Rice husk	0.173	–	Munaf and Zein (1997)
	Rice husk-polyaniline nanocomposite	24.3	–	Ghorbani et al. (2012)

[a] These reported adsorption capacities are values obtained under specific conditions. Readers are encouraged to refer to the original articles for information on experimental conditions

[b] In the unit of (mg g^{-1}) unless specified

Table 8.6 Adsorption capacities of metals by wheat based materials[a]

Metals	Adsorbent	Adsorption capacity[b]	References
Cd(II)	Wheat straw	39.22	Farooq et al. (2011)
	Wheat straw	14.56	Dang et al. (2009)
	Wheat straw	11.60	Tan and Xiao (2009)
	Wheat straw	40.48	Dhir and Kumar (2010)
	Wheat bran	51.58	Nouri and Hamdaoui (2007)
	Wheat bran	15.71	Nouri et al. (2007)
	Wheat bran	21.0	Farajzadeh and Monji (2004)
	Wheat bran	101	Özer and Pirincci (2006)
Cr(III)	Wheat straw	21.0	Chojnacka (2006)
	Wheat bran	93.0	Farajzadeh and Monji (2004)
Cr(VI)	Wheat straw	295.36	Xu et al. (2011)
	Wheat straw	47.16	Dhir and Kumar (2010)
	Wheat bran	35	Dupont and Guillon (2003)
	Wheat bran	40.8	Wang et al. (2008)
	Wheat bran	310.58	Singh et al. (2009)
	Wheat bran	0.942	Nameni et al. (2008)
Cu(II)	Wheat straw	11.43	Dang et al. (2009)
	Wheat straw-citric acid treated	78.13	Gong et al. (2008)
	Wheat bran	12.7	Dupont et al. (2005)
	Wheat bran	17.42	Aydin et al. (2008)
	Wheat bran	8.34	Basci et al. (2004)
	Wheat bran	6.85	Wang et al. (2009)
	Wheat bran	51.5	Özer et al. (2004)
	Wheat bran	15.0	Farajzadeh and Monji (2004)
Hg(II)	Wheat bran	70.0	Farajzadeh and Monji (2004)
Ni(II)	Wheat straw	41.84	Dhir and Kumar (2010)
	Wheat bran	12.0	Farajzadeh and Monji (2004)
Pb(II)	Wheat bran	87.0	Bulut and Baysal (2006)
	Wheat bran	62.0	Farajzadeh and Monji (2004)
	Wheat bran	79.4	Özer and Pirincci (2006)
Zn(II)	Wheat bran	16.4	Dupont et al. (2005)
U(VI)	Wheat straw	19.2–34.6	Wang et al. (2011)

[a] These reported adsorption capacities are values obtained under specific conditions. Readers are encouraged to refer to the original articles for information on experimental conditions

[b] In the unit of (mg g^{-1})

8.3.2 Rice Husk

Rice, a cereal grain, is the most important staple food for a large part of the world's human population, especially in Asia and the West Indies. In fact, the rice is grown on every continent except Antarctica and ranks second only to maize (corn) in terms of worldwide area and production in 2010. In rice milling industries, rice husk which is the hard outer shell of the rice grain is generated as the major by-product or waste,

Table 8.7 Adsorption capacities of metals by chitosan and chitosan composites[a]

Metal	Adsorbent	Adsorption capacity[b]	Temperature (°C)	References
As(III)	Chitosan/ceramic alumina	56.50	25	Veera et al. (2008b)
As(V)	Chitosan/ceramic alumina	96.46	25	Veera et al. (2008b)
Au(III)	Chitosan/cotton fibers (via Schiff base bond)	76.82	25	Qu et al. (2009b)
	Chitosan/cotton fibers (via C–N single bond)	88.64	25	Qu et al. (2009b)
Cd(II)	Chitosan/clay beads	72.31	25	Tirtom et al. (2012)
	Chitosan/cotton fibers (via Schiff base bond)	15.74	25	Zhang et al. (2008)
	Chitosan/glutaraldehyde	32.9	25	Vitali et al. (2008)
	Chitosan/perlite	178.6	25	Shameem et al. (2006)
	Chitosan/PVA	142.9	50	Kumar et al. (2009)
	Chitosan/xanthate	357.14	RT	Sankararamakrishnan et al. (2007)
Co(II)	Chitosan/clinoptilolite	467.90	25	Dinu and Dragan (2010)
Cr(III)	Chitosan/Reactive Blue 2	11.2	25	Vasconcelos et al. (2007)
Cr(VI)	Chitosan coated acid treated oil palm shell charcoal (CCAB)	60.25	–	Nomanbhay and Palanisamy (2005)
	Chitosan coated oil palm shell charcoal (CCB)	52.68	–	Nomanbhay and Palanisamy (2005)
	Chitosan/cellulose	13.05	25	Sun et al. 2009)
	Chitosan/ceramic alumina	153.8	25	Veera et al. (2003)
	Magnetic chitosan	69.40	–	Huang et al. (2009)
	Chitosan/montmorillonite	41.67	25	Fan et al. (2006)
	Chitosan/perlite	153.8	25	Shameem et al. (2003)
Cu(II)	Chitosan/alginate	67.66	–	Wan Ngah and Fatinathan (2008)
	Chitosan/cellulose	26.50	25	Sun et al. (2009)
	Chitosan/ceramic alumina	86.20	25	Veera et al. (2008a)
	Chitosan/clinoptilolite	574.49	–	Dragan et al. (2010)
	Chitosan/clinoptilolite	719.39	25	Dinu and Dragan (2010)
	Chitosan/cotton fibers (via Schiff base bond)	24.78	25	Zhang et al. (2008)
	Chitosan/H2fmbme	113.6	25	Vasconcelos et al. (2008)
	Chitosan/heparin	81.04	25	Coelho et al. (2007)
	Chitosan/perlite	196.07	–	Kalyani et al. (2005)
	Chitosan/perlite	104.0	25	Shameem et al. (2008)
	Chitosan/PVA	47.85	–	Wan Ngah et al. (2004)
	Chitosan/PVC	87.9	–	Srinivasa et al. (2009)
	Chitosan/Reactive Blue 2	57.0	25	Vasconcelos et al. (2007)
	Chitosan/sand	10.87	–	Wan et al. (2007)
	Chitosan/sand	8.18	–	Wan et al. (2010)
Fe(III)	Chitosan/nano-hydroxyapatite	6.75	–	Kousalya et al. (2010)

(continued)

Table 8.7 (continued)

Metal	Adsorbent	Adsorption capacity[b]	Temperature (°C)	References
Hg(II)	Chitosan/cotton fibers (via Schiff base bond)	104.31	35	Qu et al. (2009a)
	Chitosan/cotton fibers (via C–N single bond)	96.28	25	Qu et al. (2009a)
	Chitosan/glutaraldehyde	75.5	RT	Vieira and Beppu (2006)
Ni(II)	Chitosan/clay beads	32.36	25	Tirtom et al. (2012)
	Chitosan/calcium alginate	222.2	–	Vijaya et al. (2008)
	Chitosan/cellulose	13.21	25	Sun et al. (2009)
	Chitosan/ceramic alumina	78.10	25	Veera et al. (2008a)
	Chitosan/clinoptilolite	247.03	25	Dinu and Dragan (2010)
	Chitosan/cotton fibers (via Schiff base bond)	7.63	25	Zhang et al. (2008)
	Chitosan/magnetite	52.55	–	Tran et al. (2010)
	Chitosan/perlite	114.94	–	Kalyani et al. (2005)
	Chitosan/PVC	120.5	–	Srinivasa et al. (2009)
	Chitosan/silica	254.3	–	Vijaya et al. (2008)
Pb(II)	Chitosan/cellulose	26.31	25	Sun et al. (2009)
	Chitosan/cotton fibers (via Schiff base bond)	101.53	25	Zhang et al. (2008)
	Chitosan/magnetite	63.33	–	Tran et al. (2010)
	Chitosan/sand	12.32	–	Wan et al. (2010)
Th(IV)	Poly(methacrylic acid) grafted-chitosan/bentonite	110.5	30	Thayyath et al. (2010)
Zn(II)	Chitosan/cellulose	19.81	25	Sun et al. (2009)

[a] These reported adsorption capacities are values obtained under specific conditions. Readers are encouraged to refer to the original articles for information on experimental conditions

[b] In the unit of (mg g^{-1})

accounting for almost 20 % of the rice production. Throughout the world, the annual generation of rice husk was approximately 120 million tonnes in 2009, leading to serious environmental problems as the rice husk is usually disposed in the end of the production.

In nature, rice husk is tough, woody, insoluble in water, has good chemical stability and high mechanical strength. It is considered as a lignocellulosic agricultural by-product that contains approximately 32 % cellulose, 21 % hemicelluloses, 21 % lignin, 20 % silica and 3 % crude proteins (Nadzi et al. 2007). After a complete combustion process, the resulted rice husk ash consists of about 96 % silica (Rahman and Ismail 1993). The high percentage of silica coupled with a large amount of the structural polymer, lignin has made the rice husk not only resistant to water penetration and fungal decomposition, but also resistant to the best efforts of man to dispose it since husk does not biodegrade easily.

Obviously, the utilization of this abundant scaly residue will yield economic as well as environmental dividends. Therefore, exploration of possible usage of

Table 8.8 Adsorption capacities of metals by untreated and pretreated algae-based materials[a]

Metals	Algae	Adsorption capacity[b]	References
Al(III)	Sargassum fluitans-NaOH treated	0.950–3.740	Lee and Volesky (1999)
Cd(II)	Ascophyllum nodosum (B)	0.338–1.913	Holan et al. (1993)
	Ascophyllum nodosum-$CaCl_2$ treated	0.930	Yu et al. (1999)
	Ascophyllum nodosum-Divinil sulfone treated	1.139	Holan et al. (1993)
	Ascophyllum nodosum-formaldehyde treated	0.750–0.854	Leusch et al. (1995), Chong and Volesky (1995)
	Ascophyllum nodosum-formaldehyde ($3CdSO_4$, H_2O) treated	1.121	Holan et al. (1993)
	Ascophyllum nodosum-formaldehyde + urea treated	1.041	Holan et al. (1993)
	Ascophyllum nodosum-formaldehyde $Cd(CH_3COO)_2$ treated	1.326	Holan et al. (1993)
	Ascophyllum nodosum-glutaraldehyde treated	1.259	Holan et al. (1993)
	Ascophyllum nodosum-glutaraldehyde treated	0.463–0.480	Leusch et al. (1995)
	Caulerpa lentillifera (G)-dried macroalgae	0.026–0.042	Pavasant et al. (2006)
	Caulerpa lentillifera (G)-dried macroalgae	0.0381	Apiratikul and Pavasant (2008a)
	Chaetomorha linum (G)	0.48	Hashim and Chu (2004)
	Chlorella vulgaris (G)	0.30	Klimmek et al. (2001)
	Corallina officinalis (R)	0.2642	Basso et al. (2002)
	Durvillaea potatorum (B) -$CaCl_2$ treated	0.260	Matheickal et al. (1999)
	Durvillaea potatorum-$CaCl_2$ treated	1.100–1.130	Matheickal et al. (1999)
	Codium fragile (G)	0.0827	Basso et al. (2002)
	Ecklonia maxima (B) -$CaCl_2$ treated	1.150	Yu et al. (1999)
	Ecklonia radiate (B) -$CaCl_2$ treated	1.040	Yu et al. (1999)
	Fucus vesiculosus (B)	0.649	Holan et al. (1993)
	Gracilaria edulis (R)	0.24	Hashim and Chu (2004)
	Gracilaria Salicornia (R)	0.16	Hashim and Chu (2004)
	Laminaria hyperbola (B)-treated $CaCl_2$	0.820	Yu et al. (1999)
	Laminaria japonica (B)- treated $CaCl_2$	1.110	Yu et al. (1999)

(continued)

Table 8.8 (continued)

Metals	Algae	Adsorption capacity^b	References
	Lessonia flavicans (B) -treated $CaCl_2$	1.160	Yu et al. (1999)
	Lessonia nigresense (B)-treated $CaCl_2$	1.110	Yu et al. (1999)
	Padina sp.(B)	0.53	Kaewsarn and Yu (2001)
	Padina sp-$CaCl_2$ treated	0.52	Kaewsarn and Yu (2001)
	Padina tetrastomatica	0.53	Hashim and Chu (2004)
	Porphira columbina (R)	0.4048	Basso et al. (2002)
	Sargassum baccularia (B)	0.74	Hashim and Chu (2004)
	Sargassum fluitans-formaldehyde treated	0.9519	Leusch et al. (1995)
	Sargassum fluitans-glutaraldehyde treated	1.0676	Leusch et al. (1995)
	Sargassum fluitans-protonated biomass	0.710	Davis et al. (2000)
	Sargassum sp. (B)	1.40	Tobin et al. (1984)
	Sargassum natans (B)	1.174	Holan et al. (1993)
	Sargassum siliquosum (M)	0.73	Hashim and Chu (2004)
	Sargassum vulgare-protonated biomass	0.790	Davis et al. (2000)
	Ulva lactuca (G)	0.1.52	Areco et al. (2012)
Cr(IV)	Chlorella vulgaris-artificial cultivation	1.525	Dönmez et al. (1999)
Cr(VI)	Chlorella vulgaris	0.534	Aksu et al. (1997)
	Chlorella vulgaris	1.525	Dönmez et al. (1999)
	Sargassum sp.	1.3257	Cossich et al. (2002)
	Sargassum sp.	1.30	Silva et al. (2003)
	Scenedesmus obliquus	1.131	Dönmez et al. (1999)
	Scenedesmus obliquus-artificial cultivation	1.131	Dönmez et al. (1999)
Cu(II)	Ascophyllum nodosum-$CaCl_2$ treated	1.090	Yu et al. (1999)
	Ascophyllum nodosum-formaldehyde treated	0.990	Chong and Volesky (1995)
	Ascophyllum nodosum-formaldehyde treated	1.306–1.432	Leusch et al. (1995)
	Ascophyllum nodosum-glutaraldehyde treated	0.803–0.850	Leusch et al. (1995)
	Caulerpa lentillifera (G)-dried macroalgae	0.042–0.088	Pavasant et al. (2006)

(continued)

Table 8.8 (continued)

Metals	Algae	Adsorption capacity^b	References
	Caulerpa lentillifera (G)-dried macroalgae	0.112	Apiratikul and Pavasant (2008b)
	Chlorella miniata (G)	0.366	Lau et al. (1999)
	Chlorella vulgaris	0.295	Lau et al. (1999)
	Chlorella vulgaris	0.254–0.549	Aksu et al. (1997)
	Chlorella vulgaris	0.758	Dönmez et al. (1999)
	Chlorella vulgaris-artificial cultivation	0.759	Dönmez et al. (1999)
	Durvillaea potatorum-$CaCl_2$ treated	0.040–1.310	Matheickal and Yu (1999)
	Ecklonia radiate-$CaCl_2$ treated	0.070–1.110	Matheickal and Yu (1999)
	Ecklonia maxima-$CaCl_2$ treated	1.220	Yu et al. (1999)
	Laminaria hyperbola-treated $CaCl_2$	1.220	Yu et al. (1999)
	Laminaria japonica-treated $CaCl_2$	1.200	Yu et al. (1999)
	Lessonia flavicans-treated $CaCl_2$	1.250	Yu et al. (1999)
	Lessonia nigresense-treated $CaCl_2$	1.260	Yu et al. (1999)
	Padina sp-$CaCl_2$ treated	0.8	Kaewsarn (2002)
	Sargassum sp.	1.08	Silva et al. (2003)
	Sargassum fluitans-glutaraldehyde treated	1.574	Leusch et al. (1995)
	Sargassum fluitans-formaldehyde treated	1.7938	Leusch et al. (1995)
	Sargassum fluitans-NaOH treated	0.650–1.540	Lee and Volesky (1999)
	Sargassum fluitans-protonated biomass	0.800	Davis et al. (2000)
	Sargassum vulgare-protonated biomass	0.930	Davis et al. (2000)
	Scenedesmus obliquus (G)	0.524	Dönmez et al. (1999)
	Scenedesmus obliquus-artificial cultivation	0.524	Dönmez et al. (1999)
	Ulva lactuca (G)	0.34	Areco et al. (2012)
Fe(III)	Chlorella vulgaris	0.439	Aksu et al. (1997)
Ni(II)	Ascophyllum nodosum	1.346–2.316	Holan and Volesky (1994)
	Ascophyllum nodosum-formaldehyde treated	1.431–1.618	Leusch et al. (1995)

(continued)

Table 8.8 (continued)

Metals	Algae	Adsorption capacity[b]	References
	Ascophyllum nodosum-formaldehyde + CH_3COOH treated	0.409	Holan and Volesky (1994)
	Ascophyllum nodosum-formaldehyde + urea treated	0.511	Holan and Volesky (1994)
	Ascophyllum nodosum-glutaraldehyde treated	0.920–1.959	Leusch et al. (1995)
	Chlorella miniata	0.237	Lau et al. (1999)
	Chlorella vulgaris	0.205–1.017	Klimmek et al. (2001)
	Chlorella vulgaris	1.017	Dönmez et al. (1999)
	Chlorella vulgaris	0.205	Lau et al. (1999)
	Chlorella vulgaris-artificial cultivation	1.017	Dönmez et al. (1999)
	Chondrus crispus (R)	0.443	Holan and Volesky (1994)
	Codium taylori (G)	0.099	Holan and Volesky (1994)
	Cystoserta Indica (B)	0.76	Pahlavanzadeh et al. (2010)
	Durvillaea potatorum-$CaCl_2$ treated	0.17–1.13	Yu and Kaewsarn (2000)
	Fucus vesiculosus	0.392	Holan and Volesky (1994)
	Fucus vesiculosus-formaldehyde treated	0.559	Holan and Volesky (1994)
	Galaxaura marginata (R)	0.187	Holan and Volesky (1994)
	Galaxaura marginata-$CaCO_3$ treated	0.187	Holan and Volesky (1994)
	Nizmuddinia Zanardini (B)	0.76	Pahlavanzadeh et al. (2010)
	Padina australis (B)	0.37	Pahlavanzadeh et al. (2010)
	Padina gymnospora (B)	0.170	Holan and Volesky (1994)
	Padina gymnospora-$CaCO_3$ treated	0.238	Holan and Volesky (1994)
	Sargassum fluitans (B)	0.409	Holan and Volesky (1994)
	Sargassum fluitans-epichlorohyridin treated	0.337	Holan and Volesky (1994)
	Sargassum fluitans-formaldehyde treated	1.9932	Leusch et al. (1995)
	Sargassum fluitans-formaldehyde + HCl treated	0.749	Holan and Volesky (1994)
	Sargassum fluitans-glutaraldehyde treated	0.7337	Leusch et al. (1995)

(continued)

Table 8.8 (continued)

Metals	Algae	Adsorption capacity^b	References
	Sargassum glaucescens (B)	0.76	Pahlavanzadeh et al. (2010)
	Sargassum natans	0.409	Holan and Volesky (1994)
	Sargassum vulgare (M)	0.085	Holan and Volesky (1994)
	Scenedesmus obliquus	0.5145	Dönmez et al. (1999)
	Scenedesmus obliquus-artificial cultivation	0.514	Dönmez et al. (1999)
Pb(II)	Ascophyllum nodosum	1.313–2.307	Holan and Volesky (1994)
	Ascophyllum nodosum-$CaCl_2$ treated	1.150	Yu et al. (1999)
	Ascophyllum nodosum-Bis(ethenil)sulfone treated	1.733	Holan and Volesky (1994)
	Ascophyllum nodosum-formaldehyde treated	1.3755	Leusch et al. (1995)
	Ascophyllum nodosum-formaldehyde + CH_3COOH treated	1.308	Holan and Volesky (1994)
	Ascophyllum nodosum-formaldehyde + urea treated	0.854	Holan and Volesky (1994)
	Ascophyllum nodosum-glutaraldehyde treated	1.318	Holan and Volesky (1994)
	Ascophyllum nodosum-glutaraldehyde treated	0.816–0.898	Leusch et al. (1995)
	Caulerpa lentillifera (G)-dried macroalgae	0.076–0.139	Pavasant et al. (2006)
	Caulerpa lentillifera (G)-dried macroalgae	0.142	Apiratikul and Pavasant (2008a)
	Chlorella vulgaris	0.47	Klimmek et al. (2001)
	Cladophora glomerata (G)	0.355	Jalali et al. (2002)
	Chondrus crispus treated with 1-chloro-2,3-epoxipropane	1.009	Holan and Volesky (1994)
	Chondrus crispus	0.941	Holan and Volesky (1994)
	Codium taylori	1.815	Holan and Volesky (1994)
	Durvillaea potatorum-$CaCl_2$ treated	0.020–1.550	Matheickal and Yu (1999)
	Ecklonia maxima-$CaCl_2$ treated	1.400	Yu et al. (1999)
	Ecklonia radiate-$CaCl_2$ treated	0.050–1.260	Matheickal and Yu (1999)
	Fucus vesiculosus	1.105–2.896	Holan and Volesky (1994)

(continued)

Table 8.8 (continued)

Metals	Algae	Adsorption capacity[b]	References
	Fucus vesiculosus-formaldehyde treated	1.752	Holan and Volesky (1994)
	Fucus vesiculosus-formaldehyde + HCl treated	1.453	Holan and Volesky (1994)
	Galaxaura marginata	0.121	Holan and Volesky (1994)
	Galaxaura marginata-$CaCO_3$ treated	1.530	Holan and Volesky (1994)
	Gracilaria corticata (R)	0.2017–0.2606	Jalali et al. (2002)
	Laminaria hyperbola-treated $CaCl_2$	1.350	Yu et al. (1999)
	Laminaria japonica-treated $CaCl_2$	1.330	Yu et al. (1999)
	Lessonia flavicans-treated $CaCl_2$	1.450	Yu et al. (1999)
	Lessonia nigresense-treated $CaCl_2$	1.460	Yu et al. (1999)
	Padina gymnospora	0.314	Holan and Volesky (1994)
	Padina gymnospora-$CaCO_3$ treated	0.150	Holan and Volesky (1994)
	Padina tetrastomatica (B)	1.049	Jalali et al. (2002)
	Polysiphonia violacea (R)	0.4923	Jalali et al. (2002)
	Sargassum fluitans	1.594	Holan and Volesky (1994)
	Sargassum fluitans-epichlorohyridin treated	0.975	Holan and Volesky (1994)
	Sargassum fluitans-formaldehyde treated	1.8244	Leusch et al. (1995)
	Sargassum fluitans-glutaraldehyde treated	1.6603	Leusch et al. (1995)
	Sargassum hystrix (B)	1.3755	Jalali et al. (2002)
	Sargassum natans	1.221	Holan and Volesky (1994)
	Sargassum natans	1.1487	Jalali et al. (2002)
	Sargassum vulgare	1.100	Holan and Volesky (1994)
	Ulva lactuca (G)	0.61	Jalali et al. (2002)
	Ulva lactuca (G)	0.145	Areco et al. (2012)
	Undaria pinnatifida (B)	1.945	Kim et al. (1999)
Zn(II)	Ascophyllum nodosum-formaldehyde treated	0.680	Chong and Volesky (1995)
	Ascophyllum nodosum-formaldehyde treated	0.719	Leusch et al. (1995)

(continued)

Table 8.8 (continued)

Metals	Algae	Adsorption capacity[b]	References
	Ascophyllum nodosum-formaldehyde treated	0.8718	Leusch et al. (1995)
	Ascophyllum nodosum-glutaraldehyde treated	0.138–0.367	Leusch et al. (1995)
	Caulerpa lentillifera (G)-dried macroalgae	0.021–0.141	Pavasant et al. (2006)
	Chlorella vulgaris	0.37	Klimmek et al. (2001)
	Sargassum fluitans-formaldehyde treated	0.9635	Leusch et al. (1995)
	Sargassum fluitans-glutaraldehyde treated	0.9942	Leusch et al. (1995)
	Ulva lactuca (G)	0.145	Areco et al. (2012)

B brown alga, *G* green alga, *R* red alga

[a] These reported adsorption capacities are values obtained under specific conditions. Readers are encouraged to refer to the original articles for information on experimental conditions

[b] In the unit of (mmol g^{-1})

the rice husk is of great significance in many rice producing countries. It is quite unlikely to use rice husk as animal feed because of its relatively low content of total digestible nutrients (less than 10 %). Besides, the husk has a very low protein and available carbohydrates values, and yet, at the same time, high in crude fiber and crude ash. Due to its abrasive character, poor nutritive value, low bulk density and high ash content which would sometimes cause harmful effect, the rice husk cannot be considered as a safe and suitable animal feed.

Owing to its excellent properties including good heat insulation, ability in emitting smell or gases, and resistant to corrosive, the rice husk can be seen as a potential raw material used to insulate walls, floors and roof cavities. Unfortunately, the cost of building materials manufactured using rice husk as the aggregate is considerably high and not economic as compared to that of using other aggregates, hence its application as building material is not practical in real production. Recently, the rice husk ash has been used as silica source in synthesis of silica aerogel, MCM-41 and other silica- based mesoporous materials which have higher commercial value. Nevertheless, the quality of the resulted materials is hard to be controlled due to variation of silica content and presence of different elements in the rice husk ash depending on the rice species and the combustion process.

Thus, efforts have been made to use this cheap and readily available resource as a low cost adsorbent in the removal of heavy metals from aqueous environment. The high content of cellulose**,** a polymer contains three reactive hydroxyl groups has made rice husk a potential adsorbent material. However, both lignin and silica that present in rice husk tends to reduce the binding between accessible functional group

Table 8.9 Adsorption capacities of metals by bacterials[a]

Metals	Adsorbent	Adsorption capacity[b]	References
Ag(I)	Geobacillus thermodenitrificans	37.86	Chatterjee et al. (2010)
Cd(II)	Aeromonas caviae	155.3	Loukidou et al. (2004)
	Brevundimonas sp. ZF12 Strain	49.01	Masoudzadeh et al. (2011)
	Enterobacter sp.	46.2	Lu et al. (2006)
	Geobacillus thermodenitrificans	42.9	Chatterjee et al. (2010)
	Ochrobactrum anthropi	–	Ozdemir et al. (2003)
	Pseudomonas aeruginosa	42.4	Chang et al. (1997)
	Pseudomonas putida	8.0	Pardo et al. (2003)
	Pseudomonas putida	500.00	Hussein et al. (2004)
	Pseudomonas sp.	278.0	Ziagova et al. (2007)
	Sphingomonas paucimobilis	–	Tangaromsuk et al. (2002)
	Staphylococcus xylosus	250.0	Ziagova et al. (2007)
	Streptomyces pimprina	30.4	Puranik et al. (1995)
	Streptomyces rimosus	64.9	Selatnia et al. (2004a)
Co(II)	Geobacillus thermodenitrificans	69.76	Chatterjee et al. (2010)
Cr(III)	Geobacillus thermodenitrificans	70.7	Chatterjee et al. (2010)
Cr(VI)	Aeromonas caviae	284.4	Loukidou et al. (2004)
	Bacillus coagulans	39.9	Srinath et al. (2002)
	Bacillus megaterium	30.7	Srinath et al. (2002)
	Bacillus coagulans	39.9	Srinath et al. (2002)
	Bacillus licheniformis	69.4	Zhou et al. (2007)
	Bacillus megaterium	30.7	Srinath et al. (2002)
	Bacillus thuringiensis	83.3	Sahin and Öztürk (2005)
	Pseudomonas sp.	95.0	Ziagova et al. (2007)
	Pseudomonas fluorescens.	111.11	Hussein et al. (2004)
	Staphylococcus xylosus	143.0	Ziagova et al. (2007)
	Zoogloea ramigera	2	Nourbakhsh et al. (1994)
Cu(II)	Bacillus firmus	381	Salehizadeh and Shojaosadati (2003)
	Bacillus sp.	16.3	Tunali et al. (2006)
	Bacillus subtilis	20.8	Nakajima et al. (2001)
	Enterobacter sp.	32.5	Lu et al. (2006)
	Geobacillus thermodenitrificans	50.0	Chatterjee et al. (2010)
	Micrococcus luteus	33.5	Nakajima et al. (2001)
	Pseudomonas aeruginosa	23.1	Chang et al. (1997)
	Pseudomonas cepacia	65.3	Savvaidis et al. (2003)
	Pseudomonas putida	6.6	Pardo et al. (2003)
	Pseudomonas putida	96.9	Uslu and Tanyol (2006)
	Pseudomonas putida	15.8	Chen et al. (2005)
	Pseudomonas putida	163.93	Hussein et al. (2004)
	Pseudomonas stutzeri	22.9	Nakajima et al. (2001)

(continued)

Table 8.9 (continued)

Metals	Adsorbent	Adsorption capacity[b]	References
	Sphaerotilus natans	60	Beolchini et al. (2006)
	Sphaerotilus natans	5.4	Beolchini et al. (2006)
	Streptomyces coelicolor	66.7	Öztürk et al. (2004)
	Thiobacillus ferrooxidans	39.8	Liu et al. (2004)
Fe(III)	Geobacillus thermodenitrificans	79.9	Chatterjee et al. (2010)
	Streptomyces rimosus	122.0	Selatnia et al. (2004b)
Ni(II)	Bacillus thuringiensis	45.9	Öztürk (2007)
	Pseudomonas putida	556	Hussein et al. (2004)
	Streptomyces rimosus	32.6	Selatnia et al. (2004d)
Pb(II)	Bacillus sp.	92.3	Tunali et al. (2006)
	Bacillus firmus	467	Salehizadeh and Shojaosadati (2003)
	Corynebacterium glutamicum	567.7	Choi and Yun (2004)
	Enterobacter sp.	50.9	Lu et al. (2006)
	Geobacillus thermodenitrificans	32.26	Chatterjee et al. (2010)
	Pseudomonas aeruginosa	79.5	Chang et al. (1997)
	Pseudomonas aeruginosa	0.7	Lin and Lai (2006)
	Pseudomonas putida	270.4	Uslu and Tanyol (2006)
	Pseudomonas putida	56.2	Pardo et al. (2003)
	Streptomyces rimosus	135.0	Selatnia et al. (2004c)
Pd(II)	Desulfovibrio desulfuricans	128.2	De Vargas et al. (2004)
	Desulfovibrio fructosivorans	119.8	De Vargas et al. (2004)
	Desulfovibrio vulgaris	106.3	De Vargas et al. (2004)
Pt(IV)	Desulfovibrio desulfuricans	62.5	De Vargas et al. (2004)
	Desulfovibrio fructosivorans	32.3	De Vargas et al. (2004)
	Desulfovibrio vulgaris	40.1	De Vargas et al. (2004)
Th(IV)	Arthrobacter nicotianae	75.9	Nakajima and Tsuruta (2004)
	Bacillus licheniformis	66.1	Nakajima and Tsuruta (2004)
	Bacillus megaterium	74.0	Nakajima and Tsuruta (2004)
	Bacillus subtilis	71.9	Nakajima and Tsuruta (2004)
	Corynebacterium equi	46.9	Nakajima and Tsuruta (2004)
	Corynebacterium glutamicum	36.2	Nakajima and Tsuruta (2004)
	Micrococcus luteus	77.0	Nakajima and Tsuruta (2004)
	Zoogloea ramigera	67.8	Nakajima and Tsuruta (2004)
U(VI)	Arthrobacter nicotianae	68.8	Nakajima and Tsuruta (2004)
	Bacillus licheniformis	45.9	Nakajima and Tsuruta (2004)
	Bacillus megaterium	37.8	Nakajima and Tsuruta (2004)
	Bacillus subtilis	52.4	Nakajima and Tsuruta (2004)
	Corynebacterium equi	21.4	Nakajima and Tsuruta (2004)
	Corynebacterium glutamicum	5.9	Nakajima and Tsuruta (2004)
	Micrococcus luteus	38.8	Nakajima and Tsuruta (2004)
	Nocardia erythropolis	51.2	Nakajima and Tsuruta (2004)
	Zoogloea ramigera	49.7	Nakajima and Tsuruta (2004)

(continued)

Table 8.9 (continued)

Metals	Adsorbent	Adsorption capacity[b]	References
Zn(II)	Aphanothece halophytica	133.0	Incharoensakdi and Kitjaharn (2002)
	Bacillus firmus	418	Salehizadeh and Shojaosadati (2003)
	Geobacillus thermodenitrificans	48.26	Chatterjee et al. (2010)
	Pseudomonas putida	6.9	Pardo et al. (2003)
	Pseudomonas putida	17.7	Chen et al. (2005)
	Streptomyces rimosus	30.0	Mameri et al. (1999)
	Streptomyces rimosus	80.0	Mameri et al. (1999)
	Streptoverticillium cinnamoneum	21.3	Puranik and Paknikar (1997)
	Thiobacillus ferrooxidans	82.6	Celaya et al. (2000)
	Thiobacillus ferrooxidans	172.4	Liu et al. (2004)

[a] These reported adsorption capacities are values obtained under specific conditions. Readers are encouraged to refer to the original articles for information on experimental conditions

[b] In the unit of (mg g^{-1})

on the surface of rice husk and adsorbate ions/molecules. Therefore, considerable researches have been carried out to modify or treat the rice husk via different methods prior to the application in heavy metals removal. Adsorption capacities of metals by untreated and treated rice husk are presented in Table 8.5.

8.3.3 Wheat Straw and Wheat Bran

Wheat (*Triticum aestivum*) is the major food crop of the world. The World Agricultural Supply and Demand Estimates (WASDE) has estimated the total consumption of wheat worldwide was 652 million tons for year 2010. Straw and bran are generated as by-products in the wheat milling industry. Every year, over 200 million tons of wheat straw are produced and every 100 million ton of wheat can create 25 million tons of bran. In addition to their use as feed and fuel, large amounts of redundant wheat straw and bran must be disposed of. Therefore, finding new applications for these abundantly available waste materials is a challenge to the wheat production countries.

The wheat straw is a lignocellulosic agricultural waste consisting of about 34–40 % cellulose, 20–35 % hemicellulose, 8–15 % lignin and sugars as well as other compounds carrying different functional groups like carboxyl, hydroxyl, sulphydryl, amide and amine. Although the substances are almost similar, the percentage composition of different substances may vary in different parts of the world depending on the wheat species and growing conditions. Wheat straw has been used as fodder and in paper industry to produce low quality boards or packing materials. The stems are usually burnt directly in some parts of the world for fuel supply, leading to serious atmospheric pollution and wastage of resources.

The wheat bran is the shell of the wheat seed that contains most nutrients of wheat. Despite its high nutritious value, this bran is always removed in the processing of wheat into flour and discarded as waste. Most recently, wheat bran is found to be a valuable material which is applicable in fermentation industry, pharmaceutics and biomedical research. This by-product can also serve as a potential nutritious and cheap raw material for fermentation industry. In addition, its amazing properties of anti-oxidative and anti-inflammatory can bring about a revolution in the fields of melanoma and cancer research. However, more researches and investigation should be carried out to make its applications realistic in human daily life.

As attempt to fully utilize these industry by-products, both wheat straw and wheat bran have been investigated for their adsorption behaviour towards metal ions (Table 8.6). The high adsorption capability of straw is closely related to high content of cellulose, presence of different functional groups and porosity of the material. The reported metal adsorption capacities of wheat based materials could depend on the structure of wheat bran used in different studies, along with other parameters.

8.3.4 Chitin, Chitosan and Chitosan Composites

Chitin is a naturally and abundant occurring mucopolysaccharide from exoskeletons of insects, crustaceans shells, fungi cellular walls, annelids and molluscs. It is the second most abundant polymerin nature after cellulose. Chitin contains 2-acetamido-2-deoxy-β-D-glucose through a β $(1 \rightarrow 4)$ linkage. Through deacetylation process of chitin, a type of natural poly(aminosaccharide), so called chitosan is produced. The chitosan consists mainly of poly $(1 \rightarrow 4)$-2 amino-2-deoxy-D-glucose unit and this derivative biopolymer has been known as a promising polymeric material of great scientific interest due to its special characteristics, for instances, hydrophilicity, biocompatibility, biodegradability, non-toxicity, good adsorption properties and wide range of applications.

The chitosan has drawn particular attention for its feasible application in a variety of forms, from flake-types to gels, beads and fibers. Due to high content of amino and hydroxyl groups in chitosan, this by-product material has been found to be able on adsorbing several heavy metals, including copper, chromium, silver, platinum and lead physically or chemically. In fact, chitosan has binding capacities of more than 1 mmol/g for heavy metals which is far greater than that of activated carbon. The extend of metal adsorption depends strongly on the chitosan source, deacetylation degree, nature of metal ion, variations in crystallinity, amino content and solution pH.

Chitosan can either form gel or dissolve depending on the pH values. Its high sensitivity towards pH has constituted an obstacle to chitosan's performance as a biosorbent in wastewater treatment. To solve this problem, chemical modification of chitosan using cross-linking reagents, for instance glyoxal, formaldehyde, glutaraldehyde, epichlorohydrin, ethylene glycon diglycidyl ether and isocyanates have been used to stabilize chitosan in acidic solutions. Several chemical changes are possible in the chitosan polymeric matrix because of the existence of reactive amino and hydroxyl groups. It has been demonstrated that the chemical modification does not only increase the chemical stability of the adsorbent in acidic media, and especially, decrease its solubility in most mineral and organic acids, but also enhances its mechanical properties. However, the adsorption ability of the modified chitosan may be reduced after the cross-linking procedure due to increment in the rigidity of the structural conformation of the polymer.

A great number of chitosan derivatives have been obtained by introducing selected functional groups into the polymeric matrix of chitosan in order to enhance its interaction with variety of metallic ions, thus increase the adsorption capacity and selectivity for metal ions in solution. The reported chitosan derivatives are those containing nitrogen, phosphorus and sulfur as heteroatoms, and other derivatives such as chitosan crown ethers and chitosan ethylenediaminetetraacetic acid (EDTA)/diethylenetriaminepentaacetic acid (DTPA) complexes. Apart from that, chitosan composites have also been extensively investigated for heavy metals removal. Various types of substance have been used to form composite with chitosan, including activated clay, bentonite, montmorillonite, polyurethane, poly vinyl alcohol, poly vinyl chloride, kaolinite, oil palm ash and perlite. Table 8.7 shows the heavy metal removal capacities through adsorption process using these modified chitosan materials.

8.3.5 Algae

The term "algae" refers to a large and diverse assemblage of organisms that contain chlorophyll and carry out oxygenic photosynthesis. Algae are simple plant-like organisms, ranging from unicellular to multicellular forms, which are easily found in aquatic habitats, freshwater, marine and moist soil. The largest and most complex marine forms are called seaweeds. This abundantly available biomass has been extensively studied for its variety applications as fertilizer, energy sources, pollution control, pigment, stabilizing substances, nutrition and biodegradable plastic production.

Algae can be classified according to several characteristics, including the nature of the chlorophyll(s) present, the carbon reserve polymers produced, the cell wall structure, and the motility type. Although all algae consist of chlorophyll a, there are some, which contain other chlorophylls that differ in minor ways from chlorophylls a. The presence of these additional chlorophylls is typical of particular algal groups. Chrysophyta (golden-brown algae and diatoms), Euglenophyta (euglenoids, is also considered as protozoa), Pyrrophyta (dino-flagellates), Chlorophyta (green algae), Phaeophyta (brown algae) and Rhodophyta (red algae) are some of the major groups of algae.

The algal cell is surrounded by thin, rigid cell walls which are usually made of multilayered microfibrillar framework generally consisting of cellulose and intersperse with amorphous material (Madigan et al. 2000). These walls are essentially impermeable to larger molecules or to macromolecules. However, existence of pores about 3–5 nm wide on the algal cell wall has allowed low molecular-weight constituents such as water, ions, gases, and other nutrients to pass through freely for metabolism and growth.

Due to their high surface area to volume ratio, various algae have been investigated as potential materials for heavy metal removal in aqueous solutions. Actually, the metal biosorption by algae mainly depend on the components on the cell, especially through cell surface and the spatial structure of the cell wall. The cell walls of algae generally contain cellulose, alginic acid and sulphated polysaccharides. These compounds consist of several functional groups, such as carboxyl, hydroxyl, sulfate, phosphate, and amino groups which play a very important role in biosorption process of metal. The mechanism of binding metal ions by algal biomass is always affected by the biomass characteristics, species and ionic charges of the targeted metal ions, and other external environmental factors such as solution pH and temperature.

Among the three groups of algae (red, green and brown algae), brown alga is the most widely studied. This could be associated to the high sorption capability of the brown algae as compared to other two algae species (Romera et al. 2006; Brinza et al. 2007). Very often, the algae undergo treatment in different ways to enhance their sorption capacity (Romera et al. 2006). Adsorption capacities of metals by untreated and treated algae are presented in Table 8.8. In brief, algae have been proven to be both economic and eco-friendly because they are ubiquitous occurrence in nature, can be regenerated after use and have lesser volume of chemical and/or biological sludge to be disposed of.

8.3.6 Bacteria

Bacteria are a large domain of prokaryotic microorganisms. They exist at almost everywhere on the Earth, including in soil, acidic hot springs, radioactive waste, and deep in the Earth's crust, as well as in organic matter and the live bodies of animals and plants. There are about five nonillion (5×10^{30}) bacteria present on the Earth, forming a biomass that exceeds that of all plants and animals. Bacteria have simple morphology and have a wide range of shapes, ranging from spheres or ovoid (coccus) to rods (bacillus, with a cylindrical shape) and spirals (spirillum). They are recognized as microscale organisms whose single cells have neither a membrane-bounded nucleus nor other membrane-bounded organelles like mitochondria and chloroplasts. Due to differences in genetics and ecology, however, bacteria may vary in size as much as in shape. The smallest bacteria are about 0.3 μm, and a few bacteria become fairly large, e.g. some spirochetes occasionally reach 500 μm in length.

In the past decades, there has been an increasing interest to use bacteria in degrading or mineralizing several textile dyes. Bacterial decolorization was attributed to the presence of oxidoreductive enzymes, such as laccase, NADH-DCIP reductase and azoreducases in the bacteria. However, the effectiveness of decolorization using bacteria depends strongly on the adaptability and the activity of the selected bacterium.

Recently, the feasibility of bacteria as biosorbent in heavy metals was explored. It has been demonstrated that composition of cell wall of bacteria is one of the key factors influencing bacterial biosorbing properties. The anionic functional groups exist in the teichoic acids and peptidoglican of gram-positive bacteria, lipopolysaccharides and phospholipids of gram-negative bacteria are the important elements responsible for the metal binding ability of the cell wall. Besides, the metal binding ability of bacteria would be further increased with the involvement of extra-cellular polysaccharides. Usually, the availability of this compound depends on the bacterial species and growth conditions.

Advantages such as availability, small size, ability to grow under controlled conditions and resiliency to a wide range of environmental situations are some of the reasons that made bacteria gaining its popularity in the development of new biosorbents materials. Adsorption capacities of metals by bacterial are provided in Table 8.9.

8.4 Equilibrium, Continuous and Modelling Studies of Heavy Metals Adsorption

8.4.1 Batch Adsorption Experiments

An efficient contact between adsorbent and adsorbate for a period of time is desired in a batch adsorption experiment. This allows the concentration of adsorbate in solution to attain equilibrium with the adsorbate on the surface. In most of the cases, particle size, pH, concentration and agitation are the key factors for the time of equilibrium attainment. Since the last decades, porous adsorbents such as activated carbon and mesoporous silica materials are widely used in batch equilibrium operations for their extremely high surface area, bringing into more effective adsorbent-adsorbate contact and a reducing of diffusional resistance inside the pores. Separation process is always carried out after the adsorption process. The adsorbed adsorbate on the solid phase can be separated from the adsorbate residue in solution via several methods such as settling, filtration, or centrifugation. In industry, the used adsorbent is either regenerated for further use or disposed, depending on the cost involved. Both adsorption isotherm and kinetics modelling are commonly applied in discussion of batch adsorption studies.

8.4.2 Adsorption Isotherm Models in a Batch System

In general, the adsorption isotherms describe how adsorbates interact with adsorbents and therefore they are the basic as well as the most necessity in an adsorption design. The adsorption isotherms are always referred to adsorption properties and equilibrium data obtained in an adsorption system. Apparently, establishing an appropriate and correct correlation for the equilibrium data is important to understand adsorbate-adsorbent interaction, subsequently contributing to improvement of an adsorption system. Besides, the data must fit to a mathematical model for a reliable prediction on adsorption parameters. The compliance of data would also allow a quantitative comparison on adsorption activities of variety adsorption systems under different operating conditions.

During an adsorption process, adsorbate is adsorbed onto the adsorbent. At the same time, desorption process of adsorbate from the adsorbent might also occur with a slower rate. When the rate of both adsorption and desorption processes is the same, the adsorption equilibrium is said to be achieved. Usually, the equilibrium condition is characterized in graph of adsorbate concentration in solid phase versus that in liquid phase. One or more isotherm models may be used to explain the distribution of adsorbate molecules between the adsorbent and the liquid phase, which provides information of equilibrium position in the adsorption process. The suitability, so-called 'favorable' degree of an isotherm model to the adsorption system is often verified from the shape generated in isotherm graph. The isotherm model is 'favored' by the adsorption system if the value of R^2 of graph slope is equal or very close to unity. Besides, the isotherm shape also gives qualitative information on the nature of the solute–surface interaction. In adsorption system, the performance of different adsorbents is always evaluated from their maximum adsorption capacity which can be obtained from the fitted adsorption isotherm. The capacity information also allows selection of the most appropriate adsorbent for a particular adsorption application under certain conditions.

Two- and three- parameter models are widely applied in correlating adsorption equilibria in liquid phase adsorption, even though they are originally used for gas phase adsorption. The thermodynamic assumptions made and different equation parameters used within these models often provide insight into surface properties and affinity of the adsorbent as well as the adsorption mechanism. Obviously, a proper correlation of equilibrium data is crucial for an optimized adsorption condition as well as improved adsorbent's activities.

Two-Parameter Adsorption Isotherms

There are a number of available two-parameter adsorption isotherms for description of adsorption equilibria in liquid phase. However, the underlying assumptions within the model often limit the application of each model for an adsorption system. Among the models, Langmuir, Freundlich, and Brunauer-Emmet-Teller (BET) models appear as the most popular isotherms. Further, other two-parameter models such as Temkin and Dubinin-Radushkevich Jovanovic, Halsey and Hurkins-Jura are also presented in this text.

Langmuir Adsorption Isotherm

The Langmuir model has been intensively applied in quantifying the amount of adsorbate being adsorbed on an adsorbent as a function of concentration at a certain temperature in a homogenous adsorption system (Langmuir 1918). This isotherm assumes the adsorption process happens at specific homogeneous sites on the surface of adsorbate. Therefore, the Langmuir model is valid for homogenous adsorption and it is always referred to monolayer coverage of adsorbate over a homogenous adsorbent surface. For a biosorption process, all the sites on the adsorbent are equivalent and no further adsorption can occur at a site once the site has been occupied by an adsorbate molecule. Based on the assumption made, the adsorption is localized based on lattice model and no further adsorption is allowed at equilibrium where a saturation point is reached. In addition, the model makes assumption that the adsorption of each molecule has equal adsorption activation energy and adsorption enthalpy is independent of surface coverage. The Langmuir equation is written below:

$$q_e = \frac{q_{max}\, K_L\, C_e}{1 + K_L\, C_e} \tag{8.2}$$

where q_e = mass of adsorbate adsorbed/mass of adsorbent at equilibrium

q_{max} = mass of adsorbate adsorbed/mass of adsorbent for a complete monolayer

K_{L} = Langmuir constant related to the enthalpy of adsorption

C_e = concentration of adsorbate at equilibrium

Apparently, characteristic of the Langmuir isotherm can be represented by a plateau in the plot q_{e} versus C_{e}. In addition, the Langmuir isotherm is traditionally used in quantifying the maximum uptake and estimating the adsorption capacity $q_{\max}$ of different adsorbents. Since the Langmuir assumes all the surface sites possess equal affinity for the adsorbate, the $q_{\max}$ should be temperature independent. In practical, however, the presence of functional groups in the adsorbent has brought to modest changes in adsorption capacity with temperature. Besides, some other factors including the number of active sites on the adsorbent, the chemical state of the sites, the accessibility of the adsorbate to the sites and the affinity between the sites such as binding strength has greatly affected the adsorption capacity of an adsorbent in real situation.

An adsorption process can be classified as physisorption or chemisorption. In physisorption, physical forces are dominant in the bonding between adsorbates and the surface. The forces become weaken with increasing of temperature. Therefore, the exothermal nature of the adsorption process can be proven from the decrease of K_{L} value with elevating temperature (Ho and Ofomaja 2006; Shaker 2007; Padmavathy 2008; Djeribi and Hamdaoui 2008). On the other hand, the thermal energy is needed for the strong interaction between the adsorbate and the adsorbent in generating new types of electronic bonds in a chemisorption process. Thus, the rise in temperature is more favourable for the chemisorption which involves the binding of adsorbates to active sites, making it an endothermic process (Febrianto et al. 2009). Usually, the van't Hoff plots are used to further verify the exothermal or endothermal nature of the adsorption process by considering the enthalpy of adsorption. An integrated van't Hoff equation relates the Langmuir constant, K_L to the temperature as below.

$$K_\mathrm{L} = K_0 \exp\left(-\frac{\Delta H}{RT}\right) \tag{8.3}$$

where K_0 = parameter of the van't Hoff equation

H = enthalpy of adsorption

The determination of the adsorption parameters may not be easy since the Eq. 8.2 is in non-linear form. In order to overcome this problem, the Langmuir equation is often expressed in different linear forms as following:

$$\frac{C_e}{q_e} = \frac{1}{q_\mathrm{max}} C_e + \frac{1}{K_L q_\mathrm{max}} \tag{8.4}$$

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_\mathrm{max}}\right)\frac{1}{C_e} + \frac{1}{q_\mathrm{max}} \tag{8.5}$$

$$q_\mathrm{e} = q_\mathrm{max} - \left(\frac{1}{K_L}\right)\frac{q_e}{C_e} \tag{8.6}$$

$$\frac{q_e}{C_e} = K_{\mathrm{L}q\,\mathrm{max}} - K_{\mathrm{L}q\mathrm{e}} \tag{8.7}$$

As compared to the non-linear equation, the four Langmuir linear equations (Eqs. 8.4, 8.5, 8.6, and 8.7) are more favourable among the researchers due to their simplicity and convenience in acquiring isotherm data. Nevertheless, one should realise that the isotherm parameters obtained using the four Langmuir linear equations could be varied in some cases, but they are identical when the non-linear method is applied (Ho 2006).

In fact, the essential characteristics of the Langmuir adsorption isotherm can be expressed in terms of dimensionless constant equilibrium parameter, $\mathrm{R_L}$ (Hall et al. 1966). The $\mathrm{R_L}$ is also recognized as separation factor and it is defined as:

$$R_L = \frac{1}{1 + K_L C_o} \tag{8.8}$$

where C_o = maximum initial concentration of adsorbate.

The isotherm shape can be interpreted according to the value of calculated $\mathrm{R_L}$ (Table 8.10).

Even though the Langmuir adsorption is considered as conventional method in studying an adsorption system, it has suffered from some disadvantages as the model ignores adsorbate-adsorbent interactions. In fact, there are two types of adsorbate-adsorbent interaction, namely direct interaction and indirect interaction

Table 8.10 Langmuir adsorption isotherm constant equilibrium parameter, R_L

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 1$	Irreversible

present in real system. In direct interactions, the adjacent adsorbed molecules tend to make adsorbing near another adsorbate molecule more or less favourable. Meanwhile, indirect interaction influences the adsorption behaviour of the nearly sites by changing surface around the adsorbed site. Since the existence of both adsorbate-adsorbent interactions has been evidenced in heat of adsorption data, they should be taken into consideration in proper estimation of the adsorption parameters. Furthermore, the Langmuir adsorption model considers only the adsorbate of smooth and homogenous surface, making it fails to account for the rough surface of the adsorbate. Since a rough inhomogeneous surface may create different types of sites and change the properties of the sites, such as heat of adsorption, a significant deviation from this model is expected in many cases.

Freundlich Adsorption Isotherm

Freundlich isotherm (Freundlich 1906) is the oldest of the non-linear isotherms. Unlike the Langmuir isotherm which assumes homogenous site energies and limited levels of adsorption, it suggests adsorption onto heterogeneous surface. Since the multilayer adsorption is allowed in this model, concentration of adsorbate on the adsorbent surface rises with increasing of adsorbate concentration in the system. The Freundlich equation relates the concentration of an adsorbate on the surface of an adsorbent to the concentration of the adsorbate in the liquid which it is in contact. The empirical Freundlich equation is mathematically written as:

$$q_\mathrm{e} = K_\mathrm{F} C_\mathrm{e}^{1/n} \tag{8.9}$$

where q_e = mass of adsorbate adsorbed/mass adsorbent
C_e = concentration of adsorbate at equilibrium
K_F = Freundlich constant related to adsorption capacity at particular temperature
n = Freundlich constant related to adsorption intensity at particular temperature, ($n > 1$)

Equation 8.9 can also be presented in a linearized logarithmic form:

$$\log\, q_\mathrm{e} = \log\, K_\mathrm{F} + \frac{1}{n} \log\, C_\mathrm{e} \tag{8.10}$$

K_F is important in providing insight on adsorption capacity which appears as the most significant property of an adsorbent. Usually, adsorption capacity is affected by pH and temperature of the system as well as nature of the adsorbent, such as pore and particle size distribution, specific surface area, cation exchange capacity and surface functional groups. As shown in Eq. 8.10, both Freundlich constants of K_F and n can be calculated from the intercept and slope, respectively in the graph of log q_e versus log C_e. The K_F value depends on the units upon which q_e and C_e are expressed if $1/n \neq 1$. K_F is equivalent to q_e when C_e equals to 1. In the case of $1/n$ equals unity, identical adsorption energy for all sites is observed associated to linear adsorption occurrence (Site 2001). The constant n is the Freundlich equation exponent that characterizes quasi-Gaussian energetic heterogeneity of the adsorption surface (Bansal and Goyal 2005). Usually, larger value of n implies a stronger adsorbent-adsorbate interaction. For a favourable adsorption, Freundlich constant n should have values lying in the range of 1–10.

In fact, Freundlich isotherm is one of the most established isotherm models in biosorption study because it fits nearly all experimental adsorption–desorption data especially in highly heterogeneous adsorbent systems. Although Freundlich isotherm is inappropriate over a wide concentration range, this limitation is always ignored by researchers since moderate concentration is always used in most biosorption studies.

Brunauer–Emmer–Teller (BET) Model

In 1938, Stephen Brunauer, Paul Hugh Emmett, and Edward Teller had introduced the first isotherm for multimolecular layer adsorption (Brunauer et al. 1938). This adsorption theory, so called Brunauer–Emmer–Teller (BET) theory, is extension of Langmuir theory where it proposes multilayer adsorption of adsorbate on the surface of adsorbate. This BET model suggests a random distribution of sites covered by one or more adsorbate molecules by assuming the adsorbent surface consists of fixed individual sites and molecules can be adsorbed more than one layer on the surface of the adsorbent. Besides, Langmuir theory can be applied to each layer and the interaction between each adsorption layer is ignored. In other words, the same kinetics concept proposed by Langmuir is applicable to this multiple layering process, i.e., the rate of adsorption and desorption on any layer is equal.

The BET model is widely used in systems involving heterogeneous material and simple non-polar gases. However, it may not suitable for complex systems dealing with heterogeneous adsorbent such as biosorbents and adsorbates because of the assumption of all sites are energetically identical along with no horizontal interaction between adsorbed molecules. Therefore, this model should not be used in the interpretation of liquid phase adsorption data for complex solids. The simplified form of BET equation is given as following:

$$q_e = q_{\max} \frac{K_B C_e}{(C_e - C_s)\,[1 + (K_B - 1)(C_e/C_s)]} \tag{8.11}$$

where $q_{\max}$ = mass of adsorbate adsorbed/mass of adsorbent for a complete monolayer

K_B = constant related to energy of adsorption

C_s = concentration of adsorbate at saturation of all layers

After rearrangement, the Eq. 8.11 can be written into a linear form:

$$\frac{C_e}{(C_s - C_e)q} = \frac{1}{K_B q_{\max}} + \left(\frac{K_B - 1}{K_B q_{\max}}\right)\left(\frac{C_e}{C_s}\right) \tag{8.12}$$

Temkin Adsorption Isotherm

After considering the limitation of Langmuir adsorption isotherm, the Temkin model takes into accounts of indirect interactions of adsorbate-adsorbate molecules on adsorption isotherms (Temkin 1941). As the surface of adsorbent is occupied by adsorbate, the Temkin isotherm assumes that the heat of adsorption of all molecules in the layer would decrease linearly with coverage due to the indirect interactions. Thus, the Temkin model is dissimilar with Freundlich model which suggests a logarithmical decrease in adsorption. The Temkin equation is written as below:

$$q_e = \frac{RT}{b} \ln a\, C_e \tag{8.13}$$

where a = Temkin isotherm constant

b = Temkin constant related to heat of adsorption

The Temkin equation proposes the increase in degree of completion of the adsorption centres on an adsorbent may bring to a linear decrease of adsorption energy. The linearized form of Temkin equation is expressed below:

$$q_e = \frac{RT}{b} \ln a + \frac{RT}{b} \ln C_e \tag{8.14}$$

Obviously, both constants a and b can be determined from a plot of q_{e} versus ln C_{e}. The Temkin equation is useful to analyse the adsorption data at moderate concentration. Nevertheless, this equation which is originally applied in gas adsorption system, is not well-suited for a complex phenomenon involved in liquid phase adsorption. In liquid phase adsorption, the adsorbed molecules are not organized in a tightly packed structure with identical orientation like what happen in gas phase adsorption. The system becomes more complicated with the presence of solvent molecules and the formation of micelles from adsorbed molecules in liquid phase. Besides, liquid phase adsorption is also greatly influenced by other factors such as temperature, pH, solubility of adsorbate in the solvent and surface chemistry of the adsorbent. Therefore, the Temkin equation is seldom used for experimental data description of complex systems and it receives less attention as compared to three isotherms discussed previously.

Dubinin-Radushkevich Adsorption Isotherm

Dubinin and Radushkevich (D-R) adsorption isotherm has been widely used to express the adsorption isotherms in micropores (Dubinin and Radushkevich 1947). Based on the assumption made of inhomogeneous surface or constant adsorption potential, this model is applicable in estimation of porous structure of the adsorbent and the characteristics of adsorption. Besides, apparent free energy of the adsorption process can also be determined by using this model. The D-R isotherm is given by:

$$q_{\mathrm{e}} = Q_{\mathrm{m}} \exp(-K\varepsilon^2) \tag{8.15}$$

where Q_{m} = adsorption capacity of adsorbent per unit mass

K = constant related to the affinity coefficient and the adsorption energy

ε = Polanyi's adsorption potential which is correlated to temperature

The D-R equation can be also expressed in a linear form:

$$\ln q_{\mathrm{e}} = \ln Q_{\mathrm{m}} - K\varepsilon^2 \tag{8.16}$$

By plotting ln q_{e} versus ε^2, constant K and adsorption capacity, Q_{m} can be determined from the slope and the intercept, respectively. The constant K, defined as $1/\beta E$, is correlated to the affinity coefficient (β) which is closely related to the adsorbate-adsorbent interaction. It is also depends on mean free energy of adsorption (E) per mole of the adsorbate during the transportation process from infinite distance in solution to the surface of the adsorbent. Therefore, E can be calculated from the K value using the following equation:

$$E = \frac{1}{\sqrt{2K}} \tag{8.17}$$

Besides, the mean free energy can be computed using the following relationship:

$$\varepsilon = \mathrm{RT} \ln \left(1 + \frac{1}{C_e}\right) \tag{8.18}$$

Since the D-R isotherm is temperature dependent, a characteristic curve with all the suitable data lying on the same curve is expected by plotting the adsorption data at varied temperatures (ln q_{e} vs. ε^2). In other words, the applicability of the D-R equation in expressing the adsorption equilibrium data is confirmed with the attainment of the identical curve. Thus, it would be doubtful on the validity of the ascertained parameters when deviation in the characteristic curve generated from analyzed data is observed, even though the fitting procedure gives high correction value. Practically, however, the examination on the characteristic curve of biosorption systems is rarely done as the experiments are usually conducted at particular temperature. The D-R isotherm is applicable for not only single adsorbate but also bi-adsorbate adsorption system (Jaroniec and Derylo 1981). Unfortunately, the D-R isotherm is only appropriate for only an intermediate range of adsorbate concentrations since it may exhibit unrealistic asymptotic behavior.

Jovanovic Adsorption Isotherm

The Jovanovic model keeps the same assumptions contained in the Langmuir model which suggests monolayer adsorption on homogeneous solid surface. However, this model considers also the possibility of mechanical contact between the adsorbing and desorbing molecules (Wrudzinski and Wojciecbowski 1977). A general equation derived by Jovanovic is shown as below:

$$q_e = q_{max}[1 - \exp(-aCv)] \tag{8.19}$$

where C = concentration of the adsorbate in the bulk

ν = the heterogeneity parameter (with $0 < \nu < 1$) which emphasizes the allowance for

a = constant correlates to function of the sole temperature

The constant a characterizes the magnitude of the adsorbate–adsorbent interaction energy (Quinones and Guichon 1998). It is defined as (Quinones et al. 1999):

$$\mathrm{a = K\ exp(E_a/RT)} \tag{8.20}$$

where K = low-pressure equilibrium constant or Henry constant

$\mathrm{E_a}$ = characteristic energy of the distribution

The Jovanovic adsorption isotherm emphases the surface binding vibrations of an adsorbed species where the rate of desorption is proportional to the adsorbate surface coverage which can be determined from $\mathrm{q_e/q_{max}}$.

Halsey Adsorption Isotherm

The Halsey model is applicable to multilayer adsorption (Halsey 1948). Its ability to confirm the heteroporous nature of the adsorbent makes it differs from the Freundlich adsorption isotherm which is also used for multilayer adsorption. The Halsey equation is written as below:

$$\mathrm{q_e} = \mathrm{Exp}\left(\frac{\ln k_H - \ln C_e}{n}\right) \tag{8.21}$$

where k_H = Halsey isotherm constant

n = Halsey isotherm exponent

Harkin-Jura Adsorption Isotherm

The Harkin-Jura (H-J) adsorption isotherm proposes the presence of a heterogeneous pore distribution in the adsorbent (Harkins and Jura 1944). Similar to Freundlich and Hasley adsorption isotherms, this model is useful in explanation of multilayer adsorption. The H-J isotherm is expressed as below:

$$\mathrm{q_e} = \sqrt{\frac{A_H}{B_2 + \log C_e}} \tag{8.22}$$

where A_H = isotherm parameter
B_2 = isotherm constant

Three-Parameter Adsorption Isotherms

In order to have better understanding in adsorbate-adsorbent interaction and adsorption behaviour, models involving more than two parameters are necessary to interpret the data. It is very often for researchers to make comparison studies between a series of two-parameter and three-parameter isotherms in describing the equilibrium data because more than one model might be needed to explain the biosorption mechanism in some cases. Some commonly used three-parameter isotherms for the prediction of biosorption experimental data are presented.

Redlich–Peterson Adsorption Isotherm

The Redlich-Peterson (R-P) isotherm is the combination of the Langmuir and Freundlich equations (Redlich and Peterson 1959). This model proposes a non ideal monolayer adsorption and the adsorption mechanism is a hybrid of the two models. The R-P model is applicable in adsorption equilibrium data description over a wide concentration range. The R-P equation is represented below:

$$q_\mathrm{e} = \frac{K_{RP} C_e}{1 + a_{RP} {C_e}^{\beta}} \tag{8.23}$$

where K_RP, a_RP and β are the Redlich-Peterson parameters.

The exponent β ranges between 0 and 1. When $\beta = 0$, the equation resembles Henry's Law.

$$q_\mathrm{e} = \frac{K_{RP} C_e}{1 + a_{RP}} \tag{8.24}$$

If $\beta = 1$, the R-P equation is similar to Langmuir equation.

$$q_{\mathrm{e}} = \frac{K_{RP} C_e}{1 + a_{RP} C_e} \tag{8.25}$$

In most biosorption cases, the β values are close to unity. Thus, the Langmuir adsorption is the better model to correlate the adsorption data.

Equation 8.23 can also be expressed in linear form as:

$$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = \ln a_{\mathrm{RP}} + \beta \ln\ C_{\mathrm{e}} \tag{8.26}$$

Since R-P isotherm incorporates three parameters, it is not possible to obtain the parameters of the R-P isotherms from the linearized equation. To overcome this problem, the parameters of Eq. 8.26 have to be verified by maximizing the correlation coefficients between the experimental data points and those from theoretical model predictions with the solver add-in function of the Microsoft Excel. Nevertheless, the linear equation of R-P isotherm is useful in determination of the parameters of the Langmuir and Freundlich adsorption models.

Sips Adsorption Isotherm

Sips isotherm was proposed after considering the continuing increase in the adsorbed amount with rising concentration (Sips 1948). It has solved the constraint observed in Freundlich model. In fact, the Sips expression (Eq. 8.27) resembles the Freundlich adsorption isotherm, and differs only on the finite limit of adsorbed amount at adequately high concentration of adsorbate.

$$q_{\mathrm{e}} = q_{\max} \frac{(K_S C_e)^{\gamma}}{1 + (K_S C_e)^{\gamma}} \tag{8.27}$$

where K_{S} = Sips isotherm constant

On the other hand, the Sips equation, Eq. 8.27 is similar to the Langmuir equation, Eq. 8.2. An additional parameter, γ which describes heterogeneity of the system is present in the Sips equation. The heterogeneity could arise from the adsorbent or the adsorbate, or both of them. When γ equals unity, Eq. 8.27 is same with Eq. 8.5.

Toth Adsorption Isotherm

Both Sips and Freundlich equations have their limitations in describing an adsorption data at certain concentration range. The Sips equation is inappropriate for adsorption equilibria data expression the low concentration end, while the

Freundlich equation is invalid at intense concentration. In order to solve this problem, Toth isotherm which was derived from the potential theory is proposed (Toth 1971). It makes assumption that most sites have adsorption energy less than the mean value due to an asymmetrical quasi-Gaussian energy distribution with its left-hand side widened. This model obeys Henry's at low concentration and reaches an adsorption maximum at high concentration. The Toth equation is written as:

$$q_e = q_{\max} \frac{C_e}{\left[a_t + C_e^t\right]^{1/t}} \tag{8.28}$$

where a_T = adsorptive potential constant

t = heterogeneity coefficient of the adsorbent ($0 < t \leq 1$)

Toth equation is capable to characterize adsorption for heterogeneous systems as it possesses a heterogeneity coefficient, t. When $t = 1$, the surface of adsorbent is homogeneous and the Toth equation is reduced to the Langmuir equation.

8.4.3 Adsorption Kinetics Models in Batch System

The efficiency of the adsorption process is greatly affected by the rate of the adsorbate to be attached on surface of adsorbent. Obviously, an excellent adsorbent should possess not only high adsorption capacity but also fast adsorption rate. Therefore, kinetic studies involving reaction rate investigation are crucial in identifying the ideal adsorbent for a particular adsorbate. In fact, kinetic studies are also carried out to indentify factors affecting the adsorption process, leading to an optimized adsorption system.

In an adsorption process, the kinetic models are always used to examine the rate determining mechanism as well as the role of adsorption surface, chemical reaction involved and/or diffusion mechanisms. In general, the adsorption mechanism is illustrated as the following steps: (i) bulk diffusion which involves transportation of adsorbate from the bulk solution to the surface of the adsorbent; (ii) film diffusion of adsorbate through the boundary layer to the surface of the adsorbent; (iii) pore diffusion or intraparticle diffusion of adsorbate from the surface to within the particle's pores; lastly (iv) adsorption of adsorbate on the active sites that available on the internal surface of the pores. In most of the cases, the bulk diffusion in step (i) is negligible by providing sufficient stirring to avoid particle and solute gradients in the batch system. Thus, the adsorption dynamics can be approximated by three consecutive steps [(ii)–(iv)] only. A rapid uptake always occurs in adsorption process which is the step (iv) of the mechanism. This immeasurable fast process can be considered as an instantaneous process especially in the case of physical adsorption. As a result, the overall rate of adsorption process is determined by either film or intraparticle diffusion in steps (ii) and (iii), respectively, or a combination of both.

By considering the film diffusion is the rate-controlling step in adsorption mechanism, the change of adsorbate concentration with respect to time can be presented as follows:

$$\frac{dC}{dt} = -k_L A(C - C_s) \tag{8.29}$$

where C = bulk liquid phase concentration of adsorbate at any time t

C_s = surface concentration of adsorbate

k_L = external mass transfer coefficient

A = specific surface area for mass transfer

During the initial stage of adsorption, it is assumed that the transport is mainly due to film diffusion mechanism and the intraparticle resistance can be ignored. At $t = 0$, $C = C_0$ and the surface concentration of adsorbate, C_s is negligible. With the assumptions made above, Eq. 8.29 can be simplified as:

$$\left[\frac{d(C/C_0)}{dt}\right] = -k_L A \tag{8.30}$$

Unlike physical reactions, the adsorption rate may be controlled by its own kinetic rates in the case of chemical reactions. As the adsorption kinetics provide valuable insights to the practical application of the process design and operation control, a complete modeling of kinetics should consider the diffusion equations, boundary conditions and adsorption isotherm equation. It has caused a complicated system of equations. This problem is, however, possible to be resolved by separating the diffusion steps. The diffusion mechanisms can be considered independently by assuming initial adsorption rate is controlled by intraparticle diffusion and it is characterized by external diffusion.

The kinetic studies are carried out practically in batch reactions using various adsorbent dosages, particle sizes of adsorbent, initial adsorbate concentrations, agitation rate, pH values and temperatures along with different adsorbent and adsorbate types. A linear regression is used to determine the best-fitting kinetic rate equation. The compliance of experimental data to the kinetic rate equations is often confirmed using the linear least-squares method that applied to the linearly transformed kinetic rate equations. Lagergren model, pseudo-second-order kinetic model, Elovich model and intraparticle diffusion model are the four commonly applied kinetic models among the researchers.

Lagergren Model

Lagergren model, which is also recognized as pseudo-first order kinetic model, appears as simplified kinetic model which has been widely used in adsorption kinetics examination (Lagergren 1898). The well fitting of experimental data to the pseudo-first order kinetic model suggests film diffusion is the rate-limiting step. Based on solid capacity, the Lagergren first-order rate expression is presented as follows:

$$\frac{dq}{dt} = k_1(q_e - q_t) \tag{8.31}$$

where q_e = adsorption capacity at equilibrium state
q_t = adsorption capacity at time t
k_1 = rate constant of pseudo-first-order adsorption
At $t = 0$, $q_t = 0$, and at $t = t$, $q_t = q_t$, Eq. 8.31 can be integrated as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{8.32}$$

Equation 8.32 can be written in non-linear form as below:

$$q_t = q_e(1 - \exp(-k_1 t)) \tag{8.33}$$

A straight line of $\ln(q_e - q_t)$ versus t is good indicator of the applicability of this kinetic model. The q_e value obtained by this method should be compared with the experimental value to identify the deviation. A time lag resulted from external mass transfer or boundary layer diffusion at the beginning of the adsorption process may cause the difference in q_e values. If a large discrepancy in the q_e values is observed, even though the least square fitting process yields high correlation coefficient, a reaction still cannot be classified as first-order. In this case, q_e and k_1 can be estimated via non-linear procedure fitting of Eq. 8.33. On the other hand, both rate constant and equilibrium adsorbate uptake can be determined from the straight-line plots of ln ($q_e - q_t$) against t of Eq. 8.32 at different initial adsorbate concentrations.

Pseudo-Second-Order Kinetic Model

Ho and McKay introduced the pseudo-second order model on the basis of the adsorption capacity of the solid phase (Ho and McKay 1999). The well fitting of experimental data to the pseudo-second order kinetic model suggests chemisorption is the rate-limiting step. Similar to Lagergren model or pseudo-first order kinetic model, this model takes account of all the steps of adsorption including external film diffusion, intraparticle diffusion and adsorption. In particular, this pseudo-second order model is useful to the adsorption systems using various adsorbent dosages and adsorbate concentrations. This model is written as:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{8.34}$$

where k_2 = rate constant of pseudo-second-order adsorption

At $t = 0$, $q = 0$, and at $t = t$, $q_{\mathrm{t}} = q_{\mathrm{t}}$, integration of Eq. 8.34 with the boundary conditions yields

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_2 t \tag{8.35}$$

The linear form of Eq. 8.35 is shown as below:

$$\frac{t}{q} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{8.36}$$

It is noteworthy that pseudo-second order model enables the determination of adsorption capacity, pseudo-second-order rate constant, and initial adsorption rate without prior knowledge of experimental parameters.

Elovich Model

The Elovich model is a kinetic model for chemisorptions that has been widely used to describe the adsorption of gas onto solid systems (Zeldowitsch 1934; Rudzinski and Panczyk 2000). Since last decade, this model has also been applied to discuss the adsorption behaviour of heavy metal removal from aqueous solutions (Cheung et al. 2001). The Elovich equation is generally expressed as:

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{8.37}$$

Where α = initial adsorption rate
β = the desorption constant

By assuming $\alpha\beta t \gg t$ and by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. 8.36 can be simplified into (Chien and Clayton 1980):

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{8.38}$$

If the adsorption data fit the Elovich model, a plot of q_t against $\ln(t)$ should yield a linear relationship. The β and α can be calculated from the slope and intercept, respectively.

Intraparticle Diffusion Model

By assuming intraparticle diffusion is the only rate determining step, the intraparticle diffusion model correlates adsorption capacity to effective diffusivity of adsorbate within the particle (Weber and Morris 1963). The well fitting of experimental data to the intraparticle diffusion model suggests pore diffusion is the rate-limiting step. The model mathematically is expressed in the equation below:

$$q_t = f\left(\frac{Dt}{r_p^2}\right)^{1/2} = K_{WM}t^{1/2} \tag{8.39}$$

where q_t = adsorption capacity at time t

D = effective diffusivity of solutes within the particle

r_p = particle radius

K_WM = intraparticle diffusion rate constant

Theoretically, the plot of q versus $t^{1/2}$ should give a straight line passing through the origin. The slope of the straight line provides the intraparticle diffusion rate constant K_{WM}. However, detection of multi linear plots from adsorption data may imply the occurrence of some other mechanisms during the adsorption process. Accordingly, a significant external resistance to mass transfer surrounding the particles in the early stage of adsorption is evidenced by the first shaper portion. Meanwhile, the intraparticle diffusion happens in the second linear portion, which is a steady adsorption stage. Eventually, the final equilibrium stage is achieved when the rate of intraparticle diffusion becomes slow associated to extremely low solute concentration in solution in the third portion. Apparently, a good correlation of rate data in this model is important to rationalize the adsorption mechanism, subsequently to determine K_{WM} values by linearization the curve $q = f(t^{0.5})$.

The rate of diffusion within the particle is much slower compared to that of movement of the adsorbate from solution to the external solid surface. This is because of the restraining chemical attractions between adsorbate and adsorbent as well as the greater mechanical hindrance to movement exist at the surface molecules or surface layers. Usually, adsorbate molecules reach at the adsorbent surface more fast than they can diffuse into the solid adsorbent, resulting in accumulation of the adsorbate at the surface. Therefore, a (pseudo)-equilibrium may be established. Nevertheless, further adsorption of adsorbate can occur at the same rate as the surface concentration is reduced by inward adsorption.

8.4.4 Continuous Packed-Bed System in Biosorption of Heavy Metals

The batch adsorption method is only application for adsorption system involving small volumes of adsorbate. Thus, continuous flow treatments should be applied for large scale application of biosorption process. In this method, adsorbates in solution are flown continuously from either the top or the bottom of a stationary bed of solid adsorbent which is more recognized as column. Since this method has closer simulation of commercial systems in industry, it is commonly used in the assessment of the suitability of an adsorbent for a particular adsorbate. After the adsorption process, the adsorbent can be easily separated from the effluent and the used adsorbent is usually regenerated. Among the different experimental set-ups, the packed-bed column is possibly the most effective device for continuous operations.

In a down-flow packed bed column, the adsorbate solution is in contact with adsorbent when it moves through the column. As flowing down the column, adsorption process occurs where most of the adsorbate is adsorbed gradually from liquid onto the adsorbent. As a result, concentration of adsorbate in the effluent is either very low or even untraceable at the end of the column. Depending on the value of adsorbate concentration desired for its lower boundary, the length of the adsorption zone in the column is somewhat random. When more adsorbate solution is fed into the column, concentration of adsorbate in the effluent increases slowly due to equilibrium and kinetic factors. Usually, the adsorption zone will shift down the column like a slowly moving wave when the upper portion of packing adsorbent is saturated with adsorbate. Ultimately, the lower edge of the adsorption zone reaches the bottom of the column, resulting in a significant rise in adsorbate concentration in the effluent. As little additional adsorption takes place with the entire bed approaching an equilibrium state with the feed at this breakthrough point, the flow is stopped. However, one should realize that the equilibrium between adsorption and desorption process is seldom achieved under this continuous flow condition. In most cases, the breakthrough point increases with increasing of bed height, reducing of adsorbent's particle size and deceasing of flow rate.

A breakthrough curve, which is plot of adsorbate effluent concentration versus time, is applicable for description of continuous packed bed performance. The general position of the breakthrough curve along the time or volume axis is indicative of loading behaviour of the adsorbate to be removed from a solution in a fixed bed. A normalized concentration as a function of time or volume of effluent (V_{eff}) for a given bed height is used to represent the breakthrough position. In real practical, the normalized concentration is referred to the ratio of effluent adsorbate concentration to inlet adsorbate concentration (C/C_0). An adsorption isotherm is favoured with infinite adsorption rate the breakthrough curve approaches a straight vertical line. The breakthrough curve becomes less sharp as decreasing of the mass transfer rate. Since mass transfer is always finite, a breakthrough curve of S-shape would be expected. Both the breakthrough point and breakthrough curve are greatly influenced by nature of the adsorbate and the adsorbent, geometry of the column and operating conditions.

In order to evaluate and predict the dynamic behavior of a continuous packed-bed system, a number of simple mathematical models underlying different assumptions have been established. Some commonly used models in characterization of the fixed bed performance for biosorption process are presented here.

Adams–Bohart Model

The Adams-Bohart model was developed by assuming the adsorption rate is proportional to adsorbent concentration and its residual capacity (Bohart and Adams 1920). This model was originally applied to describe the relationship between C/C_o and t for the adsorption of chlorine on charcoal in fixed bed column. With the assumption of the adsorption rate is limited by external mass transfer, the model equation is expressed below:

$$\ln \frac{C}{C_0} = k_{AB} C_0 t - k_{AB} N \frac{Z}{U_0} \tag{8.40}$$

where C = adsorbate concentration remaining at each contact time

C_0 = initial adsorbate concentration

k_{AB} = Adams–Bohart kinetic constant

N = adsorbate concentration in the bulk liquid

Z = bed depth of column

U_0 = linear velocity calculated by dividing the flow rate by the column's sectional area

Equation 8.40 is generally valid in the initial part of the breakthrough as it is derived based on the assumption of low concentration field where $C < 0.15C_o$. Thus, this model is always utilized in describing the initial part of the breakthrough curve only. The plot of ln C/C_0 against t at a given bed height and flow rate provides values that characterizes operational parameters of the column. As increasing of t, concentration of metal in the bulk liquid tends to approach a saturation condition where maximum capacity of adsorption is achieved.

The Adams-Bohart model is applicable in fixed bed column of different biosorption applications due to its ability to provide solution of the differential equations for mass transfer rate in solid and liquid phases. Consequently, its overall approach is suitable for quantitative description of other systems regardless the phase of adsorbate.

Bed Depth/Service Time Model

The Bed-Depth-Service-Time (BDST) model is often used to examine the capacity of fixed bed at various breakthrough values (Bohart and Adams 1920). By assuming a direct adsorption of adsorbate onto the surface of the adsorbent, this model correlates the service time (t) with the process variables by ignoring intraparticle mass resistance and external film resistance. The BDST model states that the service time of a column is given by:

$$t = \frac{N_0}{C_0 U_0} Z - \frac{1}{K_a C_0} \ln\left(\frac{C_0}{C} - 1\right) \tag{8.41}$$

where N_0 = adsorption capacity

K_{a} = rate constant in BDST

At 50 % breakthrough $\left(\frac{C_o}{C}\right) = 2$, and $t = t_{0.5,}$ the Eq. 8.41 can be written as

$$t_{0.5} = \left(\frac{N_o}{C_o U_o}\right) Z \tag{8.42}$$

or

$$t_{0.5} = \text{constant} \times \mathrm{Z} \tag{8.43}$$

A straight line passing through the origin is expected in a plot of BDST at 50 % breakthrough against bed depth using Eq. 8.43 if the adsorption data fits the model. Obviously, this model has solved the constraint in Adams and Bohard model which is only appropriate for initial part of the breakthrough.

Yoon–Nelson Model

Yoon-Nelson (Y-N) model suggests the decrease rate in the probability of adsorption for each adsorbate molecule is comparative to the probability of adsorption of adsorbate and the probability of adsorbate breakthrough on the adsorbent (Yoon and Nelson 1984). This model can be applied without knowing the detailed information about adsorbent type, characteristics of both adsorbate and adsorbent, and physical properties of adsorption bed adsorbent. Therefore, it appears as a reasonably simple theoretical model. Expression of the Y-N equation for a single-component system is given as:

$$\ln \frac{C}{C_0 - C} = k_{YN} t - \tau k_{YN} \tag{8.44}$$

where t = time required for 50 % adsorbate breakthrough

τ = breakthrough (sampling) time

k_{YN} = Yoon and Nelson rate constant

The parameters τ and k_{YN} for the adsorbate can be obtained from the intercept and slope, respective of the ln $C/(C_0 - C)$ versus sampling time (t) plot. These values are important for the calculation of theoretical breakthrough curves for a single-component system.

Thomas Model

The Thomas model is widely used for determination of rate constant for the maximum adsorption capacity of an adsorbate in a column. This model is derived based on assumption of Langmuir kinetics of adsorption-desorption and no axial dispersion (Thomas 1944). The Thomas equation takes into account of the rate driving force obeys second order reversible reaction kinetics, and it is written as:

$$\frac{C}{C_0} = \frac{1}{1 + \exp(k_{Th}/Q(q_0X - C_0V_{eff}))} \tag{8.45}$$

Where k_{Th} = Thomas rate constant

Q = flow rate

q_0 = maximum solid-phase concentration of the solute

X = amount of adsorbent in the column

V_{eff} = effluent volume

The Thomas equation can also be presented in linear form as below:

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_{Th}q_0X}{Q} - \frac{k_{TH}C_0}{Q}V_{eff} \tag{8.46}$$

By plotting ln [$(C_0/C) - 1$] versus t at a given flow rate, the kinetic coefficient k_{Th} and the adsorption capacity of the bed q_0 can be determined. The Thomas model allows the prediction of the concentration-time profile or breakthrough curve for the effluent, hence contributing to a successful design of a column sorption process.

Clark Model

Clark (Clark 1987) proposed a new simulation for study of a continuous packed-bed system based on the (i) hypothesis of the flow is piston type (Hamdaoui 2006); and (ii) the combination of both mass transfer concept and Freundlich adsorption isotherm (Ayoob and Gupta 2007). By ignoring the phenomenon of dispersion, the equation is expressed as:

$$\frac{C}{C_0} = \left(\frac{1}{1 + Ae^{-rt}}\right)^{1/n-1} \tag{8.47}$$

with

$$\mathrm{A} = \left(\frac{C_0^{n-1}}{C_{break}^{n-1}} - 1\right)e^{rt_{break}} \tag{8.48}$$

and

$$R(n-1) = r \text{ and } R = \frac{K_{Cl}}{U_0}v \tag{8.49}$$

where C_{break} = outlet concentration at breakthrough (or limit effluent concentration)

t_{break} = time at breakthrough

n = Freundlich parameter

k_{Cl} = Clark rate constant

v = migration rate

Both constants of the model A and r of a particular adsorption process on a fixed bed and a selected treatment objective can be obtained from Eq. 8.49 by non-linear regression analysis. These values are critical for the prediction of the breakthrough curve according to the relationship between C/C_0 and t in Eq. 8.47.

Wolborska Model

Wolborska model is a simplified adsorption representation which emphasizes on the general mass transfer for the diffusion mechanism for low concentration range only for breakthrough curve (Wolborska 1989). Due to its limitation in describing the whole adsorption process, this model is seldom applied by the researchers. The equation for the mass transfer in the fixed bed adsorption is as follow:

$$\ln\left(\frac{C}{C_0}\right) = \frac{\beta_a C_0}{N_0}t - \frac{\beta_a Z}{U_0} \tag{8.50}$$

with

$$\beta_a = \frac{U_0^2}{2D}\left[\left(1 + \frac{4\beta_0 D}{U_0}\right)^{1/2} - 1\right. \tag{8.51}$$

where β_a = Kinetics coefficient of the external mass transfer
N_0 = saturation concentration
Z = height of column
U_0 = specific velocity
D = axial dispersion coefficient

Kinetics coefficient of the external mass transfer β_a can be estimated through the breakthrough curve. When the flow rate of solution through the bed is high or in short beds, axial diffusion D is negligible and $\beta_a = \beta_0$. The Wolborska model resembles Adams-Bohart model if the coefficient β_a/N_0 is equal to k_{AB}.

8.4.5 Response Surface Methodology

Response surface methodology (RSM) is a multivariate technique that mathematically fits the experimental domain studied in the theoretical design through a response function. It is used for designing experiments, building numerical models, evaluating the effects of variables and searching for the optimum combinations of factors for a system (Myers and Montgomery 2002).

Generally, the targeted response in a designed of experiments is governed by several independent variables. The response refers to the performance measure or quality characteristic of the product or process, whereas independent variables are sometimes called input variables. An experiment is a series of tests, called runs, in which changes are made in the input variables in order to identify the reasons for changes in the output response.

Conventional methods of investigating a process by varying one factor whilst maintaining all other factors involved at constant levels does not describe the combined effect of all the factors involved. This method is also time consuming and of low efficiency as it requires a number of experiments to determine the optimum levels, which are unreliable. These limitations of a classical method can be eliminated by optimising all the affecting parameters collectively by statistical technique such as RSM (Elibol 2002).

Two commonly used designs in RSM are central composite design (CCD) and Box-Behnken design (BBD) (Garg et al. 2008; Fu et al. 2009; Cerino Córdova et al. 2011). BBD is an independent quadratic design that does not contain an embedded factorial or fractional factorial design. In this design, the treatment combinations are at the center and midpoints of edges of the process space. These designs are either rotatable or near rotatable and require three levels of each factor. BBD is considered as an efficient option in RSM and an ideal alternative to CCD because it involved less input variables. Because of fewer treatment combinations, BBD is also a more time and energy saving design as compared to CCD.

Whilst CCD contains an imbedded factorial or fractional factorial design with center points that is augmented with a group of 'star points' that allow estimation of curvature. The star points represent new extreme values (low and high) for each factor in the design. The CCD is rotatable and requires five levels for each factor.

The similarity in both designs is that it allows the estimation of all the regression parameters required and represent in quantitative form as linear (first-order polynomial model), quadratic or cubic function (higher order polynomial models). The equations below show the linear and quadratic models which are most commonly used in RSM. A first-order model with n experimental runs carrying out on k design variables and a single response y can be expressed as follows:

$$y = \beta_0 + \beta_1 x_{i1} + \beta_2 x_{i2} + \ldots\ldots\ldots + \beta_k x_{ik} + \varepsilon_i (i = 1, 2, \ldots\ldots, n) \quad (8.52)$$

where y (predicted response) is a function of the design variables $x_1, x_2, \ldots, x_j$, β_0 is the constant coefficient, $\beta_1, \beta_{2\ldots}, \beta_j$ is the linear coefficients, and ε is the experimental error. This model is appropriate for describing a flat surface with or without tilted surfaces.

When there is a curvature in the response surface, the first-order model is insufficient to describe the response and in this case, a higher order polynomial such as the quadratic model may be used. This is represented by Eq. 8.53.

$$y = \beta_o + \sum_{i=0}^{n} \beta_i X_i + \sum \sum_{i<j} \beta_{ij} X_i X_j \sum_{i=1}^{n} \beta_{ii} {X_i}^2 + \in \quad (8.53)$$

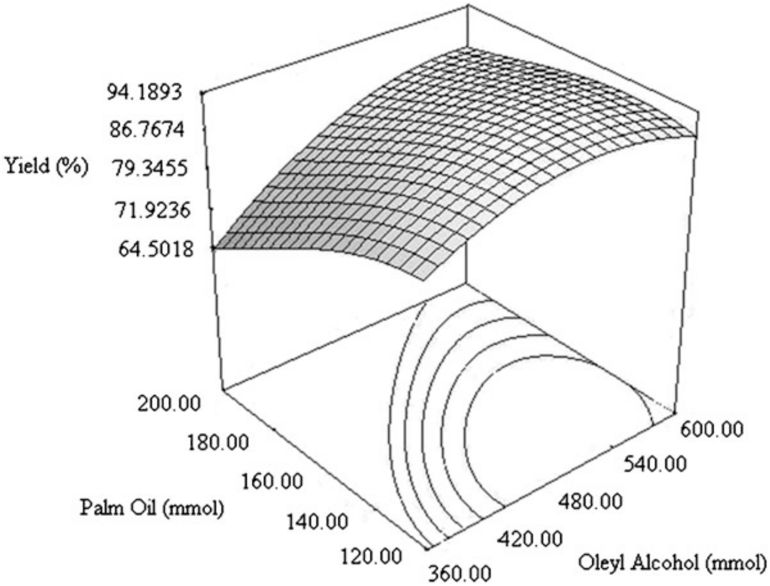

Fig. 8.1 3D response surface plot showing effect of amount of substrates on the percentage yield of palm-based wax ester production (Keng 2008)

where y is the predicted response, β_0 is the constant coefficients, β_1 is the linear coefficients of the input factor x_i, β_{ij} is the quadratic coefficients between the input factor x_i and x_j, β_{ii} is the interaction coefficients of input factor x_i and ε is the experimental error. (Box and Hunter 1957). The second-order model is important to provide a good prediction throughout the region of interest. It is rotatable so the variance of the predicted response is the same at all points. Since the objective of RSM is optimisation and as the location of the optimum is unknown prior to running the experiment, it makes sense to use the design that provides equal precisions of estimation in all directions (Tan et al. 2008).

Generally, to perform experimental optimisation with RSM, it involves three major steps: (1) design and perform the experiments; (2) response surface modeling through regression analysis; (3) optimisation and checking the adequacy of the model. In the first step, important independent input variables and desired responses with the design constrains are identified and experimental design are adopted. Such designs are generated using computer software like Statistica, SAS or Design Expert. This is followed by regression analysis and statistical analysis of variance (ANOVA) of the experimental data in order to identify parameters that are significantly affects the desired response and develop a mathematical model having the best fit to the data obtained. Lastly, optimal combination of parameters is identified and confirmation experiments are conducted to verify the optimal parameters and mathematical model generated. For visualisation of the investigated factors, contour and response surface plots in 3D are generated that show the linear, interaction and quadratic effects of two or more parameters (Fig. 8.1).

8.5 Conclusion

Removal of heavy metals from aqueous environment is indeed a challenging problem in the control of environmental pollution. A wide range of treatment technologies such as chemical precipitation, ion exchange, membrane filtration and adsorption can be employed to remove heavy metals but these treatment methods still suffer from some inherent limitations. For instance, chemical precipitation, which has been traditionally and widely used to remove heavy metals from contaminated sources, is often associated with huge sludge production. Ion exchange process is generally applicable to treat or remove heavy metals at low concentration. As for membrane filtration, problems such as membrane fouling, high maintenance cost and low permeate flux are often unavoidable. Taking all these into considerations, the adsorption process thus appeared as one of the most promising methods.

Various low cost adsorbents have been investigated intensively in order to avoid the usage of costly activated carbon. It is evident that in most of the reported works, the study is still being centralised in the maximum adsorption capacities of the materials. While most of the low cost adsorbents have shown its potential in heavy metals removal without any modifications, but it is interesting to note that their removal capabilities can generally be improved through certain chemical modifications. Also, more than one factors such as pH, contact time, initial influent concentration, temperature, adsorbent dosage and etc. can significantly affect the adsorption process.

Numerous equations based on two-parameter or three parameter adsorption isotherms have been employed to describe the adsorption process under equilibrium condition. These include Langmuir, Freundlich, Brunauer-Emmet-Teller (BET), Temkin, Dubinin-Radushkevich, Jovanovic, Hasley, Harkin-Jura, Redlich-Peterson, Sips and Toth models. As for the kinetics studies, the two commonly used rate expressions are the pseudo-first and pseudo-second order kinetic models. In most of the cases, especially those involve chemisorption, pseudo-second order kinetic model is able to provide a better description than the pseudo-first order kinetic model as the former takes the interaction of adsorbent-adsorbate through valency forces into consideration.

To overcome the limitation of batch condition which is applicable only to the treatment under equilibrium condition, it is necessary to carry out flow tests using columns to obtain a design models which would be applicable to commercial systems. Besides this, developing an appropriate mathematical model through statistical approach is also important to obtain the optimum operating condition of the adsorption system.

Several low cost adsorbents can be seen as attractive alternatives for the removal of heavy metals based on their outstanding removal ability. However, in most of the cases, attention seems to be focused on the maximum adsorption capacity of the low cost adsorbents and the model pollutants are mainly synthetic types. In order to fully utilize the application of these materials in wastewater treatment, their removal efficiency should be further tested in effluents from industries. Besides, the characterization of the adsorbents as well as the study of the sorption mechanism is equally important. More effort is required to provide insight into the direction of modeling, the effects of adsorbent recycling and regeneration and the recovery of heavy metals from wastewater. The possibility of immobilized these adsorbents can also be viewed as a feasible approach as suspended system requires a filtration step which is not suited for practical applications. If modification is needed, it is desirable to have a material with a wide range of metal affinities as this will be particularly useful for industrial effluents which carry more than one type of metals. Further research involving the combination of methodologies/system should also be encouraged as this would minimize or overcome the problem associated with a single treatment process.

References

Abo-El-Enein SA, Eissa MA, Diafullah AA, Rizk MA, Mohamed FM (2009) Removal of some heavy metals ions from wastewater by copolymer of iron and aluminum impregnated with active silica derived from rice husk ash. J Hazard Mater 172:574–579

Abo-Farha SA, Abdel-Aal AY, Ashour IA, Garamon SE (2009) Removal of some heavy metal cations by synthetic resin purolite C100. J Hazard Mater 169:190–194

Afkhami A, Saber-Tehrani M, Bagheri H (2010) Simultaneous removal of heavy-metal ions in wastewater samples using nano-alumina modified with 2,4 dinitrophenylhydrazine. J Hazard Mater 181:836–844

Agency for Toxic Substances and Disease Registry (ATSDR) (2005) Toxicological profile for nickel. U.S. Department of Health and Human Services, Public Health Service, Atlanta

Agency for Toxic Substances and Disease Registry (ATSDR) (2007) Toxicological profile for lead. U.S. Department of Health and Human Services, Public Health Services, Atlanta

Agency for Toxic Substances and Disease Registry (ATSDR) (1993) Toxicological profile for nickel (update). US Department of Health and Human Services, Public Health Service, Washington, DC, pp 1–147

Ajmal M, Rao RAK, Anwar S, Ahmad J, Ahmad R (2003) Adsorption studies on rice husk: removal and recovery of Cd(II) from wastewater. Bioresour Technol 86:147–149

Akhtar M, Iqbal S, Kausar A, Bhanger MI, Shaheen MA (2010) An economically viable method for the removal of selected divalent metal ions from aqueous solutions using activated rice husk. Colloids Surf B Biointerfaces 75:149–155

Aksu Z, Açikel Ü, Kutsal T (1997) Application of multicomponent adsorption isotherms to simultaneous biosorption of iron(III) and chromium(VI) on C. vulgaris. J Chem Technol Biotechnol 70:368–378

Al-Enezi G, Hamoda MF, Fawzi N (2004) Ion exchange extraction of heavy metals from wastewater sludges. J Environ Sci Health A Tox Hazard Subst Environ Eng 39(2):455–464

Apak R, Tutem E, Hugul M, Hizal J (1998) Heavy metal cation retention by unconventional sorbents (red muds and fly ashes). Water Res 32:430–440

Apiratikul R, Pavasant P (2008a) Batch and column studies of biosorption of heavy metals by Caulerpa lentillifera. Bioresour Technol 99:2766–2777

Apiratikul R, Pavasant P (2008b) Sorption of Cu^{2+}, Cd^{2+}, and Pb^{2+} using modified zeolite from coal fly ash. Chem Eng J 144:245–258

Areco MM, Hanela S, Duran J, Afonso MS (2012) Biosorption of Cu(II), Zn(II), Cd(II) and Pb(II) by dead biomasses of green alga Ulva lactuca and the development of a sustainable matrix for adsorption implementation. J Hazard Mater 213–214:123–132

Aroua MK, Mohamed Zuki F, Sulaiman NM (2007) Removal of chromium ions from aqueous solutions by polymer-enhanced ultrafiltration. J Hazard Mater 147:752–758

Ayala J, Blanco F, Garcia P, Rodriguez P, Sancho J (1998) Asturian fly ash as a heavy metals removal material. Fuel 77:1147–1154

Aydın H, Bulut Y, Yerlikaya C (2008) Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents. J Environ Manage 87:37–45

Ayoob S, Gupta AK (2007) Sorptive response profile of an adsorbent in the defluoridation of drinking water. Chem Eng J 133:273–281

Bade L (2007) Micellar enhanced ultrafiltration and activated carbon fibre hybrid processes for copper removal from wastewater. Korean J Chem Eng 24(2):239–245

Banerjee SS, Jayaram RV, Joshi MV (2003) Removal of nickel and zinc(II) from wastewater using fly ash and impregnated fly ash. Sep Sci Technol 38:1015–1032

Banerjee SS, Joshi MV, Jayaram RV (2004) Removal of Cr(VI) and Hg(II) from aqueous solution using fly ash and impregnated fly ash. Sep Sci Technol 39:1611–1629

Bansal RC, Goyal M (2005) Activated carbon adsorption. CRC Press, Boca Raton

Bansal M, Garg U, Singh D, Garg VK (2009) Removal of Cr(VI) from aqueous solutions using pre-consumer processing agricultural waste: a case study of rice husk. J Hazard Mater 162:312–320

Barakat MA, Schmidt E (2010) Polymer-enhanced ultrafiltration process for heavy metals removal from industrial wastewater. Desalination 256:90–93

Barreira LD, Lito PF, Antunes BM, Otero M, Lin Z, Rocha J, Pereira E, Duarte AC, Silva CM (2009) Effect of pH on cadmium (II) removal from aqueous solution using titanosilicate ETS-4. Chem Eng J 155:728–735

Basci N, Kocadagistan E, Kocadagistan B (2004) Biosorption of copper (II) from aqueous solutions by wheat shell. Desalination 164:135–140

Basso MC, Cerrella EG, Cukierman AI (2002) Empleo de algas marinas para la biosorción de metales pesados de aguas contaminadas. Avances en Energías Renovables y Medio Ambiente 6:69–74

Bayat B (2002a) Combined removal of Zinc (II) and Cadmium (II) from aqueous solutions by adsorption onto high calcium Turkish fly ash. Water Air Soil Pollut 136:6992

Bayat B (2002b) Comparative study of adsorption properties of Turkish fly ashes: II. The case of chromium (VI) and cadmium (II). J Hazard Mater 95:275–290

Bayat B (2002c) Comparative study of adsorption properties of Turkish fly ashes: I. The case of nickel(II), copper(II) and zinc(II). J Hazard Mater 95:251–273

Beolchini F, Pagnanelli F, Toro L, Vegliò F (2006) Ionic strength effect on copper biosorption by Sphaerotilus natans: equilibrium study and dynamic modelling in membrane reactor. Water Res 40:144–152

Bessbousse H, Rhlalou H, Verchére JF, Lebrun L (2008) Removal of heavy metal ions from aqueous solutions by filtration with a novel complexing membrane containing poly(ethyleneimine) in a poly(vinyl alcohol) matrix. J Membr Sci 307:249–259

Bhattacharya AK, Mandal SN, Das SK (2006) Adsorption of Zn(II) from aqueous solution by using different adsorbents. Chem Eng J 123:43–51

Bhattacharya AK, Naiya TK, Mandal SN, Das SK (2008) Adsorption, kinetics and equilibrium studies on removal of Cr(VI) from aqueous solutions using different low-cost adsorbents. Chem Eng J 137:529–541

Bhattacharyya D, Jumawan AB, Grieves RB (1979) Separation of toxic heavy metals by sulphide precipitation. Sep Sci Technol 14:441–452

Blocher C, Dorda J, Mavrov V, Chmiel H, Lazaridis NK, Matis KA (2003) Hybrid flotation – membrane filtration process for the removal of heavy metalions from wastewater. Water Res 37:4018–4026

Bohart G, Adams EQ (1920) Some aspects of the behaviour of charcoal with respect to chlorine. J Am Chem Soc 42:523–544

Bouranene S, Fievet P, Szymczyk A, Samar ME, Alain Vidonne A (2008) Influence of operating conditions on the rejection of cobalt and lead ions in aqueous solutions by a nanofiltration polyamide membrane. J Membr Sci 325:150–157

Box GEP, Hunter JS (1957) Multi factor experimental designs for exploring response surfaces. Ann Math Stat 28:195–241

Brinza L, Dring MJ, Gavrilescu M (2007) Marine micro- and macro-algal species as biosorbents for heavy metals. Environ Eng Manage J 6:237–251

Brunauer S, Emmett PH, Teller E (1938) Adsorption of gases in multimolecular layers. J Am Chem Soc 60:309–319

Bulut Y, Baysal Z (2006) Removal of Pb(II) from wastewater using wheat bran. J Environ Manage 78:107–113

Celaya RJ, Noriega JA, Yeomans JH, Ortega LJ, Ruiz-Manríquez A (2000) Biosorption of Zn(II) by Thiobacillus ferrooxidans. Bioprocess Eng 22:539–542

Cerino Córdova FJ, García León AM, Garcia Reyes RB, Garza González MT, Soto Regalado E, Sánchez González MN, Quezada Lopez I (2011) Response surface methodology for lead biosorption on Aspergillus terreus. Int J Environ Sci Technol 8(4):695–704

Cetin C, Pehlivan E (2007) The use of fly ash as a low cost, environmentally friendly alternative to activated carbon for the removal of heavy metals from aqueous solutions. Colloids Surf A Physicochem Eng Aspects 298:83–87

Chang JS, Law R, Chang CC (1997) Biosorption of lead, copper and cadmium by biomass of Pseudomonas aeruginosa PU21. Water Res 31:1651–1658

Chatterjee SK, Bhattacharjee I, Chandra G (2010) Biosorption of heavy metals from industrial waste water by Geobacillus thermodenitrificans. J Hazard Mater 175:117–125

Chen XC, Wang YP, Lin Q, Shi JY, Wu WX, Chen YX (2005) Biosorption of copper(II) and zinc(II) from aqueous solution by Pseudomonas putida CZ1. Colloids Surf B Biointerfaces 46:101–107

Chen QY, Luo Z, Hills C, Xue G, Tyrer M (2009) Precipitation of heavy metals from wastewater using simulated flue gas: sequent additions of fly ash, lime and carbon dioxide. Water Res 43:2605–2614

Cheng H (2006) Cu(II) removal from lithium bromide refrigerant by chemical precipitation and electrocoagulation. Sep Purif Technol 52:191–195

Cheung CW, Porter JF, McKay G (2001) Sorption kinetic analysis for the removal of cadmium ions from effluents using bone char. Water Res 35(3):605–612

Chien SH, Clayton WR (1980) Application of Elovich equation to the kinetics of phosphate release and sorption on soils. Soil Sci Soc Am J 44:265–268

Chipasa KB (2003) Accumulation and fate of selected heavy metals in a biological wastewater treatment system. Waste Manag 23:135–143

Choi SB, Yun YS (2004) Lead biosorption by waste biomass of Corynebacterium glutamicum generated from lysine fermentation process. Biotechnol Lett 26:331–336

Chojnacka K (2006) Biosorption of Cr(III) ions by wheat straw and grass: a systematic characterization of new biosorbents. Pol J Environ Stud 15:845–852

Chong KH, Volesky B (1995) Description of two-metal biosorption equilibria by Langmuir-type models. Biotechnol Bioeng 47:451–460

Cifuentes L, García I, Arriagada P, Casas JM (2009) The use of electrodialysis for metal separation and water recovery from $CuSO_4$–H_2SO_4–Fe solutions. Sep Purif Technol 68:105–108

Clark RM (1987) Evaluating the cost and performance of field-scale granular activated carbon systems. Environ Sci Technol 21:573–580

Coelho TC, Laus R, Mangrich AS, Fa'vere VT de, Laranjeira MCM (2007) Effect of heparin coating on epichlorohydrin cross-linked chitosan microspheres on the adsorption of copper (II) ions. React Funct Polym 67:468–475

Cossich ES, Tavares CRG, Ravagnani TMK (2002) Biosorption of chromium(III) by Sargassum sp. Biomass. Electron J Biotechnol 5:44–52

Dąbrowski A, Hubicki Z, Podkościelny P, Robens E (2004) Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. Chemosphere 56:91–106

Dang VBH, Doan HD, Dang-Vu T, Lohi A (2009) Equilibrium and kinetics of biosorption of cadmium (II) and copper (II) ions by wheat straw. Bioresour Technol 100:211–219

Davis TA, Volesky B, Vieira RHSF (2000) Sargassum seaweed as biosorbent for heavy metals. Water Res 34:4270–7278

De Vargas I, Macaskie LE, Guibal E (2004) Biosorption of palladium and platinum by sulfate-reducing bacteria. J Chem Technol Biotechnol 79:49–56

Dean JG, Bosqui FL, Lanouette KH (1972) Removing heavy metals from wastewaters. Environ Sci Technol 6(6):518–522

Dhir B, Kumar R (2010) Adsorption of heavy metals by Salvinia biomass and agricultural residues. Int J Environ Res 4:427–432

Dialynas E, Diamadopoulos E (2009) Integration of a membrane bioreactor coupled with reverse osmosis for advanced treatment of municipal wastewater. Desalination 238:302–311

Diamadopoulos E, Loannidis S, Sakellaropoulos GP (1993) As(V) removal from aqueous solutions by fly ash. Water Res 27:1773–1777

Dinu MV, Dragan ES (2010) Evaluation of Cu2+, Co2+, and Ni2+ ions removal from aqueous solution using a novel chitosan/clinoptilolite composites: kinetics and isotherms. Chem Eng J 160:157–163

Djedidi Z, Bouda M, Souissi MA, Cheikh RB, Mercier G, Tyagi RD, Blais J (2009) Metals removal from soil, fly ash and sewage sludge leachates by precipitation and dewatering properties of the generated sludge. J Hazard Mater 172:1372–1382

Djeribi R, Hamdaoui O (2008) Sorption of copper(II) from aqueous solutions by cedar sawdust and crushed brick. Desalination 225:95–112

Dönmez GC, Aksu Z, Öztürk A, Kutsal T (1999) A comparative study on heavy metal biosorption characteristics of some algae. Process Biochem 34:885–892

Dragan ES, Dinu MV, Timpu D (2010) Preparation and characterization of novel composites based on chitosan and clinoptilolite with enhanced adsorption properties for Cu2+. Bioresour Technol 101:812–817

Dubinin MM, Radushkevich LV (1947) Equation of the characteristic curve of activated charcoal. Proc Acad Sci Phys Chem USSR 55:331–333

Dupont L, Guillon E (2003) Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran. Environ Sci Technol 37:4235–4241

Dupont L, Bouanda J, Dumonceau J, Aplincourt M (2005) Biosorption of Cu(II) and Zn(II) onto a lignocellulosic substrate extracted from wheat bran. Environ Chem Lett 2:165–168

Elibol M (2002) Response surface methodological approach for inclusion of perfluorocarbon in actinorhodin fermentation medium. Process Biochem 38:667–773

Elouear Z, Bouzid Z, Boujelben J, Feki N, Jamoussi M, Montiel FA (2008) Heavy metal removal from aqueous solutions by activated phosphate rock. J Hazard Mater 156:412–420

Fan DH, Zhu XM, Xu MR, Yan JL (2006) Adsorption properties of chromium (VI) by chitosan coated montmorillonite. J Biol Sci 6:941–945

Farajzadeh MA, Monji AB (2004) Adsorption characteristics of wheat bran towards heavy metal cations. Sep Purif Technol 38:197–207

Farooq U, Khan MA, Atharc M, Kozinskia JA (2011) Effect of modification of environmentally friendly biosorbent wheat (Triticum aestivum) on the biosorptive removal of cadmium(II) ions from aqueous solution. Chem Eng J 171:400–410

Febrianto J, Kosasih AN, Sunarso J, Ju YS, Indraswati N, Ismadi S (2009) Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: a summary of recent studies. J Hazard Mater 162:616–645

Feng Q, Lin Q, Gong F, Sugita S, Shoya M (2004) Adsorption of lead and mercury by rice husk ash. J Colloid Interface Sci 278:1–8

Ferella F, Prisciandaro M, De Michelis I, Veglio' F (2007) Removal of heavy metals by surfactant-enhanced ultrafiltration from wastewaters. Desalination 207:125–133

Feroze N, Ramzan N, Khan A, Cheema II (2011) Kinetic and equilibrium studies for Zn (II) and Cu (II) metal ions removal using biomass (rice husk) Ash. J Chem Soc Pak 33:139–146

Freundlich H (1906) Adsorption in solution. Phys Chem Soc 40:1361–1368

Fu F, Wang Q (2011) Removal of heavy metal ions from wastewaters: a review. J Environ Manage 92:407–418

Fu JF, Zhao YQ, Xue XD, Li WC, Babatunde AO (2009) Multivariate-parameter optimization of acid blue-7 wastewater treatment by Ti/TiO$_2$ photoelectrocatalysis via Box-Behnken design. Desalination 243(1–3):42–51

Gan Q (2000) A case study of microwave processing of metal hydroxide sediment sludge from printed circuit board manufacturing wash water. Waste Manage 20:695–701

Garg UK, Kaur MP, Garg VK, Sud D (2008) Removal of nickel (II) from agueous solution by agricultural waste biomass using a response surface methodological approach. Bioresour Technol 99(5):1325–1331

Ghorbani M, Lashkenari MS, Eisazadeh H (2011) Application of polyaniline nanocomposite coated on rice husk ash for removal of Hg(II) from aqueous media. Synth Met 161:1430–1433

Ghorbani M, Eisazadeh H, Ghoreyshi AA (2012) Removal of zinc ions from aqueous solution using polyaniline nanocomposite coated on rice husk. Iran J Energy Environ 3(1):66–71

Ghosh P, Samanta AN, Ray S (2011) Reduction of COD and removal of Zn^{2+} from rayon industry wastewater by combined electro-Fenton treatment and chemical precipitation. Desalination 266:213–217

Gong R, Guan R, Zhao J, Liu X, Ni S (2008) Citric acid functionalizing wheat straw as sorbent for copper removal from aqueous solution. J Health Sci 54:174–178

González-Muńoz MK, Rodrguez MA, Luque S, Álvarez JR (2006) Recovery of heavy metals from metal industry wastewaters by chemical precipitation and nanoflitration. Desalination 200(1–3):742–744

Goswami D, Das AK (2000) Removal of arsenic from drinking water using modified fly-ash bed. Int J Water 1:61–70

Greenwood NN, Earnshaw A (1989) Chemistry of the elements. Pergamon Press, New York

Guo Y, Qi J, Yang S, Yu K, Wang Z, Xu H (2002) Adsorption of Cr(VI) on micro- and mesoporous rice husk-based active carbon. Mater Chem Phys 78:132–137

Gupta VK (1998) Equilibrium uptake, sorption dynamics, process development, and column operations for the removal of copper and nickel from aqueous solution and wastewater using activated slag, a low-cost adsorbent. Ind Eng Chem Res 37:192–202

Gupta VK, Ali I (2000) Utilisation of bagasse fly ash (a sugar industry waste) for the removal of copper and zinc from wastewater. Sep Purif Technol 18:131–140

Gupta VK, Ali I (2004) Removal of lead and chromium from wastewater using bagasse fly ash-a sugar industry waste. J Colloid Interface Sci 271:321–328

Gupta VK, Sharma S (2003) Removal of zinc from aqueous solutions using bagasse fly ash – a low cost adsorbent. Ind Eng Chem Res 42:6619–6624

Gupta VK, Ali I, Jain CK, Sharma M, Saini VK (2003) Removal of cadmium and nickel from wastewater using bagasse fly ash- a sugar industry waste. Water Res 37:4038–4044

Hall KR, Eagleton LC, Acrivos A, Vermeulen T (1966) Pore and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. Ind Eng Chem Fund 5(2):212–223

Halsey G (1948) Physical adsorption on non-uniform surfaces. J Chem Phys 16:931–937

Hamdaoui O (2006) Dynamic sorption of methylene blue by cedar sawdust and crushed brick in fixed bed columns. J Hazard Mater 138:293–303

Harkins WD, Jura EJ (1944) The decrease of free surface energy as a basis for the development of equations for adsorption isotherms; and the existence of two condensed phases in films on solids. J Chem Phys 12:112–113

Hashim MA, Chu KH (2004) Biosorption of cadmium by brown, green, and red seaweeds. Chem Eng J 97:249–255

Häyrynen P, Landaburu-Aguirre J, Eva Pongrácz E, Keisk RL (2012) Study of permeate flux in micellar-enhanced ultrafiltration on a semi-pilot scale: simultaneous removal of heavy metals from phosphorous rich real wastewaters. Sep Purif Technol 93:59–66

Hindmarsh JT, McCurdy RF (1986) Clinical and environmental aspects of arsenic toxicity. Crit Rev Clin Lab Sci 23:315–347

Ho Y (2006) Isotherms for the sorption of lead onto peat: comparison of linear and non-linear methods. Pol J Environ Stud 15:81–86

Ho YS, McKay G (1999) Pseudo-second order model for sorption processes. Process Biochem 34:451–465

Ho Y, Ofomaja AE (2006) Biosorption thermodynamics of cadmium on coconut copra meal as biosorbent. Biochem Eng J 30:117–123

Ho GE, Mathew K, Newman PWG (1989) Leachate quality from gypsum neutralized red mud applied to sandy soils. Water Air Soil Pollut 47:1–18

Holan ZR, Volesky B (1994) Biosorption of lead and nickel by biomass of marine algae. Biotechnol Bioeng 43:1001–1009

Holan ZR, Volesky B, Prasetyo I (1993) Biosorption of cadmium by biomass of marine algae. Biotechnol Bioeng 41:819–825

Hossain MA, Kumita M, Michigami Y, More S (2005) Optimization of parameters for Cr(VI) adsorption on used black tea leaves. Adsorption 11:561–568

Hsu TC, Yu CC, Yeh CM (2008) Adsorption of Cu^{2+} from water using raw and modified coal fly ashes. Fuel 87:1355–1359

Huang GL, Zhang HY, Jeffrey XS, Tim AGL (2009) Adsorption of chromium(VI) from aqueous solutions using cross-linked magnetic chitosan beads. Ind Eng Chem Res 48:2646–2651

Hui KK, Chao CY, Kot SC (2005) Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash. J Hazard Mater 127:89–101

Hussein H, Ibrahim SF, Kandeel K, Moawad H (2004) Biosorption of heavy metals from waste water using Pseudomonas sp. Electron J Biotechnol 17:38–46

Incharoensakdi A, Kitjaharn P (2002) Zinc biosorption from aqueous solution by a halotolerant cyanobacterium Aphanothece halophytica. Curr Microbiol 45:261–264

Inglezakis VJ, Grigoropoulou H (2004) Effects of operating conditions on the removal of heavy metals by zeolite in fixed bed reactors. J Hazard Mater B112:37–43

Iyer RS, Scott JA (2001) Power station fly ash-a review of value-added utilization outside of the construction industry. Resour Conserv Recy 31:217–228

Jalali R, Ghafourian H, Asef Y, Davarpanah SJ, Sepehr S (2002) Removal and recovery of lead using nonliving biomass of marine algae. J Hazard Mater 92:253–262

Jaroniec M, Derylo A (1981) Application of Dubinin-Radushkevich-tyoe equation for describing bisolute adsorption from dilute aqueous solutions on activated carbon. J Colloid Interface 84(1):191–195

Johan NA, Kutty SRM, Isa MH, Muhamad NS, Hashim H (2011) Adsorption of copper by using microwave incinerated rice husk ash (MIRHA). Int J Civil Environ Eng 3:211–215

Jones DJ (2012) Primary prevention and health outcomes: treatment of residential lead-based paint hazards and the prevalence of childhood lead poisoning. J Urban Econ 71:151–164

Juang R, Xu Y, Chen C (2003) Separation and removal of metal ions from dilute solutions using micellar-enhanced ultrafiltration. J Membr Sci 218:257–267

Kaewsarn P (2002) Biosorption of copper(II) from aqueous solutions by pre-treated biomass of marine algae Padina sp. Chemosphere 47:1081–1085

Kaewsarn P, Yu Q (2001) Cadmium(II) removal from aqueous solutions by pre-treated biomass of marine alga Padina sp. Environ Pollut 112:209–213

Kalyani S, Ajitha PJ, Srinivasa RP, Krishnaiah A (2005) Removal of copper and nickel from aqueous solutions using chitosan coated on perlite as biosorbent. Sep Sci Technol 40:1483–1495

Kapoor A, Viraraghavan T (1992) Adsorption of mercury from wastewater by fly ash. Adsorp Sci Technol 9:130–147

Karthikeyan KG, Elliott HA, Cannon FS (1996) Enhanced metal removal from wastewater by coagulant addition. In: Proceedings of 50th Purdue Industrial Waste Conference. 50: 259–267.

Keng PS (2008) Scale-up production of palm-based wax esters using lipozyme rm im and characterisation of the esters. Ph.D. thesis, Universiti Putra Malaysia

Kim YH, Yeon Park J, Yoo YJ, Kwak JW (1999) Removal of lead using xanthated marine brown alga, Undaria pinnatifida. Process Biochem 34:647–652

Klimmek S, Stan HJ, Wilke A, Bunke G, Buchholz R (2001) Comparative analysis of the biosorption of cadmium, lead, nickel, and zinc by algae. Environ Sci Technol 35:4283–4288

Kousalya GN, Muniyappan RG, Sairam SC, Meenakshi S (2010) Synthesis of nano-hydroxyapatite chitin/chitosan hybrid biocomposites for the removal of Fe(III). Carbohydr Polym 82:549–599

Krishnani KK, Meng X, Christodoulatos C, Boddu VM (2008) Biosorption mechanism of nine different heavy metals onto biomatrix from rice husk. J Hazard Mater 153:1222–1234

Ku Y, Jung IL (2001) Photocatalytic reduction of Cr(VI) in aqueous solutions by UV irradiation with the presence of titanium dioxide. Water Res 35:135–142

Kumar U, Bandyopadhyay M (2006) Sorption of cadmium from aqueous solution using pretreated rice husk. Bioresour Technol 97:104–109

Kumar M, Bijay PT, Vinod KS (2009) Crosslinked chitosan/polyvinyl alcohol blend beads for removal and recovery of Cd(II) from wastewater. J Hazard Mater 172:1041–1048

Kurniawan TA, Chan YSG, Lo W, Babel S (2006) Physico–chemical treatment techniques for wastewater laden with heavy metals. Chem Eng J 118:83–98

Lacour S, Bollinger J, Serpaud B, Chantron P, Arcos R (2001) Removal of heavy metals in industrial wastewaters by ion-exchanger grafted textiles. Anal Chim Acta 428:121–132

Lagergren S (1898) Zur theorie der sogenannten adsorption gelöster stoffe, Kungliga Svenska Vetenskapsakademiens. Handlingar 24:1–39

Lambert J, Rakib M, Durand G, Avila-Rodríguez M (2006) Treatment of solutions containing trivalent chromium by electrodialysis. Desalination 191:100–110

Landaburu-Aguirre J, García V, Pongrácz E, Keiski R (2006) Applicability of membrane technologies for the removal of heavy metals. Desalination 200:272–273

Langmuir I (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc 40:1361–1368

Lau PS, Lee HY, Tsang CCK, Tam NFY, Wong YS (1999) Effect of metal interference, pH and temperature on Cu and Ni biosorption by Chlorella vulgaris and Chlorella miniata. Environ Technol 20:953–961

Lee HS, Volesky B (1999) Interference of aluminum in copper biosorption by an algal biosorbent. Water Qual Res J Can 34:519–533

Lee CK, Low KS, Liew SC, Choo CS (1999) Removal of arsenic(V) from aqueous solution by quaternized rice husk. Environ Technol 20:971–978

Lee IH, Kuan Y, Chern J (2006a) Factorial experimental design for recovering heavy metals from sludge with ion-exchange resin. J Hazard Mater B138:549–559

Lee J, Kwon T, Moon I (2006b) Performance of polyamide reverse osmosis membranes for steel wastewater reuse. Desalination 189:309–322

Lenntech. Arsenic – As. Website http://www.lenntech.com/periodic/elements/as.htm#ixzz1zEkpE6Pj. Accessed 30 June 2012

Lenntech. Lead – Pb. Website http://www.lenntech.com/periodic/elements/pb.htm#ixzz1zNv6HhkP. Accessed 6 July 2012

Lenntech. Nickel – Ni. Website http://www.lenntech.com/periodic/elements/ni.htm#ixzz1zIOSNjZx. Accessed 6 July 2012

Leusch A, Holan Z, Volesky B (1995) Biosorption of heavy metals (Cd, Cu, Ni, Pb, Zn) by chemically-reinforced biomass of marine algae. J Chem Technol Biotechnol 62:279–288

Lewis AE (2010) Review of metal sulphide precipitation. Hydrometallurgy 104:222–234

Lewis A, Van Hille R (2006) An exploration into the sulphide precipitation method and its effect on metal sulphide removal. Hydrometallurgy 81:197–204

Lin CJ, Chang JE (2001) Effect of fly ash characteristics on the removal of Cu(II) from aqueous solution. Chemosphere 44:1185–1192

Lin CC, Lai YT (2006) Adsorption and recovery of lead(II) from aqueous solutions by immobilized Pseudomonas Aeruginosa PU21 beads. J Hazard Mater 137:99–105

Lin X, Burns RC, Lawrance GA (2005) Heavy metals in wastewater: the effect of electrolyte composition on the precipitation of cadmium(II) using lime and magnesia. Water Air Soil Pollut 165:131–152

Lipczynska-Kochany E, Kochany J (2009) Effect of humate on biological treatment of wastewater containing heavy metals. Chemosphere 77:279–284

Liu HL, Chen BY, Lan YW, Cheng YC (2004) Biosorption of Zn(II) and Cu(II) by the indigenous Thiobacillus thiooxidans. Chem Eng J 97:195–201

Llorens J, Pujolà M, Sabaté J (2004) Separation of cadmium from aqueous streams by polymer enhanced ultrafiltration: a two-phase model for complexation binding. J Membr Sci 239:173–181

Loukidou MX, Karapantsios TD, Zouboulis AI, Matis KA (2004) Diffusion kinetic study of cadmium(II) biosorption by Aeromonas caviae. J Chem Technol Biotechnol 79:711–719

Lu WB, Shi JJ, Wang CH, Chang JS (2006) Biosorption of lead, copper and cadmium by an indigenous isolate *Enterobacter* sp. J1 possessing high heavy-metal resistance. J Hazard Mater 134:80–86

Lu Z, Maroto-Valer MM, Schobert HH (2008) Role of active sites in the steam activation of high unburned carbon fly ashes. Fuel 87:2598–2605

Lucaci D, Visa M, Duta A (2011) Copper removal on wood-fly ash substrates-thermodynamic study. Revue Roumaine de Chimie 56(10–11):1067–1074

Luo X, Deng Z, Lin X, Zhang C (2011) Fixed-bed column study for Cu^{2+} removal from solution using expanding rice husk. J Hazard Mater 187:182–189

Madden EF, Sexton MJ, Smith DR, Fowler BA (2002) Lead. In: Sarkar B (ed) Heavy metals in the environment. Marcel Dekker, New York

Madigan MT, Martinko JM, Parker J (2000) Brock biology of microorganisms, 9th edn. Pearson Prentice Hall, Upper Saddle River

Mameri N, Boudries N, Addour L, Belhocine D, Lounici H, Grib H, Pauss A (1999) Batch zinc biosorption by a bacterial nonliving Streptomyces rimosus biomass. Water Res 33:1347–1354

Marchioretto MM, Bruning H, Rulkens W (2005) Heavy metals precipitation in sewage sludge. Sep Sci Technol 40(16):3393–3405

Marshall WE, Champagne ET, Evans WJ (1993) Use of rice milling byproducts (hulls and bran) to remove metal ions from aqueous solution. J Environ Sci Health A28:1977–1992

Masoudzadeh N, Zakeria F, Lotfabad T, Sharafi H, Masoomi F, Zahiri HS, Ahmadian G, Noghabi KA (2011) Biosorption of cadmium by *Brevundimonas* sp. ZF12 strain, a novel biosorbent isolated from hot-spring waters in high background radiation areas. J Hazard Mater 197:190–198

Matheickal JT, Yu Q (1999) Biosorption of lead(II) and copper(II) from aqueous solutions by pre-treated biomass of Australian marine algae. Bioresour Technol 69:223–229

Matheickal JT, Yu Q, Woodburn GM (1999) Biosorption of cadmium(II) from aqueous solutions by pre-treated biomass of marine alga Durvillaea potatorum. Water Res 33:335–342

Matlock MM, Howerton BS, Atwood DA (2002) Chemical precipitation of heavy metals from acid mine drainage. Water Res 36:4757–4764

McLaughlin MJ, Parker DR, Clarke JM (1999) Metals and micronutrients-food safety issues. Field Crop Res 60:143–163

Meunier N, Drogui P, Montané C, Hausler R, Mercier G, Blais J (2006) Comparison between electrocoagulation and chemical precipitation for metals removal from acidic soil leachate. J Hazard Mater B137:581–590

Mimoune S, Amrani F (2007) Experimental study of metal ions removal from aqueous solutions by complexation–ultrafiltration. J Membr Sci 298:92–98

Mimura H, Yokota K, Akiba K, Onodera Y (2001) Alkali hydrothermal synthesis of zeolites from coal fly ash and their uptake properties of cesium ion. J Nucl Sci Technol 38:766–772

Mirbagheri SA, Hosseini SN (2005) Pilot plant investigation on petrochemical wastewater treatment for the removal of copper and chromium with the objective of reuse. Desalination 171:85–93

Mishra SP, Tiwari D, Dubey RS (1997) The uptake behaviour of rice (Jaya) husk in the removal of Zn(II) ions-A radiotracer study. Appl Radiat Isot 48:877–882

Momčilović M, Purenović M, Bojić A, Zarubica A, Ranđelović M (2011) Removal of lead(II) ions from aqueous solutions by adsorption onto pine cone activated carbon. Desalination 276:53–59

Munaf E, Zein R (1997) The use of rice husk for removal of toxic metals from waste water. Environ Technol 18:359–362

Mungray AA, Kulkarni SV, Mungray AK (2012) Removal of heavy metals from wastewater using micellar enhanced ultrafiltration technique: a review. Cent Eur J Chem 10(1):27–46

Murthy ZVP, Chaudhari LB (2008) Application of nanofiltration for the rejection of nickel ions from aqueous solutions and estimation of membrane transport parameters. J Hazard Mater 160:70–77

Murthy ZVP, Chaudhari LB (2009) Separation of binary heavy metals from aqueous solutions by nanofiltration and characterisation of the membrane using Spiegler–Kedem model. Chem Eng J 150:181–187

Myers RH, Montgomery DC (2002) Response surface methodology: process and product optimization using experiments, 2nd edn. Wiley, New York

Nadzi BS, Nyahumwa C, Tesha J (2007) Chemical and thermal stability of rice husks against alkali treatment. BioResources 3(4):1267–1277

Naiya TK, Bhattacharya AK, Mandal S, Das SK (2009) The sorption of lead(II) ions on rice husk ash. J Hazard Mater 163:1254–1264

Nakajima A, Tsuruta T (2004) Competitive biosorption of thorium and uranium by Micrococcus luteus. J Radioanal Nucl Chem 260:13–18

Nakajima A, Yasuda M, Yokoyama H, Ohya-Nishiguchi H, Kamada H (2001) Copper biosorption by chemically treated Micrococcus luteus cells. World J Microbiol Biotechnol 17:343–347

Nakbanpote W, Thiravavetyan P, Kalambaheti C (2000) Preconcentration of gold by rice husk ash. Miner Eng 13:391–400

Nakbanpote W, Thiravavetyan P, Kalambaheti C (2002) Comparison of gold adsorption by Chlorella vulgaris, rice husk and activated carbon. Miner Eng 15:549–552

Nakbanpote W, Goodman BA, Thiravetyan P (2007) Copper adsorption on rice husk derived materials studied by EPR and FTIR. Colloids Surf A Physicochem Eng Aspects 304:7–13

Namasivayam C, Sangeetha D, Gunasekaran R (2007) Removal of anions, heavy metals, organics and dyes from water by adsorption onto a new activated carbon from Jatrophahusk, an agro-industrial solid waste. Trans IChemE B Process Saf Environ Prot 85(B2):181–184

Nameni M, Moghadam MRA, Aram M (2008) Adsorption of hexavalent chromium from aqueous solutions by wheat bran. Int J Environ Sci Technol 5:161–168

Nomanbhay SM, Palanisamy K (2005) Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. Electron J Biotechnol 8:43–53

Nordberg GF, Sandström B, Becking G, Goyer RA (2002) Essentiality and toxicity of metals. In: Sarkar B (ed) Heavy metals in the environment. Marcel Dekker, New York

Nourbakhsh M, Sag Y, Özer D, Aksu Z, Kutsal T, Çaglar A (1994) A comparative study of various biosorbents for removal of chromium(VI) ions from industrial waste waters. Process Biochem 29:1–5

Nouri L, Hamdaoui O (2007) Ultrasonication-assisted sorption of cadmium from aqueous phase by wheat bran. J Phys Chem A 111:8456–8463

Nouri L, Ghodbane I, Hamdaoui O, Chiha M (2007) Batch sorption dynamics and equilibrium for the removal of cadmium ions from aqueous phase using wheat bran. J Hazard Mater 149:115–125

Ortega LM, Lebrun R, Blais J, Hausler R (2008) Removal of metal ions from an acidic leachate solution by nanofiltration membranes. Desalination 227:204–216

Ozaki H, Sharmab K, Saktaywirf W (2002) Performance of an ultra-low-pressure reverse osmosis membrane (ULPROM) for separating heavy metal: effects of interference parameters. Desalination 144:287–294

Ozdemir G, Ozturk T, Ceyhan N, Isler R, Cosar T (2003) Heavy metal biosorption by biomass of Ochrobactrum anthropi producing exopolysaccharide in activated sludge. Bioresour Technol 90:71–74

Özer A, Pirincci HB (2006) The adsorption of Cd(II) ions on sulfuric acid-treated wheat bran. J Hazard Mater B137:849–855

Özer A, Özer D, Özer A (2004) The adsorption of copper (II) ions on to dehydrate wheat bran (DWB): determination of the equilibrium and thermodynamic parameters. Process Biochem 39:2183–2191

Öztürk A (2007) Removal of nickel from aqueous solution by the bacterium Bacillus thuringiensis. J Hazard Mater 147:518–523

Öztürk A, Artan T, Ayar A (2004) Biosorption of nickel(II) and copper(II) ions from aqueous solution by Streptomyces coelicolor A3(2). Colloids Surf B Biointerfaces 34:105–111

Padmavathy V (2008) Biosorption of nickel(II) ions by baker's yeast: kinetic, thermodynamic and desorption studies. Bioresour Technol 99:3100–3109

Pahlavanzadeh H, Keshtkar AR, Safdari J, Abadi Z (2010) Biosorption of nickel(II) from aqueous solution by brown algae: equilibrium, dynamic and thermodynamic studies. J Hazard Mater 175:304–310

Panday KK, Prasad G, Singh VN (1984) Removal of Cr(V1) from aqueous solutions by adsorption on fly ash-wollastonite. J Chem Technol Biotechnol 34A:367–374

Panday KK, Prasad G, Singh VN (1985) Copper(II) removal from aqueous solutions by fly ash. Water Res 19:869–873

Papandreou A, Stournaras CJ, Panias D (2007) Copper and cadmium adsorption on pellets made from fired coal fly ash. J Hazard Mater 148:538–547

Papandreou A, Stournaras CJ, Panias D, Paspaliaris I (2011) Adsorption of Pb(II), Zn(II) and Cr(III) on coal fly ash porous pellets. Miner Eng 24:1495–1501

Pardo R, Herguedas M, Barrado E, Vega M (2003) Biosorption of cadmium, copper, lead and zinc by inactive biomass of Pseudomonas Putida. Anal Bioanal Chem 376:26–32

Pattanayak J, Mondal K, Mathew S, Lalvani SB (2000) A parametric evaluation of the removal of As(V) and As(III) by carbon-based adsorbents. Carbon 38:589–596

Paul Chen J, Mou H, Wang LK, Matsuura T (2006) Membrane filtration. In: Wang LK, Hung Y-T, Shammas NK (eds) Handbook of environmental engineering, volume 4: advanced physicochemical treatment processes. The Humana Press, Totowa, pp 203–259

Pavasant P, Apiratikul R, Sungkhum V, Suthiparinyanont P, Wattanachira S, Marhaba TF (2006) Bioresour Technol 97:2321–2329

Pengthamkeerati P, Satapanajaru T, Singchan O (2008) Sorption of reactive dye from aqueous solution on biomass fly ash. J Hazard Mater 153:1149–1156

Petrus R, Warchoł JK (2005) Heavy metal removal by clinoptilolite. An equilibrium study in multicomponent systems. Water Res 39:819–830

Pillai MG, Regupathi I, Kalavathy MH, Murugesan T, RoseMiranda L (2009) Optimization and analysis of nickel adsorption on microwave irradiated rice husk using response surface methodology (RSM). J Chem Technol Biotechnol 84:291–301

Polowczyk I, Bastrzyk A, Sawinski W, Kozlecki T, Rudnicki P, Sadowski Z (2011) Sorption properties of fly ash from brown coal burning towards arsenic removal. Tech Trans Chem 8:135–142

Puranik PR, Paknikar KM (1997) Biosorption of lead and zinc from solutions using Streptoverticillium cinnamoneum waste biomass. J Biotechnol 55:113–124

Puranik PR, Chabukswar NS, Paknikar KM (1995) Cadmium biosorption by Streptomyces pimprina waste biomass. Appl Microbiol Biotechnol 43:1118–1121

Qu RJ, Sun CM, Fang M, Zhang Y, Ji CN, Xu Q (2009a) Removal of recovery of Hg(II) from aqueous solution using chitosan-coated cotton fibers. J Hazard Mater 167:717–727

Qu RJ, Sun CM, Wang MH, Ji CN, Xu Q, Zhang Y (2009b) Adsorption of Au(III) from aqueous solution using cotton fiber/chitosan composite adsorbents. Hydrometallurgy 100:65–71

Quinones I, Guiochon G (1998) Extension of a Jovanovic–Freundlich isotherm model to multicomponent adsorption on heterogeneous surfaces. J Chromatogr A 796:15–40

Quinones I, Stanley B, Guiochon G (1999) Estimation of the adsorption energy distributions for the Jovanovic–Freundlich isotherm model with Jovanovic local behaviour. J Chromatogr A 849:45–60

Rahman IA, Ismail J (1993) Preparation and characterization of a spherical gel from a low-cost material. J Mater Chem 3:931–934

Rahmanian B, Pakizeh M, Maskooki A (2012) Optimization of lead removal from aqueous solution by micellar-enhanced ultrafiltration process using Box-Behnken design. Korean J Chem Eng 29(6):804–811

Rao M, Parwate AV, Bhole AG (2002) Removal of Cr^{6+} and Ni^{2+} from aqueous solution using bagasse and fly ash. Waste Manage 22:821–830

Rao M, Parwate AV, Bhole AG, Kadu PA (2003) Performance of low-cost adsorbents for the removal of copper and lead. J Water Supply Res Technol AQUA 52:49–58

Redlich OJ, Peterson DL (1959) A useful adsorption isotherm. J Phys Chem 63:1024

Ricou P, Lecuyer I, Cloirec PL (1999) Removal of Cu^{2+}, Zn^{2+} and Pb^{2+} by adsorption onto fly ash and fly ash/lime mixing. Water Sci Technol 39:239–247

Rivas BL, Palencia M (2011) Removal-concentration of pollutant metal-ions by water-soluble polymers in conjunction with double emulsion systems: a new hybrid method of membrane-based separation. Sep Purif Technol 81:435–443

Romera E, Gonzalez F, Ballester A, Blazquez ML, Munoz JA (2006) Biosorption with algae: a statistical review. Crit Rev Biotechnol 26:223–235

Roy D, Greenlaw PN, Shane BS (1993) Adsorption of heavy metals by green algae and ground rice hulls. J Environ Sci Health A28:37–50

Rubin CH, Esteban E, Jones R, Noonan G, Gurvich E, Utz S, Spirin V, Revich B, Kruchkov G, Jackson RJ (1997) Childhood specific lead poisoning in Russia: a site-specific pediatric blood lead evaluation. Int J Occup Environ Health 3:241–248

Rudzinski W, Panczyk T (2000) Kinetics of isothermal adsorption on energetically heterogeneous solid surfaces: a new theoretical description based on the statistical rate theory of interfacial transport. J Phys Chem 104(39):9149–9162

Şahin Y, Öztürk A (2005) Biosorption of chromium(VI) ions from aqueous solution by the bacterium Bacillus thuringiensis. Process Biochem 40:1895–1901

Salam OEA, Reiad NA, Elshafei MM (2011) A study of the removal characteristics of heavy metals from wastewater by low-cost adsorbents. J Adv Res 2:297–303

Salehi E, Madaeni SS, Heidary F (2012) Dynamic adsorption of Ni(II) and Cd(II) ions from water using 8-hydroxyquinoline ligand immobilized PVDF membrane: isotherms, thermodynamics and kinetics. Sep Purif Technol 94:1–8

Salehizadeh H, Shojaosadati SA (2003) Removal of metal ions from aqueous solution by polysaccharide produced from Bacillus firmus. Water Res 37:4231–4235

Sankararamakrishnan N, Sharma AK, Sanghi R (2007) Novel chitosan derivative for the removal of cadmium in the presence of cyanide from electroplating wastewater. J Hazard Mater 148:353–359

Savvaidis I, Hughes MN, Poole RK (2003) Copper biosorption by Pseudomonas cepacia and other strains. World J Microbiol Biotechnol 19:117–121

Selatnia A, Bakhti MZ, Madani A, Kertous L, Mansouri Y (2004a) Biosorption of Cd2+ from aqueous solution by a NaOH-treated bacterial dead Streptomyces rimosus biomass. Hydrometallurgy 75:11–24

Selatnia A, Boukazoula A, Kechid N, Bakhti MZ, Chergui A (2004b) Biosorption of Fe3+ from aqueous solution by a bacterial dead Streptomyces rimosus biomass. Process Biochem 39:1643–1651

Selatnia A, Boukazoula A, Kechid N, Bakhti MZ, Chergui A, Kerchich Y (2004c) Biosorption of lead (II) from aqueous solution by a bacterial dead Streptomyces rimosus biomass. Biochem Eng J 19:127–135

Selatnia A, Madani A, Bakhti MZ, Kertous L, Mansouri Y, Yous R (2004d) Biosorption of Ni2+ from aqueous solution by a NaOH-treated bacterial dead Streptomyces rimosus biomass. Miner Eng 17:903–911

Sen AK, De AK (1987) Adsorption of mercury(II) by coal fly ash. Water Res 21:885–888

Shahalam AM, Al-Harthy A, Al-Zawhry A (2002) Feed water pretreatment in RO systems in the middle east. Desalination 150:235–245

Shaker MA (2007) Thermodynamic profile of some heavy metal ions adsorption onto biomaterial surfaces. Am J Appl Sci 4:605–612

Shameem H, Abburi K, Tushar KG, Dabir SV, Veera MB, Edgar DS (2003) Adsorption of chromium(VI) on chitosan-coated perlite. Sep Sci Technol 38:3775–3793

Shameem H, Abburi K, Tushar KG, Dabir SV, Veera MB, Edgar DS (2006) Adsorption of divalent cadmium (Cd(II)) from aqueous solutions onto chitosan-coated perlite beads. Ind Eng Chem Res 45:5066–5077

Shameem H, Tushar KG, Dabir SV, Veera MB (2008) Dispersion of chitosan on perlite for enhancement of copper(II) adsorption capacity. J Hazard Mater 152:826–837

Sharma N, Kaur K, Kaur S (2009) Kinetic and equilibrium studies on the removal of Cd^{2+} ions from water using polyacrylamide grafted rice (Oryza sativa) husk and (Tectona grandis) saw dust. J Hazard Mater 163:1338–1344

Silva EA, Cossich ES, Tavares CG, Cardozo Filho L, Guirardello R (2003) Biosorption of binary mixtures of Cr(III) and Cu(II) ions by Sargassum sp. Braz J Chem Eng 20:213–227

Singh KK, Hasan HS, Talat M, Singh VK, Gangwar SK (2009) Removal of Cr(VI) from aqueous solutions using wheat bran. Chem Eng J 151:113–121

Sips RJ (1948) On the structure of a catalyst surface. Chem Phys 16:490–495

Site AD (2001) Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants: a review. J Phys Chem Ref Data 30:187–439

Smith CJ, Livingston SD, Doolittle DJ (1997) An international literature survey of "IARC Group I carcinogens" reported in mainstream cigarette smoke. Food Chem Toxicol 35:1107–1130

Srinath T, Verma T, Ramteke PW, Garg SK (2002) Chromium (VI) biosorption and bioaccumulation by chromate resistant bacteria. Chemosphere 48:427–435

Srinivasa RP, Vijaya Y, Veera MB, Krishnaiah A (2009) Adsorptive removal of copper and nickel ions from water using chitosan coated PVC beads. Bioresour Technol 100:194–199

Srivastava NK, Majumder CB (2008) Novel biofiltration methods for the treatment of heavy metals from industrial wastewater. J Hazard Mater 151:1–8

Srivastava VC, Mall ID, Mishra IM (2008) Removal of cadmium(II) and zinc(II) metal ions from binary aqueous solution by rice husk ash. Colloids Surf A Physicochem Eng Aspects 312:172–184

Srivastava VC, Mall ID, Mishra IM (2009) Competitive adsorption of cadmium(II) and nickel(II) metal ions from aqueous solution onto rice husk ash. Chem Eng Process Process Intensification 48:370–379

Sun XQ, Peng B, Jing Y, Chen J, Li DQ (2009) Chitosan(chitin)/cellulose composite biosorbents prepared using ionic liquid for heavy metal ions adsorption. Separations 55:2062–2069

Surchi KMM (2011) Agricultural wastes as low cost adsorbents for Pb removal: kinetics, equilibrium and thermodynamics. Int J Chem 3:103–112

Tan G, Xiao D (2009) Adsorption of cadmium ion from aqueous solution by ground wheat stems. J Hazard Mater 164:1359–1363

Tan IAW, Ahmad AL, Hameed BH (2008) Adsorption of basic dye on high-surface-area activated carbon prepared from coconut husk: equilibrium, kinetic and thermodynamic studies. J Hazard Mater 154:337–346

Tangaromsuk J, Pokethitiyook P, Kruatrachue M, Upatham ES (2002) Cadmium biosorption by Sphingomonas paucimobilis biomass. Bioresour Technol 85:103–105

Tarley CRT, Ferreira SLC, Arruda MAZ (2004) Use of modified rice husks as a natural solid adsorbent of trace metals: characterisation and development of an on-line preconcentration system for cadmium and lead determination by FAAS. Microchem J 77:163–175

Temkin MI (1941) Adsorption equilibrium and the kinetics of processes on nonhomogeneous surfaces and in the interaction between adsorbed molecules. Zh Fiz Chim 15:296–332

Thayyath SA, Sreenivasan R, Abdul Rauf T (2010) Adsorptive removal of thorium(IV) from aqueous solutions using poly(methacrylic acid)-grafted chitosan/bentonite composite matrix: process design and equilibrium studies. Colloids Surf A Physicochem Eng Aspects 368:13–22

Thomas HC (1944) Heterogeneous ion exchange in a flowing system. J Am Chem Soc 66:1664–1666

Tirtom VN, Dincer A, Becerik S, Aydemir T, Celik A (2012) Comparative adsorption of Ni(II) and Cd(II) ions on epichlorohydrin crosslinked chitosan-clay composite beads in aqueous solution. Chem Eng J 197:379–386

Tiwari DP, Singh DK, Saksena DN (1995) Hg(II) adsorption from solutions using rice-husk ash. J Environ Eng 121:479–481

Tobin JM, Cooper DG, Neufeld RJ (1984) Uptake of metal ions by Rhizopus arrhizus biomass. Appl Environ Microbiol 47:821–824

Toth J (1971) State equations of the solid gas interface layer. Acta Chem Acad Hung 69:311–317

Tran HV, Tran LD, Nguyen TN (2010) Preparation of chitosan/magnetite composite beads and their application for removal of Pb(II) and Ni(II) from aqueous solution. Mater Sci Eng 30:304–310

Tunali S, Çabuk A, Akar T (2006) Removal of lead and copper ions from aqueous solutions by bacterial strain isolated from soil. Chem Eng J 115:203–211

Uslu G, Tanyol M (2006) Equilibrium and thermodynamic parameters of single and binary mixture biosorption of lead (II) and copper (II) ions onto Pseudomonas putida: effect of temperature. J Hazard Mater 135:87–93

Vasconcelos HL, Fa'vere VT, Goncalves NS, Laranjeira MCM (2007) Chitosan modified with reactive blue 2 dye on adsorption equilibrium of Cu(II) and Ni(II) ions. React Funct Polym 67:1052–1106

Vasconcelos HL, Camargo TP, Goncalves NS, Laranjeira MCM, Fa'vere VT (2008) Chitosan crosslinked with a metal complexing agent: synthesis, characterization and copper(II) ions adsorption. React Funct Polym 68:572–579

Veeken AHM, Akoyo L, Hulshoff Pol LW, Weijma J (2003) Control of the sulfide (S^{2-}) concentration for optimal zinc removal by sulfide precipitation in a continuously stirred tank reactor. Water Res 37:3709–3717

Veera MB, Krishnaiah A, Jonathan LT, Edgar DS (2003) Removal of hexavalent chromium from wastewater using a new composite chitosan biosorbent. Environ Sci Technol 37:4449–4456

Veera MB, Krishnaiah A, Ann JR, Edgar DS (2008a) Removal of copper(II) and nickel (II) ions from aqueous solutions by a composite chitosan biosorbent. Sep Sci Technol 43:1365–1381

Veera MB, Krishnaiah A, Jonathan LT, Edgar DS, Richard H (2008b) Removal of arsenic (III) and arsenic (V) from aqueous medium using chitosan-coated biosorbent. Water Res 42:633–642

Vieira RS, Beppu MM (2006) Interaction of natural and crosslinked chitosan membranes with Hg(II) ions. Colloids Surf A 279:196–207

Vijaya Y, Srinivasa RP, Veera MB, Krishnaiah A (2008) Modified chitosan and calcium alginate biopolymer sorbents for removal of nickel (II) through adsorption. Carbohydr Polym 72:261–271

Visa M, Isac L, Duta A (2012) Fly ash adsorbents for multi-cation wastewater treatment. Appl Surf Sci 258:6345–6352

Vitali L, Laranjeira MCM, Goncalves NS, F'avere VT (2008) Spray-dried chitosan microspheres containing 8-hydroxyquinoline-5 sulphonic acid as a new adsorbent for Cd(II) and Zn(II) ions. Int J Biol Macromol 42:152–157

Volesky B, Holan ZS (1995) Biosorption of heavy metals. Biotechnol Prog 11:235–250

Von Burg R (1997) Nickel and some nickel compounds. J Appl Toxicol 17:425–431

Wan Ngah WS, Fatinathan S (2008) Adsorption of Cu(II) ions in aqueous solution using chitosan beads, chitosan–GLA beads and chitosan–alginate beads. Chem Eng J 143:62–72

Wan Ngah WS, Kamari A, Koay YJ (2004) Equilibrium kinetics studies of adsorption of copper (II) on chitosan and chitosan/PVA beads. Int J Bio Macromol 34:155–161

Wan MW, Kan CC, Lin CH, Buenda DR, Wu CH (2007) Adsorption of copper (II) by chitosan immobilized on sand. Chia-Nan Annu Bull 33:96–106

Wan MW, Kan CC, Buenda DR, Maria LPD (2010) Adsorption of copper(II) and lead(II) ions from aqueous solution on chitosan-coated sand. Carbohydr Polym 80:891–899

Wang S, Li H (2007) Kinetic modelling and mechanism of dye adsorption on unburned carbon. Dye Pigments 72:308–314

Wang LH, Lin CI (2008a) Adsorption of chromium (III) ion from aqueous solution using rice hull ash. J Chin Inst Chem Eng 39:367–373

Wang LH, Lin CI (2008b) Adsorption of lead(II) ion from aqueous solution using rice hull ash. Ind Eng Chem Res 47:4891–4897

Wang XS, Li ZZ, Sun C (2008) Removal of Cr(VI) from aqueous solutions by low cost biosorbents: marine macroalgae and agricultural by-products. J Hazard Mater 153:1176–1184

Wang XS, Li ZZ, Sun C (2009) A comparative study of removal of Cu(II) from aqueous solutions by locally low-cost materials: marine macroalgae and agricultural by-products. Desalination 235:146–159

Wang X, Xia L, Tan K, Zheng W (2011) Studies on adsorption of uranium(VI) from aqueous solution by wheat straw. Environ Prog Sust Energ 31(4):566–576. doi 10.1002/ep.10582

Warchoł J, Petrus R (2006) Modeling of heavy metal removal dynamics in clinoptilolite packed beds. Micropor Mesopor Mater 93:29–39

Weber WJ, Morris JC (1963) Kinetic of adsorption on carbon from solution. J Sanit Eng Div ASCE 89SA2:31–59

Wen Y, Tang Z, Chen Y, Gu Y (2011) Adsorption of Cr(VI) from aqueous solutions using chitosan-coated fly ash composite as biosorbent. Chem Eng J 175:110–116

Weng CH, Huang CP (1990) Removal of trace heavy metals by adsorption onto fly ash. In: Proceedings of the 1990 ASCE Environmental Engineering Specialty Conference. Division of Environmental Engineering, American Society of Civil Engineers (ASCE). Arlington, pp 923–924

Weng CH, Huang CP (1994) Treatment of metal industrial wastewater by fly ash and cement fixation. J Environ Eng 120:1470–1487

Weng CH, Huang CP (2004) Adsorption characteristics of Zn(II) from dilute aqueous solution by fly ash. Colloids Surf A Physicochem Eng Aspects 247:137–143

Wolborska A (1989) Adsorption on activated carbon of p-nitrophenol from aqueous solution. Water Res 23:85–91

Wong KK, Lee CK, Low KS, Haron MJ (2003a) Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions. Chemosphere 50:23–28

Wong KK, Lee CK, Low KS, Haron MJ (2003b) Removal of Cu and Pb from electroplating wastewater using tartaric acid modified rice husk. Process Biochem 39:437–445

Wrudzinski W, Wojciecbowski BW (1977) On the Jovanovic model of adsorption. Colloid Polym Sci 255:859–880

Xu X, Gao BY, Tan X, Yue QY, Zhong QQ, Li Q (2011) Characteristics of amine-crosslinked wheat straw and its adsorption mechanisms for phosphate and chromium (VI) removal from aqueous solution. Carbohydr Polym 84:1054–1060

Yadava KP, Tyagi BS, Panday KK, Singh VN (1987) Fly ash for the treatment of Cd(II) rich effluents. Environ Technol Lett 8:225–234

Yamanaka K, Ohtsubo K, Hasegawa A (1996) Exposure to dimethylarsenic acid, a main metabolite of inorganic arsenic, strongly promotes tumorigenesis initiated by 4-nitroquinolone 1 oxide in the lungs of mice. Carcinogenesis 17:767–770

Yan-Chu H (1994) Arsenic distribution in soils. In: Nriagu JO (ed) Arsenic in the environment, part 1: cycling and characterization. Wiley, New York, pp 17–49

Ye H, Zhu Q, Du D (2010) Adsorptive removal of Cd(II) from aqueous solution using natural and modified rice husk. Bioresour Technol 101:5175–5179

Ye H, Zhang L, Zhang B, Wu G, Du D (2012) Adsorptive removal of Cu(II) from aqueous solution using modified rice husk. Int J Eng Res Appl 2(2):855–863

Yoon YH, Nelson JH (1984) Application of gas adsorption kinetics. I. A. Theoretical model for respirator cartridge service time. Am Ind Hyg Assoc J 45:509–516

Yu Q, Kaewsarn P (2000) Adsorption of Ni^{2+} from aqueous solutions by pretreated biomass of marine macroalga Durvillaea potatorum. Sep Sci Technol 35:689–701

Yu Q, Matheickal JT, Yin P, Kaewsarn P (1999) Heavy metal uptake capacities of common marine macro algal biomass. Water Res 33:1534–1537

Zeldowitsch J (1934) Über den mechanismus der katalytischen oxydation von CO an MnO_2. Acta Physicochem URSS 1:364–449

Zhang GY, Qu RJ, Sun CM, Ji CN, Chen H, Wang CH (2008) Adsorption for metal ions of chitosan coated cotton fiber. J Appl Polymer Sci 110:2321–2327

Zhou M, Liu Y, Zeng G, Li X, Xu W, Fan T (2007) Kinetic and equilibrium studies of Cr(VI) biosorption by dead Bacillus licheniformis biomass. World J Microbiol Biotechnol 23:43–48
Ziagova M, Dimitriadis G, Aslanidou D, Papaioannou X, Litopoulou Tzannetaki E, Liakopoulou-Kyriakides M (2007) Comparative study of Cd(II) and Cr(VI) biosorption on Staphylococcus xylosus and Pseudomonas sp. in single and binary mixtures. Bioresour Technol 98:2859–2865
Zulkali MMD, Ahmad AL, Norulakmal NH, Sharifah NS (2006) Comparative studies of oryza sativa L. Husk and chitosan as lead adsorbent. J Chem Technol Biotechnol 81:1324–1327