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Heavy Metals Removal Using Adsorption and Nanofiltration Techniques

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The removal of some heavy metals Cu (II), Cd(II), Mn(II), Pb(II) As(III), and As(V) from water solution using absorption and nanofiltration membrane techniques is presented. The influence of temperature, sorbent mass, solution pH, flow rate and sorbent chemical modification in the adsorption process are discussed. Among the listed sorbents the best performers for higher initial heavy metal concentration are: montmorillonite, kaolin, tobermorite, magnetite, silica gel and alumina that removed more than 80% from a solution of initial concentration range 1–100 ppm for cadmium, chitosan coated magnetic nanoparticles modified with α-ketoglutaric acid removed >95% from a solution of initial concentration 200 ppm for copper, polymeric cation exchanger containing nano-Zr(HPO_3-S)$_2$ absorbs 98% of lead with initial concentration 80 ppm, acid modified carbon black has absorption efficiency of ∼80% with initial concentration 200 ppm of As(V); and polonite sorbent absorb 98.7% of manganese with initial concentration 0.01 ± 0.031 ppm. For the nanofiltration (NF) membrane, research showed removal efficiencies around 97% for cadmium (initial concentration C_0 = 500 ppm), 99.9% for copper (C_0 = 12000 ppm), 84% lead (C_0 = 0.64 ppm, 93% As (V) and 89% As (III) (total arsenic concentration = 600 ppm) and 98% for Mn (C_0 =310 ppm).

KEYWORDS Sorbents, binding sites, heavy metals, absorption, nanofiltration

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INTRODUCTION

Limited water resources and increased demands have triggered a worldwide campaign for innovative water management practices. The use of effective technologies, such as membranes, for wastewater treatment containing heavy metals will allow the implementation of water recycling systems in industrial facilities. As a result, wastewater discharge fees and freshwater supply payments will decrease. For removal of heavy metals from wastewater, a wide variety of treatment techniques are available such as ion exchange, reverse osmosis and nanofiltration, precipitation, coagulation/co-precipitation and adsorption. The selection of a particular treatment depends on a number of factors, for example, waste type, contaminant concentration, level of cleanup required and economics (1).

Use of these techniques can be practical and cost-effective only with concentrated wastewater but they will be ineffective when applied to low concentration wastewater that contain heavy ions less than 100 ppm (2). Furthermore, in the adsorption process the adsorbent can be considered as cheap or low cost if it is abundant in nature, require little processing or is a by-product of waste material (3). Many natural and/or synthetic adsorbents can effectively remove dissolved heavy metals; most of them show some disadvantages such as poor adsorption capacity, a low efficiency/cost ratio, and ineffectiveness at high metal concentration. The NF process can overcome the problem of high concentration; however, it has the disadvantages of cost and membrane fouling. Some researchers (e.g., flotation and microfiltration membrane (4) and flotation and nanofiltration/reverse osmosis membrane (5) combine different separation processes for heavy metal removal in order to minimize the limitations of using them alone. Nguyen et al. (6) combined the adsorption process (nanoscale sorbent) with the nanofiltration process to achieve very high treatment efficiency. This review the treatments of the heavy metals cadmium, arsenic, copper, manganese and lead using adsorption and membrane filtration is highlighted. The influence of performance factors and sorbent modification is also reported.

CADMIUM TREATMENT

Cadmium (Cd) like other heavy metals can be introduced into surface waters in amounts significant to human health by industrial effluents (7). The major sources of cadmium are industrial waters such as metal plating, cadmium-nickel batteries, phosphate fertilizer, mining, pigments, stabilizers and alloys (8). Cadmium is a non-essential and non-beneficial element for plants and animals. Ingestion of soluble cadmium compounds above the maximum permissible level can cause a number of health problems. Itai-itai disease, renal damage, emphysema, hypertension and testicular atrophy are

all harmful effects (9). According to Baird and Cann (10) the maximum contaminant level (MCL) of cadmium is 5 ppb in the United States (The U.S. Environmental Protection Agency (EPA)) and Canada, but this standard level was decreased to 3 ppb by World Health Organisation (WHO) in 1993(11).

Adsorption

Adsorption is a mass transfer process in which a substance is transferred from a liquid phase to the surface of a solid and becomes bound by physical and or chemical interactions (12). The most common and effective method for removal of heavy metals is activated carbon, but this is not attractive due to the high regeneration cost (13). Biosorption is the process that uses biomass, either living or dead microorganisms, to remove heavy ions from industrial wastewater. Many researchers reported that several kinds of microorganisms (fungi, bacteria and algae) and bio-sludge of activated sludge systems adsorb both organic and inorganic matter from wastewater (14–18). Dead bioadsorbents are more favorable as they are not affected by the heavy metals, cost less, can be regenerated and reused and are easier to operate and maintain (16).

The removal of heavy metals from aqueous solution using biomass is based on metal sorption. Basically, the process of biosorption requires a solid phase (the sorbent) and a liquid phase (the solvent, water) containing a dissolved metal ions) to be sorbed (sorbate). The metal ions are attracted and bonded to the sorbent due to the high affinity of the sorbent for the ions through a complex process that depends on various mechanisms involving ion exchange, chemisorptions, complexation, adsorption on the surface and pores, chelation and adsorption by physical forces which is a result of concentration gradient and diffusion through cell wall and membrane (19). Figure 1 illustrates these mechanisms.

For removal of cadmium, various adsorbents were used and some of these were summarised by Balkaya and Cesur (8) and Ngah and Hanafiah (3), together with their adsorption capacities.

Sorbents from plants. Ngah and Hanafiah (3) listed many low-cost adsorbents obtained from plants for removal of cadmium. The researchers discussed the modification or chemical treatment of these adsorbents. In general they found that chemically modified plant wastes show higher adsorption capacities than unmodified forms and this probably due to a higher number of active binding sites, better ion-exchange properties and formation of new functional groups. For example, modification of rice husk with sodium hydroxide raised the adsorption by almost double (Tarley et al., 2004 in (3)). Özer et al. (in (3)) found that wheat bran had a much higher surface area when treated with sulfuric acid, and he suggested that acid causes this change by increasing the conversion of macropores to micropores.

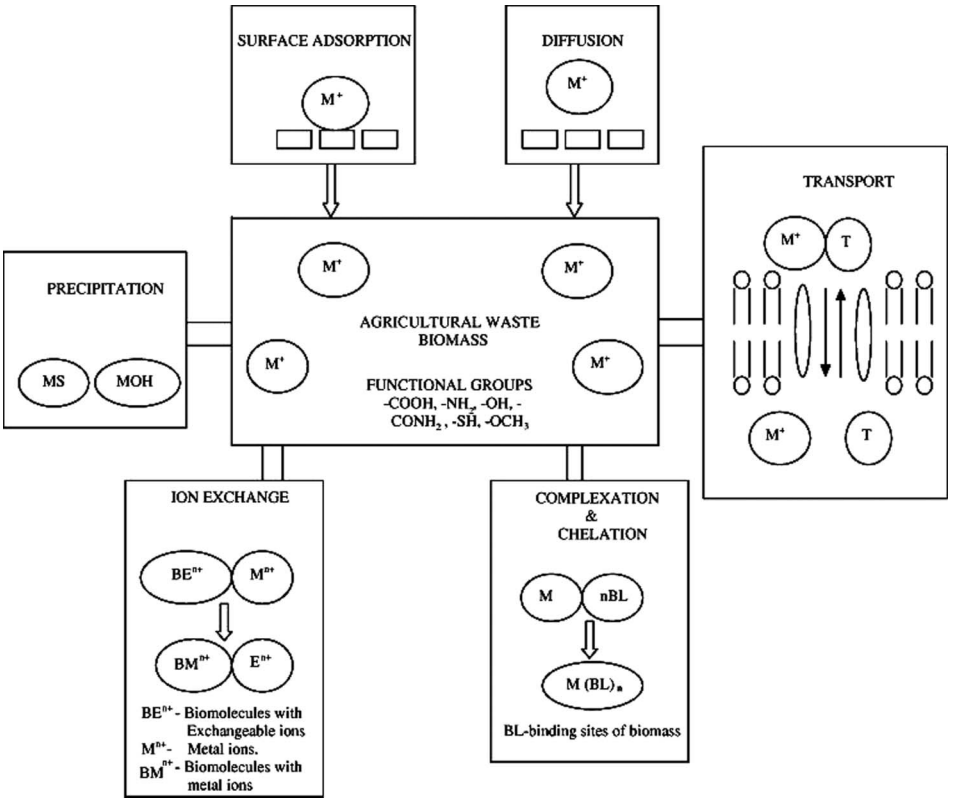

FIGURE 1 Mechanism of biosorption (19).

To produce a low-cost modified sorbent, both the chemical cost and the method of treatment have to be taken into consideration. Also it is recommended, because the modification might change the properties of the adsorbent, that characterisation studies of parameters such as surface area, pore size, porosity, pH zeta point charge (pH_{ZPC}), etc. should be undertaken. Also, as a part of understanding the mechanism of metal absorption on modified plant waste, spectroscopic analysis should be done for example Fourier Transform Infrared (FTIR), Energy Dispersive Spectroscopy (EDS), X-ray Absorption Near Edge Structure (EANES) Spectroscopy and Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy (3).

According to Ngah and Hanafiah (3) the highest capacity for Cd(II) was 313mg/g, which was obtained by Junior et al. (in ref. 3) using sugar-cane bagasse treated with triethylenediamine. This high capacity was caused by a greater number of nucleophilic sites (amide groups) as a result of chemical modification by the triethylenetetramine. The amide group is a result of a reaction between the carboxylic acid group (which was originally

hydroxyl group in sugarcane and converted to carboxylic group by using succinic anhydride) with an amine group. However, pre-treating of sugarcane bagasse with methanol instead of triethylenediamine did not show a good adsorption of cadmium. This was probably because methanol acts as an extracting agent for the phenolic group found in the sugarcane bagasse (20), which means less binding sites, although Ibrahim et al. (21) considered methanol as a washing agent only.

Another modified plant waste adsorbent used for removal of Cd(II) is Eucalyptus bark (Ghodbane et al. (1)). In this study the influence of temperature on the sorption isotherms of cadmium was also been studied. When the temperature was raised from 20 to 50°C, the sorption capacity increased. The $\Delta G°$ values were negative, which indicates that sorption of cadmium onto eucalyptus was spontaneous in nature.

Minamisawa et al. (22) elucidated the effect of the type of coffee and the roasting degree of coffee beans on adsorption of copper and cadmium. In the study, they also compared the adsorption capacity with that of other common adsorbents such as activated carbon. The adsorption experiments were carried by a batch method and with initial concentration of 5 ppm of metal ions. The results showed that the adsorption for both metal ions were above 90% for all used coffee beans. The adsorption capacity is similar to that of chitosan, zeolite and activated carbon and higher than those of cerite and chitin.

Jamali et al. (23) explored the adsorption behavior of hazelnut shell and its ash for cadmium ions from aqueous solution as a function of appropriate equilibrium time, amount of adsorbent, concentration of adsorbate, pH and sorbent particle size using a batch system. As a result, the removal efficiency increased with increasing solution pH but above pH about 6 the removal efficiency decreased. At pH 6, with a contact time of 3 hours and initial concentration of 30 ppm, the maximum adsorption was about 98.2% for hazelnut shell and 99.1% for hazelnut shell ash.

Mineral oxides sorbents. Aluminium oxide was used by Sen and Sarzali (24) as a sorbent. This is a useful sorbent due to its high surface area and mechanical strength and its acid-base properties. Aluminium oxide is also beneficial in terms of efficiency and economy. This study illustrated that the amount of adsorbed cadmium ion increased with initial metal concentration, contact time and with the solution pH but decreased with adsorbent dosages or masses.

Katsumata et al. (25) investigated the removal of Cd(II), Cr(VI), Cu(II) and Pb(II) (initial concentration 1 ppm) from wastewater with economical materials Montmorillonite, kaolin, tobermorite, magnetite, silica gel and alumina by the column method. In all adsorbents, the removal efficiency of Cd(II) tended to increase with increasing pH value. With these adsorbents

and with a cadmium (II) concentration range 1–100 ppm, high removal efficiency (>80%) was obtained. However, the removal percentage decreased gradually with increasing cadmium (II) concentration (>100 ppm).

Kalfa et al. (26) synthesised a new solid phase extractor, nano-scale diboron/titanium dioxide composite material for removal of cadmium from different samples. They used a column model and a variety of different analytical parameters. The recovery of Cd under the optimum conditions was found to be around 96% at a 95% confidence level (adsorption capacity = 49 mg/g). This nanocomposite material shows many advantages. One major advantage is the high surface area and fine grain size. In addition, it is not necessary to load complexing or chelting agent or microorganisms onto the sorbent, which minimises contamination by reagents. Furthermore, repeated use of sorbent (it was observed that the column could be used for up to 100 runs) without a decrease in the recovery of Cd(II) was possible. Also, in acidic medium, the sorbent has the capability of reducing the potential for metal hydroxide precipitation. However the main disadvantage of using this material is the duration time of the preconcentration step and also that higher adsorption efficiency is restricted to cadmium at low concentration (0.1 ppm).

Due to the many advantages of SiO_2 and TiO_2 (i.e., the high surface area of silica as well as the photocatalytic ability of TiO_2) as sorbent for removal of heavy metals, Ismail et al. (27) used mixed oxide TiO_2: SiO_2 as sorbent to get the benefit of both. Statistically designed experiments, employing the Box–Behnken method (Box and Behnken 1960; Cornell and Montgomery 1996), were applied to determine optimum conditions in terms of pH, shaking time, and metal ions concentrations.

The sorption results showed that pH is the most significant factor. The extent of sorption increases dramatically with increasing the pH. They explained this sorption behavior in terms of the surface charge as well as the species present in solution. At high pH, the surface charge of TiO_2-SiO_2 is more negative due to the presence of OH^- groups which leads to formation of hydroxyl complexes. Formation of such hydroxyl compounds at higher pH is responsible for the uptake of the metal ions from the solution. Whereas, the low degree of sorption at low pH can be related to the competition of cations (Ni^{2+}, Cd^{2+}) and protons (H^+) for the same sites, as well as the repulsion between ions with the same surface charge. The study also examined the effect of reuse of TiO_2-SiO_2 on metal ions sorption. The results showed that the TiO_2-SiO_2 sorbent still sorbed at 100% of Cd^{2+} after 10 runs, while the Ni^{2+} sorption decreased sharply after 6 cycles.

Modified oxides sorbent (bonded or coated). Aguado et al. (28) used amino functional mesoporous silica absorbent to remove cadmium ions. Functionalization of mesoporous silica with organic chains containing one,

two, three amino groups had been synthesised using two methods: grafting and co-condensation. The results of this study showed that materials prepared by co-condensation had negligible metal adsorption capacity, whereas, amine-grafted materials adsorb significant amounts of the metal ions used, Cd(II) being one of them. With an initial aqueous solution of 100 ppm, removal of Cd^{2+} ion varied from approximately 30% to around 75%, depending on the amino functional groups present on the sorbent.

Liu et al. (29) developed a novel low-cost magnetic sorbent material prepared by coating magnetic Fe_3O_4 nanoparticles with humic acid (HA) for the removal of toxic Hg(II), Pb(II), Cd(II) and Cu(II) from water. Fe_3O_4/HA was synthesised by a co-precipitation procedure with cheap and environmentally friendly iron salts and HA. The Fe_3O_4/HA was able to remove over 99% of Hg(II) and Pb(II) and over 95% of Cu(II) and Cd(II) in natural and tap water at optimized pH. Leaching back of the Fe_3O_4/HA sorbed heavy metals in water was found to be negligible. The presence of some coexisting ions (Ca^{2+} and PO_4^{3-}) has no effect on the sorption of heavy metals to Fe_3O_4/HA.

Other sorbents. Sarı and Tuzen (30) studied the biosorption potential of *A. rubescens* biomass in the removal of Pb(II) and Cd(II) ions from aqueous solution as a function of pH, biomass dosage, contact time, and temperature. The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were applied to describe equilibrium isotherms. The best fitted model was Langmuir model. At certain conditions of pH 5.0, contact time of 30 min and a temperature of 20°C, the biosorption capacity of *A. rubescens* biomass was found to be 38.4 mg/g for Pb(II) and 27.3 mg/g for Cd(II).

As pH was increased from 2 to 4, the biosorption efficiency was increased from 40% to 80% for Pb(II) biosorption and from 35% to 70% for Cd(II) ion. However, the maximum biosorption was found to be 98% for Pb(II) and 97% for Cd(II) ions at pH 5. Thermodynamic calculations showed that the nature of the biosorption of Pb(II) and Cd(II) ion onto *A. rubescens* biomass at 20–50°C was exothermic and spontaneous.

The adsorption of cadmium on phosphogypsum, which is a waste material from the manufacture of the phosphoric acid by a wet process, was studied by Balkaya and Cesur (8). They found that the maximum adsorption capacity of lime-preconditioned phosphogypsum was higher than most adsorbents listed in his table. The cadmium removal by lime, raw phosphogypsum and lime-preconditioned phosphogypsum was compared and the results showed that the lime-preconditioned phosphogypsum was a more suitable adsorbent for removal of Cd(II).

Maximum adsorption of cadmium ion was found in the pH range of 9.5 and 11.5, which means that pH is a critical parameter for cadmium uptake. The Langmuir and Freundlich models were used to describe the

adsorption process of cadmium, but the adsorption isotherms fit better using the Freundlich equations.

Zhang et al. (31) used polymeric hybrid sorbent (called ZrPS-001) that was fabricated by impregnating $Zr(HPO_3S)_2$ (ZrPS) nanoparticles within a porous polymeric cation exchanger D-001. In this study the effect of Ca^{2+} on Pb^{2+}, Zn^{2+} and Cd^{2+} uptake by ZrPS-001 was examined. The result showed that the removal efficiency of all the metals onto ZrPS-001 was slightly influenced by the calcium ion. Both continuous batch sorption and column sorption showed high removal of the metals used. The sorption order was $Pb^{2+} > Cd^{2+} > Zn^{2+}$.

Most studies found that adsorption is dependent on contact time, initial metal concentration, sorbent dose, initial pH and temperature. However the adsorption process also depends on the metal species and the properties of the sorbent. The sorbents used at low metal initial concentration ($\leq$100 ppm) showed the efficiency of modified sorbent is better than that of unmodified sorbent. The improved efficiency is dependent on the method of modification and the chemical used. Some of the adsorbents used for the removal of cadmium(II) ion are listed in Table 1.

Membrane Filtration

Nanofiltration (NF) is a process that lies between reverse osmosis (RO) and ultrafiltration (UF). The mechanism of separation involves steric (sieving)

TABLE 1 Adsorbents Used for Removal of Cadmium

Adsorbent	Initial concentration	Results	Reference
Sugarcane bagasse	NA*	189 mg/g	(3)
Sodium bicarbonate		189 mg/g	
Ethylenediamine		313 mg/g	
Triethylenetetramine methanol		7 mg/g	
Eucalyptus bark	100 ppm	15 mg/g at 20°C, 16 mg/g at 50°C	(1)
Coffee beans	5 ppm	>90%	(22)
Hazelnut shell ash.	30 ppm	99.1%	(23)
A. Rubescens biomass	10 ppm	97%	(30)
Lime-preconditioned phosphogypsum	50 ppm	132 mg/g (99%)	(8)
Aluminium oxide	30 ppm	127 mg/g	(24)
Montmorillonite, kaolin, tobermorite, magnetite, silica gel and alumina	1–100 ppm	>80%	(25)
Nano-scale diboron/titanium dioxide	0.1 ppm	Above 95%	(26)
TiO_2-SiO_2	5 ppm	≈100%	(27)
Amino functional mesoporous silica	100 ppm	<80%	(28)
Humic acid-coated Fe_3O_4 nanoparticles (Fe_3O_4/HA)	≈1.0 ppm	>91%	(29)
ZrPS-001	45 ppm	~87 %	(31)

*NA: not available.

and electrical (Donnan) effects. A Donnan potential is created between the charged anions in the NF membrane and co-ions in the effluent to reject the latter (32). Descriptions of solute transport in membranes were originally given by the irreversible thermodynamic model. In this model the membrane was considered as a black box; no membrane structural or electrical parameters were acquired, and limited information about the transport mechanisms inside the membrane could be obtained. The solution-diffusion model was later proposed. The model considers that each permeate dissolves in the membrane and is transported by diffusion due to its gradient in chemical potential through a non-porous membrane.

The solute flux is independent of permeation pressure while the solvent flux increases proportionally to it. Retention must therefore increase with pressure. This was confirmed for metals, some ions and saccharides. For NF membranes, there is some debate about the existence of discrete pores (33). In this case the solution–diffusion model is incomplete, and a convection term should be included that takes account of solute transport through membrane pores because of applied pressure gradient across the membrane (34). Details about the solute mass transfer theory is shown elsewhere (35, 36).

Various types of commercial NF membranes are available and their separation performance varies greatly. Most NF membranes are thin-film composite membranes of hydrophobic polymers with negatively charged groups incorporated (included) (36–38).

Reverse osmosis (RO) and nanofiltration (NF) were initially developed for the production of drinking water from saline and brackish water. Membrane processes such as RO, NF and UF are becoming the standard technologies used for water purification for both the public and in industry despite their higher cost when compared with other techniques. There are several advantages of using membranes in water and wastewater treatment. They are flexible, scalable, modular and relatively easy to operate and maintain. Use of these membranes will also enable industry to comply with the effluent standards limits obliged by environmental regulation (Paul and Sikdar, 1998 in (39)).

Kurniawan et al. (40) presented the types of membrane filtration employed for heavy metal removal. These membranes were ultrafiltration, nanofiltration and reverse osmosis. They reported that UF can remove more than 90% with a metal concentration of 10 to 112 ppm at pH ranging from 5 to 9.5 and at 2–5 bar. For high removal efficiency, the metal concentration is most important in the case of NF (2000 mg/l) than that of RO membrane (21–200 mg/l). These efficiencies do, however, depend on the characteristics of the membrane.

Abu Odais and Moussa (39) used both RO and NF for the treatment of wastewater containing copper and cadmium. The membrane unit used to carry out the experiments consists of a module containing two tubular

TABLE 2 Nanofiltration Membranes Used in Removal of Cadmium

Type of membrane	Initial concentration	Removal efficiency%	Reference
AFC30, AFC40 (thin-film composite membranes with negatively charged groups)	33 ppb	94% (AFC30) 91% (AFC40)	(37)
Polyamide	25–200 ppm 500 ppm($CuSO_4$+$CdSO_4$)	82–97% (average 90%) 97%	(39)

spiral-wound membranes arranged in series. The system contains a plunger pump, which provides high pressure. The results showed that the removal efficiency of Cd^{2+} by NF ranged from 82% to 97% and that for Cu^{2+} ranged from 84% to 90%. On the other hand, the average removal efficiency by RO for both Cu^{2+} and Cd^{2+} was 97% and 98.5%, respectively. The effectiveness of RO and NF membranes in treating wastewater solution containing multi-metals (copper and cadmium) was also determined. The results showed that the RO was capable of treating wastewater with an initial concentration of 500 ppm and reducing the metal ion concentration to about 3 ppm (99.4% removal), while the average removal efficiency of NF was less at 97%.

Linde and Jönsson (37) investigated the possibility of using nanofiltration membrane to treat a saturated high salt content landfill leachate. They used two types of tubular NF membranes, AFC30 and AFC40. Most of the heavy metals such as cadmium, zinc, lead and chromium were relatively highly rejected (>70%) compared with the monovalent cations (potassium and sodium) that were rejected poorly (<10%). The AFC40 membrane showed a higher flux but a lower retention than the AFC30 membrane. However, the difference in retention of the heavy metals was very small. Finally some of the NF membranes used to remove cadmium and their performance are listed in Table 2.

ARSENIC TREATMENT

Arsenic is a toxic semi-metallic element that can be fatal to humans. In the environment it exists in several forms. Both organic and inorganic forms of arsenic are found in natural waters. It is the inorganic arsenic species that are the dominant form found in most groundwater and surface water sources. Inorganic arsenic has variable oxidation states (−3, 0, +3 and +5) (41). The inorganic forms of arsenic are more toxic than the organic forms and the trivalent inorganic forms are more toxic then the pentavalent inorganic

forms, although some of the +5 form is converted by reduction to the +3 form in the human body.

The greater toxicity of As(III) is due to its ability to be retained in the body longer since it becomes bound to thiol groups in one of several enzymes. The subsequent inactivity of the enzymes decreases energy production in the cell and thus the cell is damaged (10). Environmental arsenic exists mainly as sulfides of the general formula As_2S_3 and other ores. On heating of these ores, arsenic sublimes and oxidises to form arsenic (III) oxide (42). The use of arsenic compounds includes as wood preservatives, as pesticides and as pigments. Arsenic can get into air, water, and the ground from wind-blown dust. It may also get into water from runoff (10).

Medical research indicates that exposure to arsenic in drinking water causes urinary, bladder, lung and skin cancers, muscular weakness, loss of appetite, gastrointestinal disorders, nerve tissue injuries and Blackfoot disease. Because of these health problems, the Environmental Protection Agency (EPA) recommended in 2001 that the arsenic standard level in drinking water be reduced from 50 ppb to 10 ppb. This recommendation became effective in February 2002 with a compliance date for January 2006 (43).

Adsorption

Sorbents from plants. Budinova et al. (44) used a low-cost activated carbon from bean pods waste for the removal of As(III) from aqueous solutions at different initial concentrations and pH values. The prepared biomass-derived carbon showed that the adsorption capacity of As (III) is 1 mg/g. The researcher described a unique combination of high basicity that bean-pods-derived carbon possesses, which is due to the large amount of oxygen-containing functional groups of basic nature and high mineral matter content. The presence of these functional groups in the sorbent enhances the adsorption process. In general, the role of the oxygen functional groups during the adsorption process is to contribute to the carbon basicity and/or to form complexes with As (III) ions. The removal of As (III) increases with the pH, and reaches a maximum around pH 7.7.

As the pH increases beyond 8, a decrease is observed in the uptake of As (III) particularly in strongly basic solutions (pH 12). This behavior (pH 8–12) is attributed to the changes in the carbon surface of the sorbent. This change occurs as the positive charged nature of the carbon surface gradually decreases as the pH increases. Moreover, the arsenic species in solution are also affected by pH. Below pH 7, the neutral form (H_3AsO_3) is predominant in the solution. As pH increases, the amount of negative arsenic species ($H_2AsO_3^-$ and $HAsO_3^{2-}$) rises.

Pandey et al. (45) found that a biomass derived from the plant Momordica Charantia was very efficient in arsenic (III) adsorption under different conditions. The parameters used were contact time (5–150 min), pH (2–11), concentration of adsorbent (1–50 g/l) and concentration of adsorbate (0.1–100 mg/l). They observed that the pH had a strong effect on biosorption capacity and the optimum pH for arsenic adsorption was 9. The sorption efficiency of As(III) removal was 88% (uptake capacity is 0.88 mg As(III)/g of biomass) at a concentration of 0.5 mg/l of As(III) solution. The Isotherm studies were performed for As(III) ion using Freundlich and Langmuir adsorption isotherms.

Cornejo et al. (46) investigated a method based on steel wool (as a source of zero-valent iron) lemon juice (as citric source) and solar radiation for the removal of arsenic. The method was evaluated using water from the Camarones River, Atacama Desert in northern Chile, in which the arsenic concentration ranges between 1 and 1.3 mg/l. The optimal conditions when using solar radiation to remove arsenic from natural water from the Camarones River are: 1.3 g/l of steel wool and one drop (ca. 0.04 ml) of lemon juice. Under these conditions, removal percentages are higher than 99.5% and the final arsenic concentration is below 0.01 ppm.

The results showed that the presence of the citrate in combination with solar exposure is very important and the absence of one effected the arsenic removal. For example in the absence of citrate only 74% of removal was obtained after 2 hours. This can be explained by the formation of the photo-sensitive Fe-CIT complex that promotes radical generation followed by the release of Fe (III) into the solution and consequent formation of iron (III) hydroxide that adsorbs the arsenic. Still, citrate by itself was found to have a negative effect on arsenic removal, probably because high citrate concentrations would inhibit iron hydroxide formation.

Murugesan et al. (47) examined tea fungus, a waste produced during black tea fermentation for its capacity to remove metal ions from groundwater samples. Autoclaved tea fungal mat and autoclaving followed by $FeCl_3$ pretreated tea fungal mat were investigated for removal of As(III), As(V) and Fe(II) from ground water samples collected from Kolkata, West Bengal, India. The results showed that the $FeCl_3$ treated tea fungal mat and autoclaved fungal mat were efficient in removing As(III), As(V) and Fe(II) from groundwater samples. $FeCl_3$-treated tea fungal mat performed better because iron has an affinity towards arsenic in forming arsenic-iron oxides. In batch mode studies, the adsorption was dependent on contact time, initial metal ion concentration and biosorbent dosage. $FeCl_3$ pretreated and autoclaved fungal mats removed 100% of As(III) and Fe(II) after 30 min contact time and 77% of As(V) after 90 min contact time. The optimum adsorbent dosage was 1.0 g/50 ml of water sample.

For the removal of arsenic from aqueous media at various conditions, Amin et al. (48) examined the use of rice husk adsorption technology without any pre-treatment. Adsorption column methods showed the complete removal of both As(III) and As(V) under the following conditions: initial As concentration, 0.1 mg/L; rice husk amount, 6 g; average particle size, 780 and 510 μm; treatment flow rate, 6.7 and 1.7 ml/min; and pH, 6.5 and 6.0, respectively. RH was evaluated for treatment of As-contaminated Bangladeshi groundwater (total arsenic in the samples were 270 and 595 ppb). The removal efficiencies with 100 mL of 1 M KOH were 96%.

A chemical modification of orange juice residue (OJR) with the substitution of phosphate groups on the alcoholic analogy of cellulose, which was further loaded with iron(III) was used to study the removal of As. Arsenic(III) adsorption was found to perform better at alkaline condition (pH = 7–11), while that of arsenic(V) was at acidic condition (pH = 2–6). Maximum adsorption capacity for As(V) and As(III) was 70.43 and 68.18 mg/g at their optimum pH values 3.1 and 10.0, respectively (49).

Mineral oxides sorbents. Guo et al. (50) used batch and column systems for arsenic species, As(V), As(III) and dimethylarsinic acid (DMA), adsorption from aqueous solution using natural hematite and siderite solids. On both materials, As(V) was preferentially adsorbed in the batches and first reached equilibrium, followed by DMA and As(III). The arsenic adsorption took place more slowly on natural hematite and natural siderite compared with ferrihydrite, which was studied by Raven et al. (51) in removal of As(V) and As(III). Guo et al. (2008) found that natural hematites oxidised As(III) to As(V), which was enhanced by the presence of Mn^{4+} and Fe^{3+} in the samples.

This, as the researcher said, gives an explanation of the decrease in the As(III) concentration of hematite batches before its adsorption. Hematite showed the highest efficiency for As retention in the batch experiments, whereas siderite showed a better performance in removing As in the packed column experiments. The result indicates that the combination of siderite and hematite would promote the column performance in removing arsenic from aqueous solution.

Pena et al. (52) examined the adsorption mechanism of As(V) and As(III) on nanocrystalline TiO_2 using a combination of macroscopic and microscopic techniques including X-ray absorption fine structure (EXAFS), Fourier transform infrared (FTIR) and electrophoretic mobility (EM) measurements. The results showed that greater than 98% of the As(V) was removed by TiO_2 in the pH range from 4 to 9.5 and when the pH was increased to 11.8 this adsorption decreased to about 10%. On the other hand, As (III) removal increased from 72 to 95% when the pH was increased from 4.5 to 9.5. The maximum uptake of As(III) occurred at about pH 9.5.

Gupta and Ghosh (53) used hydrous nanostructure iron(III)-titanium (IV) binary mixed oxide to remove As(III) and As(V) from aqueous solution. This removal was studied at pH 7.0 (±1) with variation of contact time, solute concentration and temperature. A comparison of rate constant values estimated from either of the kinetic equation analyses suggests that the rate of As(III) sorption by NHITO is faster than As(V) at all of the temperatures studied and the favorable temperature is 303 (±1.6)K.

The Langmuir capacity (q_m, mg/g) value of the material is 85.0 (±4.0) for As(III) and 14.0 (±0.5)for As(V). The higher sorption of As(V) compared with the As(III) is presumably due to chemisorptions with ion-exchange. The effect of phosphate and sulfate ions on arsenic sorption was significant on As(V) removal and insignificant on As(III) removal. In the case study, they found that a fixed bed NHITO column gave 3.0, 0.7 and 4.5 L of treated water (As content ≤0.01 mg/l) from separate As(III) and As(V) spiked (0.35 ±0.02 mg/l) natural water samples and from high arsenic (0.11 ± 0.01 mg/l) groundwater, respectively, when the input flow rate was (0.06 l/h).

Modified oxides sorbent (bonded or coated). Because of recent information on the high toxicity of methylated arsenicals and the abundance of organic arsenic species in the fresh water environment researchers have concentrated on its removal. Pokhrel and Viraraghavan (54) utilised iron oxide-coated *A. niger* biomass to examine the parameters influencing dimethylarsinic acid (DMA) removal from an aqueous solution. The factors examined were the concentration of DMA in solution, the mass of the adsorbent, the solution temperature and Ca^{2+}, Fe^{2+}, SO_4^{2-}, and Cl^- ions in solution.

As a result of this study, they concluded that DMA can be removed from water using iron oxide-coated *A. niger* biomass with an efficiency of approximately 50%. Although in an earlier investigation of As(III) and As(V) removal by the iron-coated biomass showed that almost 95% of the As(V) and 75% of the As(III) were removed at a pH of 6 (55). The factors influencing the adsorption of DMA by iron oxide-coated biomass were found to be in the following order (based on the magnitude): presence of Ca^{2+} ions in solution > the DMA concentration > solution temperature > presence of SO_4^{2-} in solution > presence of Fe^{2+} in solution > the mass of adsorbent > the presence of Cl^- in solution.

Novel adsorbent nanomaterials have been used by others. White et al. (56) used magnetic γ-Fe_2O_3 nanoparticles coated with poly-L-cysteine for chelation of As(III) and others metals. In this study the adsorption capacities of functionalized and unfunctionalized γ-Fe_2O_3 nanoparticles was compared. PLCys-nano showed large binding capacities for all tested metals, and in the case of As(III) the capacity (25.55 ± 4.35 mg metal/g Fe_2O_3) is larger than adsorption capacity obtained for the unfunctionalized γ-Fe_2O_3 nanoparticle (12.29 ± 2.62 mg metal/g Fe_2O_3). The As(III)

recovery for PLCys-Nano was very poor (22%) compared with the other metals.

Dliyanni et al. (2000, 2003) (in (57)) synthesized a nanostructure adsorbent, akaganéite-type β-FeO(OH) by precipitation from aqueous solution of Fe(III) chloride and ammonium carbonate for arsenic removal. When 0.5 g /l akaganéite was used at 298 K, the maximum load capacity was found to be about 100–120 mg As(V) per g of akaganéite.

Other sorbents. Duas et al. (58) tested five sorption materials (activated carbon AC, Zirconium-loaded activated carbon Zr-AC, Absorptionsmittel 3 AM3, iron-hydroxide granulates GIH and zero-valent elemental iron Fe^0) for the removal of two inorganic species of arsenic (arsenite and arsenate) using batch and column modes. For As(V) the sorption kinetics onto the materials followed the sequence Zr-Ac >> GIH = AM3 > Fe^0 > AC, while for As(III) the order was AC >> Zr-AC = AM3 = GIH = Fe^0. From the batch experiments the uptake capacities for Zr-AC was in the same order as the GIH (5.2 mg/g) and a little higher than the one for AM3 (about 5 mg/g).

The column tests showed that arsenite was completely removed (below 10 ppb) by the three sorbent materials GIH, AM3 and Zr-AC investigated. For arsenate, the sorption capacity results of the column experiments were, 2.8 mg/g for Zr-AC, 2.3 mg/g for GIH and 2.0mg/g for AM3. From the results of this study the authors stated that pure activated charcoal is not suitable for sorption reactions without modification but it has the ability of forcing the oxidation of arsenite to arsenate.

Borah et al. (41, 59) reported that commercial carbon black revealed excellent sorption ability for the removal of As(V) from aqueous phase with a sorption performance of more than 90%. In addition, an acid modified carbon black showed a removal of 93% of As(V) from a 50mg/l solution. The modification of the sorbent creates acidic functional groups, which were confirmed by FTIR analysis. The sorption performance has been found to be strongly dependent on the solution pH with a maximum at pH 5.0. The effect of temperature on sorption performance of As(V) onto the modified carbon black was investigated in the temperature range of 27–70°C. The results showed that the temperature has a positive effect on sorption increasing the extent of removal with temperature up to the optimum temperature.

Using a low-cost adsorbent, Chen et al. (60) described the removal of As(V) on bone char in a batch system as a function of pH, adsorbent, dosage and contact time. As a result, the maximum As(V) removal achieved was 99.18% at the initial As(V) concentration of 0.5 mgl^{-1} and pH 10. The results suggested that the removal of As(V) on bone char was a complex mechanism. Both co-precipitation and ion exchange took place between calcium hydrogen arsenate and hydroxylapatite in aqueous solution. These processes are shown in the following equations:

Adsorption:

$$Ca_{10}(PO_4)_6(OH)_2 + Ca^{2+} + HAsO_4^{2-} \rightarrow Ca_{10}(PO_4)_6(OH)_2 \cdot Ca(HAsO_4)$$

Ion exchange:

$$Ca_{10}(PO_4)_6(OH)_2 + HAsO_4^{2-} \rightarrow Ca_{10}(PO_4)_6(HAsO_4) + 2OH^-$$

Guerra et al. (61) used Na-magadiite (M_{synt}) in unmodified and chemically modified form in an adsorption process for arsenic(III) at pH 2.0 and temperature 298 ± 1 K. The chemical modification process was developed with organofunctionalization with N-propyldiethylenetrimethoxysilane (M_{NPTM}) and bis[3-(triethoxysilyl)propyl]tetrasulfide (M_{3TPT}) the maximum adsorption values are 412.07, 828.63 and 1052.65 mg/g for M_{synt} matrices M_{3TPT} and M_{NPTM}, respectively. The researcher explained that the degree of adsorption depends on the combination of the reactive basic centres and the corresponding cation properties, and the adsorption capacities increased with an increase of reactive basic centres in the pendant organic chains of the intercalated silylating agent.

Because layered double hydroxides (LDHs) have large surface areas and high anion exchange capacities, researchers have used them to develop rapid and cost-effective methods for removal of arsenic from contaminated water. Wang et al. (62) synthesized Mg/Al–NO_3 LDHs with a Mg:Al ratio of 2:1, 3:1 and 4:1 using a constant-pH co-precipitation method. They found that the molar ratios exhibited significant differences in their arsenate adsorption characteristics due to different nitrate orientations in their interlayers. The maximum adsorption of As on 2:1, 3:1 and 4:1 LDHs were 116.88, 80.92 and 26.97 mg/g, respectively.

The interlayer nitrate in 4:1 LDH is parallel to the hydroxide sheets, and the resulting small interlayer space restricts the access of arsenates to the interlayer binding sites. On the other hand, the interlayer nitrates in both 2:1 and 3:1 LDHs, is perpendicular to the hydroxide sheets and so this can be replaced by arsenate more readily, relative to their counterparts with a horizontal orientation. As a result, arsenate adsorption by 2:1 and 3:1 LDHs appears on both the external and interlayer surfaces.

So, in general, we can say that the ability of the sorbent to remove arsenic depends on the particular arsenic species. The removal efficiency of As(III) was better at alkaline pH in contrast to As(V), which was better at acidic conditions. The presence of the functional groups (reactive basic centres) and their orientation in the sorbent surface affects the adsorption capacity of the sorbent. Some sorbents show high efficiency for As(III) compared with As(V) however this can be attributed to the oxidation of As(III) to As(V). Some of the sorbents used for the removal of arsenic from water are summarized (Table 3), although there are many others (63–67).

TABLE 3 Adsorbents Used for Arsenic Removal

Adsorbent	As species	Initial concentration	Results	Ref.
Low-cost activated carbon from bean pods	As(III)	20 ppm	≈80% (pH ≈7.7)	(44)
Biomass derived from plant Mamordica Charatia	As(III)	0.5 ppm	88%	(45)
Steel-wool + Lemon juice + solar radiation	As	≈1 ppm	>99.5% Final As con. < 0.01 ppm	(46)
Waste–tea fungal biomass	As(III) and As(V)	1.3 and 0.9 ppm	treated FM work better than the non-treated. $FeCl_3$ pretreated and autoclaved FM removed 100% of As(III) (30 min contact time) 77% of As(V) (90 min contact time)	(47)
Rice husk	As(III) and As(V)	0.1 ppm	Very excellent removal of both As(III) and As(V)	(48)
Orange juice residue (OJR) (modified PO_4^{3-} groups)	As(III) and As(V)	NA	As(V) 70 mg/g (pH = 3.1) As(III) 68 mg/g (pH = 10.0)	(49)
Natural hematite (NH) and natural siderite (NS)	As(V), As(III) and DMA	0.2–2 ppm	NH better in batch systems NS better in column systems As(V)removal > DMA > As(III).	(50)
Nanocrystalline TiO_2	As(V) and As(III)	1.0 ppm	>98% of the As(V) (pH 4 to 9.5) As (III) 95% (pH 9.5)	(52)
Hydrous nanostructure iron(III)-titanium(IV) binary mixed oxide solution	As(V) and As(III)	5–250 ppm	As(III) 85 mg/g	(53)

(*Continued*)

TABLE 3 (Continued)

Adsorbent	As species	Initial concentration	Results	Ref.
			As(V) 14 mg/g	
Nano-sized magnetite, Fe_3O_4	As(V)	0.1 ppm	≈98% (11nm, 15m^2/l)	(68)
Iron-oxide- coated *A.nigar* biomass	DMA	0.05–0.5 ppm	≤50%	(54)
	As(III)	0.1 ppm	75%	(55)
	As(V)		95%	
Magnetic γ-Fe_2O_3 nanoparticles coated with poly-L-cysteine	As(III)	1 ppm	PLCys-nano (26 ± 4 mg/g) γ -Fe_2O_3 nanoparticles (12 ± 3 mg /g)	(56)
Akaganéite-type β-FeO(OH) nanomaterials	As(V)	NA	~100–120 mg/ g	Dliyanni et al., 2000, 2003 (in (57))
Granular activated carbon (GIH)	As(III) and As(V)	5–100 ppm	- Batch experiments	(58)
Zirconium loaded activated carbon (Zr-AC)		<0.01 ppm	Zr-AC = GIH = 5.2mg/g, AM3 ≈ 5mg/g	
			- Column experiments	
			Zr-AC ≈ 2.8 mg/g, GIH = 2.3 and AM3 = 2 mg/g	
Absorptionsmittel 3 (AM3)	As(V)	<50 ppm	Both >90%	(59)
Commercial carbon black (CB-C) and its H_2SO_4-modified form(CB-S)		≈200 ppm	CB-S ≈80%	(41)
		50 ppm	CB-C > 75%	
		100 ppm	93%	
			≈ 84%	

Acid modified carbon black (HNO_3 + H_2SO_4)				
Bone Char	As(V)	0.5 ppm	Excellent recovery 99%	(60)
Na-magadiite	As(III)	25 ppm	412 mg/g	(61)
Unmodified(M_{synt})			829 mg/g	
Modified (M_{3TPT})			1053 mg/g	
Modified (M_{NPTM})				
Mg/Al-NO_3 LDH	As(V)	7.5–150 ppm		(62)
Mg: Al ratio				
2: 1			117 mg/g	
3: 1			81 mg/g	
4: 1			27 mg/g	

Membrane Filtration

Nanofiltration is a method that can be used to purify water in order to meet the standard level of arsenic in the drinking water. Choong et al. (57) stated that many workers used this method for arsenic removal.

Waypa et al. (69) investigated the effectiveness of reverse osmosis (RO) and nanofiltration (NF) membranes in removing arsenic from synthetic freshwater and source water under certain conditions. These operational conditions included applied pressure and feedwater temperature and solution chemical composition, arsenic oxidation state, pH and the presence of co-occurring inorganic solutes. The results showed that the average removal efficiency of about 97% for As(V) and around 96 % for As(III)at an initial concentration of 0.05 ppm.

Applied pressure and co-occurring inorganic solutes had little effect on arsenic removal. Similarly, variations in solution pH from 4 to 8 also had no affect the removal of arsenic species by the tested membranes. However, an increase in feed water temperature decreased arsenic removal by a small percentage.

Urase et al. (70) examined a negatively charged NF membrane for arsenic removal. Experiments were conducted with groundwater to which arsenate, arsenite and DMA were added (total arsenic concentration 0.6 ppm). Authors found that rejection of arsenite increased with pH while arsenate removal was almost stable (the degree of increase with pH was smaller compared to the arsenite). The rejection of arsenite As(Ill) was increased from 50% at pH 3 to 89% at pH 10, while the rejection of arsenate was increased from 87% at pH 3 to 93% at pH 10.

The rejection of dimethyl arsinic acid was more than 98% regardless of the pH. This was explained using the extended Nernst-Planck equation which showed that electrically charged membranes generally have a higher rejection for charged solutes than for non-charged solutes.

Brandhuber and Amy (71) investigated and evaluated a variety of membrane processes for their ability to reject arsenic under a range of conditions. This study matched the proper membrane to the characteristics of the source water (arsenic species, arsenic size distribution and co-occurrence of organic or inorganic species in the water). Arsenic speciated as As(V) can be effectively treated by RO and NF whereas for As(III) only RO membranes or tight NF membranes appear to be able to sustain high removal rates for arsenic. Pretreatment of water containing As(III) with ferric coagulants followed by microfiltration is possible, but greater coagulant doses will be required compared to As(V). The selection of membranes may be influenced by the presence of arsenic in the particulate or dissolved form.

Seidal et al. (72) studied the difference in rejection between As(III) and As(V) using a loose NF membrane. The removal of As(V) increased from 60

to 90%, while the rejection of As(III) decreased from 28 to 5% as the feed water concentration was increased from 0.01 to 0.316 ppm.

Sato et al. (73) found that NF membranes could remove more than 95% of As (V) and 75% of As (III) (both initial concentration = 0.05 ppm) without any chemical additives. Sand filtration systems however, could not remove As(III) without its pre-oxidation to As(V). Both pentavalent and trivalent arsenic removal using NF membranes was unaffected by source water chemical composition. Furthermore, for all NF membranes investigated, in the pressure range of 0.3–1.1 MPa, pentavalent arsenic removal efficiency exceeded 85%, while trivalent arsenic proved to be far more difficult to remove. This is because As(III) exists in a neutral molecular form whilst As(V) exists in a negatively monovalent form.

Due to the extremely small particle size, large surface area and high in situ reactivity, the combination of nanoscale zero valent iron with membrane is believed to lead to very high treatment efficiency. Nguyen et al. (6) performed experiments using microfiltration (MF) and nanofiltration (NF) alone and in combination with in-line nanoscale zero valent iron addition to investigate the effectiveness of a new hybrid membrane system in removing arsenic. In this study the membranes used were NTR 729HF polyvinyl alcohol/polyamide NF and polyvinyl alcohol MF.

Results showed the removal of arsenic by membrane filtration is highly dependent on the arsenic species and the properties of the membrane. Nanofilter (NTR729HF, 700 MW cutoff) removed 81% of As(V) and 57% of As(III) from 500 ppb arsenic solution whereas the microfilter (PVA, pore size of 0.4 mm) removed only 37% of As(III) and 40% of As(V). When a small amount of nZVI (0.2 g nZVI/L) was added in the water, both microfiltration (MF) and nanofiltration (NF) could remove the majority of the arsenic (more than 90%). Finally, this method is suitable when high quality effluent is necessary.

Figoli et al. (74) studied the removal of pentavalent arsenic from synthetic water by using two commercial nanofiltration (NF) spiral-wound membrane modules (N30F by Microdyn-Nadir and NF90 by Dow Chemical). The influence of main operating parameters such as feed concentration, pH, pressure and temperature on the As rejection and permeate flux of both membranes, was investigated.

They observed that an increase of pH and a decrease of operating temperature and arsenic feed concentration determined a higher efficiency of As removal for both membranes, whereas the pressure slightly affected the As rejection of the N30F membrane (it reduced at higher TMP). For all the investigated operating conditions, the As rejection of the NF-90 membrane (above 91%) was higher than the N30F membrane (above 74%). This phenomenon was explained in terms of a lower molecular weight cut-off for

theNF-90 membrane (≈200 Dalton) in comparison with the N30F membrane (400 Dalton).

Another application for using membrane was investigated by Bey *et al.* (75). In that synthesised poly (vinylidene fluoride) (PVDF) membrane was applied in removal of As(V) by non-dispersive solvent extraction using Aliquat-336 (tricaprylmethylammouium chloride) as extractant. The effect of temperature, initial arsenic concentration, pH of the feed solution and membrane properties was studied. As a result, the extraction was affected mainly by the pH and the thickness of the membranes.

In general, the selection of the membrane is affected by arsenic species, size distribution (particulate or dissolved form) and the pH of the treated water**.** The successful application of membrane technology to the removal of arsenic will depend upon matching the correct membrane to the characteristics of the water. The material and the properties of the membrane and its conditions during an experiment (surface area, applied pressure, initial concentration and temperature) play an important role in the membrane efficiency**.** A **c**ombination of membrane with another separation method, such as coagulation and adsorption, enhances the removal efficiency. Some of the NF membranes used to remove arsenic and their performance are listed in Table 4.

COPPER TREATMENT

Copper has an attractive golden color and is one of the most important metals. It is malleable and ductile and a good conductor of heat and electricity (second only to silver in electrical conductivity). The most important alloys of copper are brass and bronze (42). Common oxidation states of copper include the less stable copper(I) state, Cu^{+}; and the more stable copper(II) state, Cu^{2+}, which forms blue or blue-green salts and solutions. Under unusual conditions, a 3+ state and even an extremely rare 4+ state can be obtained. Copper is an essential trace nutrient to all high plant and animal life. In animals, including humans, it is found primarily in the bloodstream, as a co-factor in various enzymes and also in copper-based pigments. However, in sufficient amounts, copper can be poisonous and even fatal to organisms (76).

Copper is introduced into the environment from copper mining and smelting, brass manufacture, electroplating industries and excessive use of copper based agricultural-chemicals. In 1993 WHO set the maximum acceptable copper concentration in drinking water at 2 mg/l (11).

Copper is not a biodegradable metal; because of this, it can accumulate in plants and animals. The excessive intake of copper by man leads to severe mucosal irritation, widespread capillary damage, hepatic

TABLE 4 Nanofiltration Membranes Used in Removal of Arsenic

Type of membrane	Initial concentration	Removal efficiency %	Reference
Tight NF, thin-film composite	0.05 ppm	≈97% As(V), ≈96% As(III)	(69)
Aromatic polyamide ES-10	0.6 ppm (each 0.2 ppm)	As(III) 89%, As(V) 93%, DMA 98%	(70)
NF70 4040-B (300 Da) Aromatic polyamide NF2 HL-4040F1550 (300 Da) Thin film composite	As(V) 26 ppb As(III) 19 ppb	As(V) 95%, As(III) 40%	(71)
A sulfonated polysulfone thin film composite BQ01	0.316 ppm	As(V) 90%, As(III) 5%	(72)
Aromatic polyamide (ES-10), polyvinyl alcohol(NTR-7250 and NTR-729HF)	≈ 0.05 ppm	As(V) 93–99.6% (NTR-729HF, ES-10) and >70% (NTR-7250) As (III) >75% (ES-10), < 22% (NTR-7250 and NTR-729HF)	(73)
NTR 729HF polyvinyl alcohol/polyamide NF	0.5 ppm	As(V)81%, As(III) 57% nZVI (0.2 g nZVI/L) + NF) >90%	(6)
Polyamide thin-film compositeNF90- 2540 and Hydrophilized polyethersulfone N30F-2440	0.1–1 ppm	As(v), NF-90 >90% N30F ≥74%	(74)

and renal damage, central nervous problems followed by depression, gastrointestinal irritation, and possible necrotic changes in the liver and kidney (Coton et al., 2004 in (77)).

Adsorption

Sorbents from plants. Madhava Rao et al. (78) studied the removal of copper and others metals from aqueous solution by activated carbon prepared from *Ceiba pentandra* hulls by controlling parameters such as equilibrium time, solution pH and adsorbent dose. The adsorption sites in this adsorbent are the C=O and S=O functional groups. The maximum adsorption capacity of copper was calculated from Langmuir isotherm and found to be 20.8 mg/g. in this study the effect of HCl concentration on desorption was also examined. They found that with an increase in HCl concentration the desorption also increased but attained a constant with 0.2 M HCl with a maximum copper desorption of 90%. A comparison of

this activated carbon with activated carbon prepared from *Phaseolus aureus* hulls (ACPAH) by Madhava Rao et al. (79), showed a similar maximum adsorption capacity Cu(II) 19.5 mgg^{-1}.

Mohan and Sreelakshmi (80) reported using fixed bed columns to study for copper and other metal removal with raw rice husk (RRH) and phosphate-treated rice husk (PRH). Column bed depth was investigated in this study. It was observed that the uptake of heavy metals increased with the increase in bed depth and concluded this was due to increasing contact time. The metal uptake capacity for PRH was more than that of RRH due to the increase of surface charge as a result of the presence of phosphate groups and thus more binding site for the adsorption. Wong et al. (81, 82) used a tartaric acid modified rice husk (TARH) using batch and column modes.

The sorption capacities of the TARH column for Cu (31.85 mg/g) agreed closely with the levels obtained from batch equilibrium studies (29.0 mg/g). Application of Langmuir isotherm in column modes indicated that there was no significant difference in the sorption capacity of TARH for Cu and the other metals in synthetic solution and wastewater. In addition the authors found that a decrease in sorbent particle size led to an increase in the sorption of metal ions and that the metal uptake was reduced in the presence of competitive cations and chelators.

Zheng et al. (83) used areca waste (AW), a food waste, as metal biosorbent for copper removal. AW is a suitable choice as the food waste is readily available and the cellulosic matrix is rich with metal binding active sites. They found that pH was a most effective variable with a removal efficiency for Cu^{2+} of 96.46% under optimized conditions of dosage mass, metal ion concentration and contact time. This study also suggested surface adsorption and ion-exchange as the two mechanisms responsible for the adsorption process of Cu and Cd.

Amarasinghe and Williams (84) investigated the potential of tea waste from Sri Lankan tea for the removal of copper and lead ions. Both batch and fixed bed column experiments were performed to determine the adsorption factors. For the copper uptake or removal, comparing this adsorbent with the others, low-cost adsorbents such as sawdust (85, 86), rice husk (80–82), sunflower stalks (87), cassava waste biomass (88), tree leaves (Baig et al., 1999 in (84)), unmodified tree barks (Martin-Dupoint et al., 2002 in (84)), melon seeds husks (Okieimen and Onyenkpa, 1989 in (84)), wheat bran (Farajzadeh and Monji, 2004 and Özer et al., 2004 in(3)) and carrot residues (Nasernejad et al., 2005 in (3)), they found that the tea waste performed the best. They also explained the lower adsorption capacity of Cu compared to Pb by the hydration enthalpy by concluding that the more the cation is hydrated the stronger its hydration enthalpy and the less it could interact with the adsorbent.

Şengil et al. (77) studied the biosorption of Cu(II) from aqueous solutions by valonia tannin resin as a function of particle size, initial pH, contact time and initial metal ion concentration. In order to determine the best fit equation for the biosorption of copper ions onto valonia tannin resin, the experimental data were analysed using four sorption kinetic models – the pseudo–first- and second-order equations, the Elovich and the intraparticle diffusion model equation. Results showed that the pseudo–second-order equation provides the best correlation for the biosorption process although predicted q_t (the amount of Cu(II) adsorbed at time t) values deviate from the experimental data points.

The Elovich equation also fits the experimental data well although its correlation coefficients are lower than those of pseudo–second-order. The equilibrium data were analysed using Langmuir, Freundlich and Temkin isotherms. The Langmuir isotherm was the best. In this study the researchers suggested that the adsorption mechanism was partly a result of ion exchange or complexation between the Cu^{2+} ions and phenolic groups on the valonia tannin resin surfaces.

Iftikhar et al. (89) investigated the use of rose waste biomass in Cu(II) and Cr(III) removal. In that, the effects of pH, sorbent dose, size, initial metal concentration, content time and temperature on Cu(II) and Cr(III) biosorption are described. The Cu(II) and Cr(III) biosorption capacity of rose biomass varies with temperature and the maximum adsorption capacities of 55.79 mg/g for Cu(II) and 67.34mg/g for Cr(III) at 303 ± 1K were found. pH 5 was the optimum sorption for Cu(II) and Cr(III). The calculated thermodynamic parameters showed that reactions were exothermic and spontaneous. Over 98% of Cu(II) and Cr(III), at an initial concentration of 100 mg/L, was removed in only the first 20 minutes.

Mineral oxides sorbents. Some of mineral oxides sorbent for removal of copper are TiO_2 nanoparticles (90) and natural kaolinite (91).

Modified oxides sorbent (bonded or coated). Liu et al. (92) prepared nanometer TiO_2 immobilized on silica gel by a sol–gel method. The adsorptive potential of immobilized nanometer TiO_2 for the removal of trace Cd, Cr, Cu and Mn was investigated using a microcolumn. The adsorption capacity of immobilized nanometer TiO_2 for Cd, Cr, Cu and Mn was found to be 2.93, 2.11, 6.69 and 2.47 mg/g, respectively. The packed microcolumn could be used up to at least 20 adsorption–elution cycles without a decrease in the performance. A flow rate of 2.0 mL/min was employed as the recoveries of the analytes decreased slightly when the flow rate was over 2.0 ml/min. At high pH, the OH− on the surface provides sites for binding cations. Thus, the highest recovery was obtained in the pH range of 8–9. However Liang et al. (90) used TiO_2 nanoparticles for preconcentration of trace amounts of Cu, Mn and Ni. The adsorption capacity of nanometer TiO_2 was found as 6.862, 7.747, 2.143 and 1.996 mg g^{-1} for Cu, Cr, Mn and Ni, respectively. Liu et al. used immobilized TiO_2 because nanometer TiO_2 easily aggregated

into larger particles. The effect of this aggregation is loss of sorbent activity and a subsequent reduction in sorbent recovery.

Huang and Chen (93) developed a novel magnetic nano-adsorbent by covalently binding polyacrylic acid (PAA) onto the surface of Fe_3O_4 nanoparticles, which was then modified by amino-functionalization using diethylenetriamine(DETA) via carbodiimide activation. They reported the adsorption of various metal cations (Ag^+, Cu^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Fe^{2+}, Fe^{3+}) and anions ($AuCl^{4-}$, $PdCl_4^{2-}$, $HCrO_4^-$) by the amino-functionalized magnetic nanoparticles in aqueous solutions at 25 °C. As a result they found that the amino-functionalized magnetic nanoparticles exhibited a significantly higher capability of adsorbing metal cations compared to the (PAA) coated magnetic nanoparticles. In general, the amino-functionalized magnetic nanoparticles had higher adsorption capability for both cations and anions compared with the naked iron oxide nanoparticles. Both Cu(II) and Cr(VI) followed the Langmuir isotherm equation with the maximum adsorption capacities of 12.43 mg/g for Cu(II) and 11.24 mg/g for Cr(VI).

Zhou and Nie (94) used a magnetic nanoadsorbent, chitosan-coated magnetic nanoparticles (CCMNPs), modified with a biodegradable and eco-friendly biological reagent, α-ketoglutaric acid (α-KA) to remove toxic Cu^{2+} ions from aqueous solution. The best adsorption conditions for Cu^{2+} from aqueous solution were determined at various initial ion concentration, initial pH, contact time and adsorbent concentration. The maximum adsorption capacity (q_{max}) for Cu^{2+} ions was estimated to be 96.15 mg/g, which was higher than that of pure CCMNPs (60.61 mg/g).

Other sorbents. Xue et al. (95) illustrated the adsorption of Cd(II), Cu(II), Pb(II), and Zn(II) onto basic oxygen furnace slag (BOF slag) in single and multi-element solution systems as a function of pH and concentration, in a matrix solution of 0.01M $NaNO_3$. In the adsorption edge experiments (as a function of pH) the selectivity sequence of these metals was Zn > Cu > Pb > Cd in single-element systems, whereas the sequence was Pb > Cu > Zn > Cd in the multi-element system. For adsorption isotherms (as a function of concentration), the selectivity sequence was Cu > Zn > Pb > Cd in single-element system and Cu > Cd > Pb > Zn in multi-element system.

Adsorption of heavy metals onto BOF slag was described using the extended constant-capacitance surface complexation model. This model assumed different reaction mechanisms in order to explain the adsorption behavior for copper, cadmium, lead and zinc. At low pH, all these metals adsorbed onto permanent charge sites by ion exchange reactions. Adsorption onto variable charge sites occurred at higher pH by forming inner-sphere complexes at crystal edges and octahedral alumina faces. The hydroxyl species of Cu, Pb and Zn were adsorbed by forming monodentate inner-sphere complexes, whereas adsorption of Cd on variable charges occurred by forming bidentate complexes.

The literature shows that there are many adsorbents that have been used in removal of copper from aqueous solution, some of these adsorbents were listed by researchers Ngah and Hanafiah (3), Sud et al. (19) and Bhattacharyya and Gupta (63) and some are listed in Table 5.

Membrane Filtration

As mentioned before in the cadmium treatment, Abu Qdais and Moussa (39) used both RO and NF for the treatment of wastewater containing copper and cadmium. Tanninen et al. (96) reported the rejection of copper ion from a very acidic copper solution ($CuSO_4$,25 g/l with 8 wt.% H_2SO_4) at high temperature (40°C) and high pressure (20–40 bar) using various flat-sheet NF membranes and for a period of 2 months. The membranes used were: NF270, Desel-5 DK, Desel KH, BPT-NF-1 and BPT-NF-2. The best overall copper retention at 30 bar was achieved by the Desel KH (92–95%) and by BPT-NF-2 (60–88%). The NF-270 membrane showed complete copper retention (99.5%) during the first 2 weeks and after 27 days its retention was almost zero.

Chaabane et al. (97) used a spiral wound module for copper removal from both synthetic solution and the wastewater of an electric cable factory. Concentration polarization is one of the limiting nanofiltration factors studied and Chaabane et al showed that the concentration polarization phenomenon occurs at 3.5 bar at a recirculation flux of 103L/h. They also showed that the retention of the membrane for copper is reduced by increasing the metal concentration and increased by increasing the transmembrane pressure.

Castelblanque and Salimbeni (98) studied the recovery of copper from the cleaning baths in a copper electro deposition plant using Osmonics-DESAL nanofiltration membrane. As a result, the recovery of copper was 99.8% compared with that of traditional ion exchange method (recovery 55%). The highest recovery (highest concentration of copper in the brine about 60g/l) give an evidence of lower copper concentration in permeate (few ppm). The retention of the membrane was beyond 99.9%.

Sudilovskiy et al. (5) studied treatment of wastewater containing Cu^{2+} with NF and RO. They found that the influence of feed water concentration and temperature on NF is greater than for RO. For both RO and NF as the concentration of copper increased the rejection increased. They also studied membranes integrated with flotation. There are two ways of combining membranes with flotation. The first one (membrane then flotation) can be characterized by greater recovery, lower rejection, lower energy and lower reagent consumption.

The second one (flotation then membrane), on the contrary, shows lower recovery, higher rejection, higher energy and higher reagent consumption. To estimate the applicability of the first combination, the silt density index (SDI) of the feed wastewater must be measured. If the SDI

TABLE 5 Adsorbents Used for Removal of Copper from Aqueous Solution

Adsorbent	Initial concentration	Results	Reference
Activated carbon prepared from *Ceiba pentandra* hulls	80 ppm	21 mg/g	(78)
Activated carbon prepared from *Phaseolus aureus* hulls (ACPAH)	20–200 ppm	20 mg/g	(79)
Raw rice husk (RRH) and phosphate treated rice husk (PRH).	10 ppm	The metal uptake capacity for PRH was more than that of RRH	(80)
Tartaric acid modified rice husk (TARH)	100–450 ppm	The sorption capacities (column) = 32 mg/g (Single solution), 16 ppm (bi-metal solution) (batch) = 29 mg/g	(81, 82)
Areca waste (AW)	8 ppm	97 %	(83)
Tea waste	50 ppm	77 %(1g sorbent)	(84)
Valonia tannin resin	100 ppm	44 mg/g	(77)
Rose waste biomass	10–640 ppm	56 mg/g 48 mg/g(C_0 Cu^{2+} = 60ppm)	(89)
Nanometer TiO_2	Trace element (0.5–10 ppm)	Cu = 7 mg/g, Cr = 8 mg/g, Mn = 2 mg/g and Ni = 2 mg/ g	(90)
Immobilized nanometer TiO_2	10 ppm	Cd = 2.9 mg/g, Cr = 2 mg/g, Cu = 6.7 mg/g and Mn = 2.5 mg/g.	(92)
Amino-functionalization of PAA-coated Fe_3O_4 nanoparticles	600 ppm (5ml solution)	≈ 12 mg/g pH ≈5	(93)
Chitosan-coated magnetic nanoparticles (CCMNPs), modified α-ketoglutaric acid (α-KA)	200 ppm	>90% at 5 g/L dose of α-KA-CCMNPs	(94)
Humic acid coated Fe_3O_4 nanopaticles (Fe_3O_4/HA)	≈1 ppm	>95%	(29)
Basic oxygen furnace slag (BOF slag)	Cu (6.4–254 ppm) Zn (6.5–262 ppm) Pb (21–829 ppm) Cd (11–450 ppm)	Adsorption edge experiments Zn > Cu > Pb > Cd (single-element) Pb > Cu > Zn > Cd (multi-element). Adsorption isotherms, Cu > Zn > Pb > Cd in (single-element) Cu > Cd > Pb > Zn (multi-element)	(95)

TABLE 6 Nanofiltration Membranes Used in Removal of Copper

Type of membrane	Initial concentration	Removal efficiency %	Reference
Spiral wound, Polyamide	25–200 ppm 500 ppm ($CuSO_4$+$CdSO_4$)	84 to 96 (average 90) 97	(39)
NF270, Desel-5 DK, Desel KH, BPT-NF-1 and BPT-NF-2	25g/l $CuSO_4$(Cu^{2+} = 9613 ppm)	Desel KH (92–95%) BPT-NF-2 (60–88%) BPT-NF-1(≈71–85%) NF-270 (0–99.5 %) Desel KH (≈29–85%)	(96)
Negatively charged microporous NF, Nanomax50	$CuCl_2$ = 1345 ppm Cu^{2+}[200 ppm] +(Cd^{2+},Ca^{2+}) [100 ppm] Cu^{2+} [200 ppm] + (Cd^{2+},Ca^{2+}, NaCl)[100 ppm]	≈66(p = 3.0 bar) ≈46(p = 3.0 bar) ≈50(p = 3.0 bar)	(97)
Osmonics-DESAL NF	$CuSO_4.5H_2O$ 50g/l, [cu] =12.7g/l (12,700 ppm)	99.9%	(98)
Spiral-wound ERN-B-45-300 Vladipor PA	≈50 ppm	>95 (3.8 bar) >95, >99	(5)
Combination of NF/RO and flotation	–		

is below 5, then the first combination is applicable. The rejection of copper in the membrane/flotation combination was more than 95%, while in the flotation/membrane was more than 99%. A summary of some NF membranes used in removal of manganese is found in Table 6.

MANGANESE TREATMENT

Manganese exists in several different oxidation states ranging from 0 to +7, although it is almost always found in nature in its +2, +3, and +4 state. Mn(II) is readily soluble in water whereas Mn(III) is more unstable and has a tendency to precipitate or dissociate to Mn(II) or Mn(IV) unless chelated to another molecule. Mn(IV) is insoluble and can be detected by the presence of a visible brown or black precipitate in neutral solutions. The oxidation of Mn(II) to Mn(IV) by aeration alone is a slow process unless the pH is raised above neutrality (99). Generally manganese removal methods required the use of strong oxidizing agents such as potassium permanganate, chlorine, hypochlorite, chlorine dioxide or ozone (100). The major disadvantages of these oxidizers are the generation of other pollutants or toxins.

Manganese is a major element that can be found everywhere on earth. It is naturally occurring and is found in rock, soil and water. The major anthropogenic sources of environmental manganese are municipal wastewater discharges, sewage sludge, mining and mineral processing, emission from alloy, steel and iron production, combustion of fossil fuels and fuels additives. Manganese is one of the three toxic essential trace elements, which means that it is necessary for humans to survive, but it is also toxic when concentrations are present too high in a human body.

When people do not consume the recommended daily allowances their health will decrease. But when the uptake is too high, health problems will also occur (101). Long-term exposure to dust or fumes of manganese compounds may cause chronic manganese poisoning. Manganese effects occur mainly in the respiratory tract and in the brain. Symptoms of manganese poisoning include hyperirritability, violent acts, hallucinations, decreases of libido and coordination. Manganese can also cause Parkinson's disease (102).

The presence of manganese at higher concentrations (above 0.1 ppm) in water causes; an unpleasant taste, deposits on food during cooking, stains on sanitary ware, discoloration of laundry, deposits on plumbing fittings and cooking utensils, and will foster the growth of micro-organisms in water supply systems. The European Commission recommends an upper limit of 0.05 ppm for manganese in drinking water (99).

Adsorption

Sorbents from plants. Budinova et al. (44) explored the potential application of low-cost activated carbon derived from bean pods waste. The research investigated the removal of arsenic and manganese ions from aqueous solutions at different initial concentrations and pH values. Adsorption for both ions follows Langmuir-type isotherm, the maximum adsorption capacities were 23.4 mg/g for Mn (II) and 1.0 mg/g for arsenic (III). The results of the effect of pH on removal of Mn (II) on bean pods carbon showed that the removal of manganese increases sharply between pH 2 and 4. The maximum uptake is reached in pH >4, and this maxima is maintained as the pH of the solution increase. On the other hand, the removal of As (III) increases with the pH of the system, and it reached a maximum at pH around 8. At pH above this value a sharp decrease was obtained.

Güzel et al. (103) determined the order of biosorption of Cu(II), Ni(II),Co(II), and Mn(II) ions that were absorbed onto modified carrot residues (MCR) in a batch system. The effect of temperature and the equilibrium contact times for the adsorption process were investigated. Results showed that the sorption capacities were higher at higher temperature. From the values of q_m at different temperatures, the order of the sorption capacity

is: Cu(II) > Ni(II) > Co(II) > Mn(II) with Mn(II) having a sorption capacity of 3.871 mg/g.

Mineral oxides sorbents. Yavuz et al. (91) used natural kaolinite to remove Mn(II), Co(II), Ni(II), and Cu(II) from aqueous solution. The results showed that heavy metals are easily and rapidly adsorbed by kaolinite according to the following order: Cu(II) > Ni(II) > Co(II) > Mn(II). Langmuir adsorption capacities of Mn(II) were 0.446 mg/g at 298 K and 0.461 mg/g at 313 K. The values of the calculated enthalpy (ΔH), free energy (ΔG) and entropy (ΔS) show that adsorption of heavy metal on kaolinite was an endothermic process and the process of adsorption was favored at high temperatures.

As mentioned in the section on copper treatment section, nanometer-size TiO_2 and immobilized TiO_2 were used as sorbent for the removal of trace manganese. In addition nanomaterial Al_2O_3 (104) and CeO_2 (105) were also used. Vassileva et al. prepared two ceria; CeO_2 samples with different surface areas, C-1 and C-2. The adsorption capacities of C-1 and C-2 for a particular metal cation; Cd^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+} and Pb^{2+}; were generally similar and ranged from 4mg/g for cobalt to 13 mg/g for lead.

Modified oxides sorbent (bonded or coated). García-Mendieta et al. (106) determined, using single and binary systems, the sorption properties of a Mexican zeolitic tuff for the removal of iron and manganese from aqueous solutions. The effect of the treatment of the tuff with NaCl solutions and the role of pH in the sorption process were also investigated. It was observed that the treatment of the zeolitic tuff with sodium chloride solutions improved the sorption performance for manganese from aqueous solutions.

It was found that the amount of both iron and manganese found in the zeolitic tuff in the binary system is lower than in the single system, which means that they compete for the sorption sites. Also, at pH 6 the sorption of iron in the single system is higher than manganese and in the binary system the opposite behavior was observed. Despite this difference, the equilibrium time for the sorption of manganese and iron was similar in both single and binary systems. The researchers concluded that ion exchange was the main mechanism responsible for manganese removal and precipitation for iron removal at pH 6.0.

Taffarel and Rubio (107) used a Chilean zeolite (Ch-zeolite) as an adsorbent for manganese ions from aqueous solution. A near neutral pH influenced significantly the manganese ions adsorption capacity and the best results were obtained at pH 6–6.8. Results also showed that the adsorption capacity of the activated zeolites increased in comparison to natural zeolite. Maximum adsorption capacity depended on the activation type and decreased in this order: NaCl ≈ NaOH > Na_2CO_3 > NH_4Cl > natural.

Other sorbents. Silva et al. (108) studied the biosorption of Cr, Cu, Mn and Zn ions by *Pseudomonas aeruginosa* AT18 strains (isolated from sites contaminated with petroleum) in single and complex solutions at a pH range of 3–7.72 units. *Pseudomonas aeruginosa* AT18 capacity for the sorption of manganese is low (22.39 mg/g) in comparison to the Cr^{3+}, Cu^{2+} and Zn^{2+} ions in individual solution. However, the adsorption of Mn^{2+} ions by *P. aeruginosa* AT18 in the individual solution of this metal was similar to that of the solution containing mixtures of Cr^{3+}, Cu^{2+}, Mn^{2+} and Zn^{2+} with 20% removal at pH 7.0.

Renman et al. (109) used six filter materials (opoka, sand, polonite, limestone, two types of blast furnace slag: amorphous slag coarse ASC, crystalline slag coarse CSC, crystalline slag very coarse CSVC) in removal and accumulation of some metal from domestic wastewater. The tendency for removing metals among the materials studied here followed the order Polonite > ASC > opoka > CSC > limestone > CSVC > sand. All columns were able to remove 53%–83% of Zn except those filled with sand. Only the three blast furnace slags (ASC, CSC, CSVC) were able to remove Ni. Polonite removed over 98% of dissolved Mg and Mn in the wastewater, while ASC showed reasonably efficient removal of Cu. Some of the sorbents used for the removal of Mn(II) ion from aqueous solution are listed in Table 7.

Membrane Filtration

Literature searches have revealed a limited number of studies for manganese removal using nanofiltration and in these studies the concentration of manganese was low depending in the source of the water used. Lipp and Baldauf (110) used nanofiltration in combination with limestone filtration for treating of soft spring water that contained high amounts of humic substances and trace components of some heavy metal such as manganese. The membrane used rejected completely the cations manganese, iron and aluminium. NF filtrate was followed by further treatment (CO_2 dosage + limestone filtration) in order to fit the pH value. Ericsson et al. (111) reported also about 90% retention of low manganese initial concentration.

Soares et al. (112) investigated the removal of manganese from waste water containing higher concentration of manganese. In this study NF membrane was able to reject 98% of manganese with an initial concentration of 310ppm and RO reject 99% with initial concentration of 529 ppm. Summary of some NF membranes used in removal of manganese is found in Table 8.

TABLE 7 Adsorbents Used for Removal of Manganese

Adsorbent	Initial concentration	Results	Reference
Activated carbon derived from bean pods waste	5 ppm	≈ 5 mg/g (pH ≈4–6.5)	(44)
Modified carrot residues (MCR)	NA*	4 mg/g.	(103)
Raw rice husk and phosphate treated rice husk (PRH).	10 ppm	uptake capacity for PRH > RRH	(80)
Natural kaolinite	Stock solution. 1029 ppm	adsorption capacities = 0.45 mg/g at 298 K and 0.46 mg/g at 313 K	(91)
Nanometer TiO_2	Trace amount 0.01 ppm	2 mg/ g	(90)
Nanomaterial Al_2O_3	–	–	(104)
CeO_2	1–20 ppb	8.3 mg/g(C-1), 8.2 mg/g (C-2)	(105)
Immobilized nanometer TiO_2	Trace amount 0.01 ppm	3 mg /g	(92)
Mexican zeolitic tuff and NaCl treated zeolitic tuff	2.5–100 ppm	NaCl treated zeolitic tuff > zeolitic tuff	(106)
Chilean zeolite (Ch-zeolite)	5–600 ppm	Activated zeolites > natural zeolite. depend on the activation type (NaCl ~ NaOH > Na_2CO_3 > NH_4Cl > natural)	(107)
Pseudomonas aeruginosa AT18	49 ppm	22 mg/g (20%)	(108)
Opaka	10.9 ± 3.1 μg/l	62 %	(109)
Polonite		99 %	
Amorphous slag coarse ASC		84 %	
Limestone		45 %	

*NA : not available.

TABLE 8 Nanofiltration Membranes Used in Removal of Manganese

Type of membrane	Initial concentration	Removal efficiency %	Reference
Polyamide/polysulfone	0.1 ppm	>90%	(110)
DOW NF 45	0.03–0.12(average 0.06 ppm)	≈90%	(111)
DESAL DL 5	0.03–0.15 (average 0.04 ppm)	≈91%	
GE- Osmonices NF (HL, DL and DK)	310 ppm	98%	(112)

LEAD TREATMENT

Lead is a soft, malleable metal, also considered as one of the heavy metals. It has a bluish-white color when freshly cut, but tarnishes to a dull greyish color when exposed to air. Lead is used in building construction, fuels, lead-acid batteries, bullets and shot, glazes, pigments, pesticide and is part of solder, fusible alloys and radiation shields. (10, 113).

Lead is one of the most useful of all the metals and is easy to work with. It has been used since antiquity because of its wide distribution and its ease of extraction. However, it is also a metal that has very damaging effects on human health. It can enter the human body through the uptake of food (65%), water (20%) and air (15%) (114). The presence of lead in drinking water even at low concentrations may cause diseases such as anaemia, encephalopathy, hepatitis and nephritic syndrome (Lo et al., 1999 in (80)). E.U. limit for lead in drinking water is 50 μg/L (0.05 mg/l) (114).

Adsorption

Similar to copper, many studies are found for the removal of lead; Ngah and Hanafiah (3), Sud et al. (19) and Bailey et al. (115) discussed and listed some of the low-cost sorbents used. Bhattacharyya and Gupta (63) also discussed in their review the adsorption of lead by clay (Kaolinite and montmorillonite) and other adsorbents.

Sorbents from plants. Madhava Rao et al. (79) investigated the removal of lead [Pb(II)], zinc [Zn(II)], copper [Cu(II)], and cadmium [Cd(II)] from aqueous solutions using activated carbon prepared from *Phaseolus aureus* hulls (ACPAH). The influence of various parameters such as pH, initial concentration of metal ion, contact time, and adsorbent dose on the removal efficiency of the ACPAH was studied. The sorption isotherms were studied using Langmuir, Freundlich, Dubinin Radushkevich (D–R), and Temkin isotherm models. The maximum adsorption capacity values of ACPAH for metal ions were 21.8 mg/g for Pb(II), 21.2 mg/g for Zn(II), 19.5 mg/g for Cu(II), and 15.7 mg/g for Cd(II).

Arslanoglu et al. (116) used, in batch systems, a carboxyl groups rich material prepared from lemon to remove Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} from an aqueous solution. Results revealed that sorption of metal ions onto adsorbent is strongly dependent on solution pH; the sorption of metal ions sharply decreases with decreasing pH. The effect of the temperature results showed that the sorption capacity is reduced at higher temperature for all the metals investigated and that indicates the exothermic nature of the adsorption process. Furthermore, the negative values in free energy for metal sorption indicate the process was spontaneous. The order of metal binding capacity calculated from Langmuir isotherm at 25°C was Pb^{2+} (313 mg/g) > Cd^{2+} (129 mg/g) > Cu^{2+} (81 mg /g) > Ni^{2+} (71 mg/g) > Zn^{2+} (63 mg/g) >Cr^{3+} (34 mg/g).

Mineral oxides sorbents. Similar to manganese ion, ceria CeO_2 was used as a solid phase extractor for lead(II) ions. The adsorption capacities of ceria towards Pb(II) was 9.89 mg/g on the C-1 and 13.33 mg/g on the C-2 (105).

Modified oxides sorbent (bonded or coated). As described in arsenic removal, White et al. (56) used magnetic γ-Fe_2O_3 nanoparticles coated with poly-L-cysteine for lead chelation. The metal binding capacity on PLCys-Nano γ-Fe_2O_3 and unfunctionalized γ-Fe_2O_3 nanoparticles as determined by ICP-MS for Pb ions were 14.7 ± 2.5 mg/g and 18.6 ± 1.7 mg/g, respectively. Lead recovery for PLCys-Nano was 67%.

D'Couto (68) investigated adsorption of Pb (II) and As (V) on nano-sized magnetite, Fe_3O_4. This sorbent was synthesised by two methods, lab-synthesis and home-synthesis. In this study two different particle sizes with three different total surface areas were used. In the experiments of various concentration, the adsorption of Pb(II) onto magnetite nanoparticles was relatively inefficient (i.e., below 40%), compared to As(V) adsorption. Adsorption of Pb(II) onto 11nm and 20–30 nm magnetite of different surface areas showed a strong dependence on particle size.

Adsorption of lead onto 20–30nm magnetite reached over 90%, whereas adsorption onto 11 nm remained low (<30%). The competitive adsorption experiments between Pb(II) and As(V) with the powdered magnetite nanoparticles showed that As (V) adsorption is 95% compared to Pb(II) which is <60%. Adsorption of Pb(II) is not significantly affected by the presence of As(V). Adsorption of As(V) onto home or kitchen synthesised magnetite showed initial adsorption reaching 90%. This indicates that the kitchen synthesised magnetite has a sorption capacity but this needs further study.

Chaari et al. (117) studied the adsorption of Pb^{2+} ions onto Tunisian smectite-rich clay (sampled in Jebel Aïdoudi in El Hammaarea (meridional Atlas of Tunisia)) in aqueous solution by a batch system. Four smectitic clay samples: untreated clay (UC), hydrochloric activated clay (HAC), sulfuric

activated clay (SAC) and thermic activated clay (TAC) were used. HAC and SAC samples enhanced the adsorption capacity under the same conditions compared to the untreated clay minerals due to the increase of surface area. The uptake of Pb^{2+} by SAC was very high when compared to that by HAC, because clay minerals are more soluble in sulfuric acid than hydrochloric acid. HAC and SAC removed as much as 50.18 and 65.12% of Pb^{2+} ions respectively, whereas UC could remove only 41.32%. The removal of lead by the TAC sample at 100 °C was 54.22%, but this percentage decreased with increased temperature. A comparative study between activated carbon and SAC showed that the adsorption capacity of SAC was better than that for activated carbon.

Adebowale et al. (118) considered the kinetic and thermodynamic study of the adsorption of Pb(II) and Cd(II) on tripolyphosphate-modified Kaolinite clay (TPP). The sorption capacity of the adsorbent increased with Increasing temperature and initial metal ion concentration. From the results this study suggested that two mechanisms could be responsible for the adsorption of Pb^{2+} and Cd^{2+} onto TPP-modified Kaolinite clay adsorbent: film-diffusion controlled mechanism and chemisorption. Both the rate of adsorption of Pb^{2+} and the sorption capacity of TPP-Kaolinite clay for both Pb^{2+} and Cd^{2+} were reduced in binary solutions of both metal ions at different concentrations. However, binary solutions of both metal ions enhanced the rate of adsorption of Cd^{2+}.

Eren et al. (119) explored adsorption characteristics for removal of Pb(II) from aqueous solution by the use of raw bentonite clay (RB), acid activated bentonite (AAB) and manganese oxide-coated bentonite (MCB). The adsorption process was studied as a function of the initial Pb(II) concentration, solution pH, ionic strength, temperature and inorganic ligand (Cl^-). The Langmuir monolayer adsorption capacities of RB, AAB and MCB in 0.1M KNO_3 solution (Ionic strength = 0.1 M) were estimated as 16.70, 8.92 and 58.88 mg/g, respectively.

Whereas in absence of KNO_3 (Ionic strength = 0), capacities were estimated as 64.29, 40.14 and 123.64 mg/g. in this study, when they compared the q_m value of the MCB used in their work with those obtained in the literature (carbon nanotube; $q_m \approx 26.24$ mg/g and Mn oxide-coated carbon nanotube; $q_m = 78.74$ mg/g) they found that MCB is more effective for lead(II) removal (123.64 mg/g in absence of KNO_3 and 58.88 mg/g with 0.1M KNO_3 solution). They also observed that Pb(II) adsorption behavior in the bentonite suspensions is influenced by both aqueous speciation and surface ligand complexation of Pb(II) ions.

Other sorbents. Apiratikul and Pavasant (120) investigated biosorption of Cu(II), Cd(II), and Pb(II) by a dried green macroalga *Caulerpa lentillifera* in batch and column systems. The maximum sorption capacity of this biomass was in this order Pb^{2+} (29 mg/g) >Cu^{2+} (8 mg/g) > Cd^{2+} (5 mg/g). In this study the researchers found that during sorption Ca(II), Mg(II), and

Mn(II) ions from the algal biomass were released, which means that ion exchange was one of the main sorption mechanisms.

Elouear et al. (121) investigated the removal characteristics of lead, cadmium, copper and zinc ions from aqueous solution by activated phosphate rock under different variables such as contact time, solution pH, initial metal concentration and temperature. The activation was undertaken with 1M sodium hydroxide and 1M nitric acid. The results showed that, adsorption capacity of activated phosphate rock (APR) was better than phosphate rock (PR).

The sorption of metals ions depends on the pH of the metal solutions and a maximum retention of Cd^{2+}, Cu^{2+} and Zn^{2+} occurs at pH in the range 4 to 6 whereas that of Pb^{2+} is between pH 2 and 3. The maximum sorption capacity of the investigated cations was in this order Pb^{2+} (PR 12.78 mg/g, APR 15.47 mg/g) $>Cd^{2+}$ (PR 10.46 mg/g, APR 13.56 mg/g) $>Cu^{2+}$ (PR 9.76 mg/g, APR 13.28 mg/g) $>Zn^{2+}$ (PR 8.54 mg/g, APR 12.26 mg/g). The sorption of these ions onto both PR and APR was favored at higher temperatures.

Ozdes et al. (122) used a waste mud (WM) obtained from a Cu–Zn mine as an adsorbent, for the removal of lead ions from aqueous solutions. In order to increase the adsorption capacity of the waste mud, it was activated with NaOH. Adsorption studies were applied in a batch system as a function of several parameters such as solution pH, contact time, initial Pb(II) concentration, activated-waste mud (*a*-WM) concentration and temperature. Adsorption capacity for Pb(II) was found to be 24.4mg/g for a 10g/l concentration of *a*-WM. The negative value of $\Delta G°$ and positive $\Delta S°$ showed that the adsorption of Pb(II) ions on *a*-WM was feasible and spontaneous. The positive value of $\Delta H°$ confirmed that the nature of the adsorption was endothermic. The *a*-WM can be reused at least five times for further adsorption processes. Some of the used sorbents for the removal of Pb(II) ion from aqueous solution are listed in Table 9.

Membrane Filtration

Soares et al. (112) investigated rejection and permeate flux measurements of a high sulfate concentration effluent for lead, cadmium, manganese and zinc using three nanofiltration membranes called HL, DL and DK and three reverse osmosis membranes called AD, SE and AG. Results show that the reverse osmosis membranes are capable of rejecting 100% of lead, 94 to 100% of cadmium, 94 to 99% of manganese and 94 to 98% of zinc. The retention of nanofiltration membranes was 84% for lead, 95% to 98% for cadmium, 96 to 98% for manganese and 95 to 98% for zinc. In nanofiltration tests, DK membrane showed better rejection for heavy metals. While in the reverse osmosis tests higher rejections were obtained with AD membrane.

TABLE 9 Adsorbents Used for Removal of Lead

Adsorbent	Initial concentration	Results	Reference
Activated carbon prepared from *Phaseolus aureus* hulls (ACPAH)	20–200 ppm	22 mg/g	(79)
A carboxyl groups-rich material prepared from lemon	207–5180 ppm	312 mg/g	(116)
Ceria CeO_2	0.001–0.02 ppm	10 mg/g	(105)
• C-1		13 mg/g	
• C-2			
Magnetic γ-Fe_2O_3 nanoparticles	1 ppm		(56)
• PLCys-Nano		15 ± 3 mg/g	
• unfunctionalized γ-Fe_2O_3 nanoparticles		19 ± 2 mg/g	
Nano-sized magnetite, Fe_3O_4	0.1 ppm	>90% (20–30nm)	(68)
Tripolyphosphate-modified Kaolinite clay (TPP)	60–1000 ppm	~ 82 mg/g at 323K and 1000 ppm	(118)
Tunisian smectite-rich clay	NA*	41 %.	(117)
• untreated clay (UC)		50 %	
• hydrochloric activated clay (HUC)		65 %	
• sulfuric activated clay (SAC)		54 % at 100 °C	
• thermic-activated clay (TAC)			
Bentonite clay	2–207 ppm	64 mg/g	(119)
• raw bentonite (RB)		40 mg/g	
• acid activated bentonite (AAB)		124 mg/ g	
• Manganese oxide-coated bentonite(MCB).		~ 98 %	
ZrPS-001	80 ppm	>99%	(31)
Humic acid coated Fe_3O_4 nanoparticles (Fe_3O_4/HA)	≈1 ppm	98%	(29)
A. rubescens biomass	10ppm	29 mg/g	(30)
A dried green macroalga *Caulerpa lentillifera*	20.7–248.6 ppm	(PR) 13 mg/g (APR) 16 mg/g	(120)
Phosphate rock (PR) and activated phosphate rock (APR)	10–500 ppm		(121)
Activated-waste mud (*a*-WM)	235 ppm	82%	(122)

*NA : not available.

TABLE 10 Nanofiltration Membranes Used in Removal of Lead

Type of membrane	Initial concentration	Removal efficiency %	Reference
GE- Osmonices NF (HL, DL and DK)	0.64 ppm	84%	(112)
NF50 M10 capillary nanofiltration membrane(polyethersulfone/polyamide)	3 ppb	83%	(123)

Sayed et al. (123) used direct capillary nanofiltration to treat raw domestic wastewater under continuous and stable process conditions. Direct capillary nanofiltration showed high retention in removal of total bacterial count, phosphate, nitrate, COD, BOD, iron and lead and lower retention for removal of Manganese and ammonia. Some of the NF membranes used for the removal of lead are in Table 10.

The advantages and disadvantages of adsorption and nanofiltration membrane techniques for the removal of heavy metals (Cd, Cu, As, Mn and Pb) are summarised in Table 11. It can be seen from the table that NF membrane is more effective than adsorption technique for the high concentrated and multi-metals solution (concentrated industrial effluent). For less concentrated solution the adsorption technique is better. Although of these, the properties of both sorbent and NF membrane have to be taken into consideration.

CONCLUSIONS

- In general chemical modification improved the adsorption capacity of the adsorbents probably due to a higher number of active binding sites, better ion exchange properties and formation of new functional groups that favor metal uptake. However, the method used for the modification affects this improvement.
- As modification can change the properties of the adsorbent, some characterisation studies of the sorbent such as surface area, pore size, porosity, pH_{ZPC}, etc. should be carried out.
- The adsorption capacity of the sorbent varies between the metals and this may depend on the reactivity (coordination number, electronegativity, charge transfer . . .) and/or on the hydration enthalpy of the metal.
- Although many of the natural and/or synthetic adsorbents can effectively remove dissolved heavy metals, most of them show some disadvantages such as poor adsorption capacity, a low efficiency/cost ratio, and ineffectiveness for high metal concentration
- Presence of competitive cations and chelators reduced metal uptake.
- A decrease in sorbent particle size led to an increase in the sorption of metal ions.

TABLE 11 Advantages and Disadvantages of Adsorption and Nanofiltration Techniques for the Removal Of Heavy Metals (Cd, Cu, As, Mn and Pb)

Techniques	Advantages	Disadvantages
Adsorption	- Cheap or low cost if the sorbent is abundant in nature, require little processing or is a by product of waste material. - Easily operated using column or batch experiments. - Some sorbent or biomass show higher uptake capacity with long lifetime that can be enough to be used in a continuous industrial process (124).	- Ineffectiveness at high metal concentration (>100 ppm) - The adsorption behaviors (removal) of metals in single and multi-element systems are different. In some cases and with multi-solution some metal will be exchanged by the others and this of course depending on the metal and its affinity for the binding sites (95, 124)
NF membrane	- Effective for higher metal concentration (up to 12,000 ppm) (98) - NF are capable of treating waste water containing more than one heavy metal with higher removal efficiency (mostly >80%) - The removal efficiency of metals in single and multi-element systems are nearly similar (39, 97)	- Cost and membrane fouling - Not suitable for monovalent cations.

- The adsorption process is affected by a variety of factors: initial metal concentration, initial solution temperature, solution pH, flow rate, sorbent mass and contact time. These different factors depend on the sorbate and the sorbent; for example,

  Temperature affects the adsorption rate by altering the rate of molecular interactions and solubility, if solubility of the adsorbate increases with increase in temperature, then the chemical potential decreases and so a decrease in adsorption results.
  The effect of pH on the adsorption capacity depends on the surface charge or zeta potential of the sorbent at different pH and presence of different electrolyte.
  The effect of sorbent mass depends on the availability of the binding sites. Normally the number of sites available for sorption increases by increasing the sorbent dose. However this is not always the case, as high adsorbent dosage can result in aggregates of sorbent forming rather than the number of active sites increasing. In addition, as aggregation occurs electrostatic interferences that diminish attractions between the adsorbing solute and the surface of the sorbent may result (20).
- The adsorption mechanism can be a result of ion exchange or/ and complexation or co-precipitation.
- Some sorbents showed highest efficiency in removing metal ion in batch experiments whereas others showed a better performance in packed column experiments.
- Removal of heavy metal by membrane filtration is highly dependent on the species of metal and properties of the membrane.
- Combination of nanoscale sorbent with membrane leads to very high treatment efficiency. In general membrane fabricated by nanomaterials are more effective in terms of selectivity, permeate flux and retention (115).
- Nanometer material oxide showed relatively high chemical stability towards the action of acidic solutions and can be re-used up to a certain number of cycles depending on the sorbent and the sorbate.
- In general, RO membranes are more effective for heavy metal removal compared with NF and UF membranes.
- NF and RO are capable of treating wastewater containing more than one heavy metal.
- Membrane filtration in combination with flotation showed a high rejection and a low liquid discharge.
- NF membrane can be used in any types of water and it can treat inorganic effluent with a metal concentration of more than 10000ppm. Also NF shows high rejection towards divalent cations compared with monovalent cations.
- NF membranes are widely used in removal of arsenic and copper compared with the others metal such as manganese and lead.

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NOMENCLATURE

C_0:	initial concentration (ppm)
q_t:	amount of metal absorbed at time t (mg/g)
q_{max}or q_m:	maximum absorption capacity (mass of adsorbed solute completely required to saturate a unit mass of adsorbent), (mg/g)
pH_{zpc}:	pH zeta point charge
$\Delta G°$:	Gibbs free energy
$\Delta S°$:	entropy
$\Delta H°$:	enthalpy

ABBREVIATIONS

- AAB:	acid-activated bentonite
- AC:	activated carbon.
- ACPAH:	activated carbon *Phaseolus aureus* hulls
- AM3:	absorptionsmittel 3
- APR:	activated phosphate rock
- ASC:	amorphous slag coarse
- AW:	areca waste
- BOD:	biological oxygen demand
- CB-C:	commercial carbon black
- CB-S:	H_2SO_4- Commercial carbon black
- CCMNPs:	Chitosan-coated magnetic nanoparticles
- Ch-zeolite:	Chilean zeolite
- COD:	carbon oxygen demand
- CSC:	crystalline slag coarse
- CSVC:	crystalline slag very coarse
- DETA:	diethylenetriamine
- DMA:	dimethylarsinic acid
- D–R:	Dubinin–Radushkevich model
- EANES:	X- ray absorption near edge structure
- EDS:	energy dispersive spectroscopy
- EM:	electrophoretic mobility
- EXAFS:	extended X-ray absorption fine structure
- Fe^0:	zero-valent elemental iron)

- FTIR: Fourier transform infrared
- GIH: iron-hydroxide granulates
- HAC: hydrochloric activated clay
- LDHs: layered double hydroxides
- M_{3TPT}: Na –magadiite with bis[3-(triethoxysilyl)propyl]tetrasulfide
- MCB: manganese oxide-coated bentonite
- M_{NPTM}: Na–magadiite modified with N-propyldiethylenetrimethoxysilane
- M_{synt}: Na –magadiite
- NH: natural hematite
- NHITO: hydrous iron(III)–titanium(IV) bimetal mixed oxide
- NS: natural siderite
- PAA: polyacrylic acid
- PLCys-nano: magnetic γ-Fe_2O_3 nanoparticles coated with poly-L-cysteine
- PR: phosphate rock
- PRH: phosphate rice husk
- RB: raw bentonite clay
- RRH: raw rice husk
- SAC: sulphuric-activated clay
- SDI: silt density index
- TAC: thermally activated clay
- TARH: tartaric acid rice husk
- TPP: tripolyphosphate
- UC: untreated clay
- Zr-AC: zirconium-loaded activated carbon
- ZrPS-001: $Zr(HPO_3S)_2$ nanoparticles fabricated by a porous polymeric cation exchanger D-001
- α-KA: α-ketoglutaric acid

REFERENCES

1. Ghodbane, I., Nouri, L., Hamdaoui, O., and Chiha, M. (2008) Kinetic and equilibrium study for the sorption of cadmium(II) ions from aqueous phase by eucalyptus bark. *Journal of Hazardous Materials*, 152: 148–158.
2. Volesky, B. (1990) *Biosorption of Heavy Metals*. CRC Press: Boca Raton, FL.
3. Ngah, W. S. W., and Hanafiah, M. (2008) Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresource Technology*, 99: 3935–3948.
4. Blocher, C., Dorda, J., Mavrov, V., Chmiel, H., Lazaridis, N. K., and Matis, K. A. (2003) Hybrid flotation - membrane filtration process for the removal of heavy metal ions from wastewater. *Water Research*, 37: 4018–4026.
5. Sudilovskiy, P. S., Kagramanov, G. G., and Kolesnikov, V. A. (2008) Use of RO and NF for treatment of copper containing wastewaters in combination with flotation. *Desalination*, 221: 192–201.

6. Nguyen, V. T., Vigneswaran, S., Ngo, H. H., Shon, H. K., and Kandasamy, J. (2009) Arsenic removal by a membrane hybrid filtration system. *Desalination*, 236: 363–369.
7. Hammer, J. (1996) *Water and wastewater technology*. Prentice-Hall Inc.: Englewood Cliffs, New Jersey.
8. Balkaya, N., and Cesur, H. (2008) Adsorption of cadmium from aqueous solution by phosphogypsum. *Chemical Engineering Journal*, 140: 247–254.
9. Leyva-Ramos, R., Rangel-Mendoza-Baron, J. R., Fuentes-Rubio, L., and Guerrero-Coronado, R. M. (1997) Adsorption of cadmium(II) from aqueous solution onto activated carbon. *water Sci. Technol*., 35: 205–210.
10. Baird, C. and Cann, M. (2008) *Environmental Chemistry*. W.H. Freeman and Company: New York.
11. WHO (2003) *Guidelines for Drinking Water Quality. Chemical Facts sheets*. [Accessed 24 June 2010].
12. Kurniawan, T. A., and Babel, S. (2003) *A research study on Cr(VI) removal from contaminated wastewater using low cost adsorbents and commercial activated carbon*. In *Proceeding of the 2nd International Conference on Energy Technology Towards a clean Environment (RCETE)*: Phuket, Thailand.
13. Xuejiang, W., Ling, C., Siqing, X., Jianfu, Z., Chovelon, J.-M., and Renault, N. J. (2006) Biosorption of Cu(II) and Pb(II) from aqueous solution by dried activated sludge. *Minerals Engineering*, 19: 968–971.
14. Ozer, A., Ozer, D., Dursun, G., and Bulak, S. (1999) Cadmium(II) adsorption on Cladophora crispata in batch stirred reactors in series. *Waste Management*, 19: 233–240.
15. Alasheh, S. and Duvnjak, Z. (1995) Adsorption of Copper and Chromium by Aspergillus-Carbonarius. *Biotechnology Progress*, 11: 638–642.
16. Al-Qodah, Z. (2006) Biosorption of heavy metal ions from aqueous solutions by activated sludge. *Desalination*, 196: 164–176.
17. Chang, Y. K., Chang, J. E., Lin, T. T., and Hsu, Y. M. (2002) Integrated copper-containing wastewater treatment using xanthate process. *Journal of Hazardous Materials*, 94: 89–99.
18. Gulnaz, O., Saygideger, S., and Kusvuran, E. (2005) Study of Cu(II) biosorption by dried activated sludge: effect of physico-chemical environment and kinetics study. *Journal of Hazardous Materials*, 120: 193–200.
19. Sud, D., Mahajan, G., and Kaur, M. P. (2008) Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions—A review. *Bioresource Technology*, 99: 6017–6027.
20. Julkunen-Tiitto, R. (1985) Phenolic constituents in the leaves of Northern Willows: Methods for the analysis of certain phenolics. *J. Agric. Food Chem*., 33: 213–217.
21. Ibrahim, S. C., Hanafiah, M. A. K. M., and Yahya, M. Z. A. (2006) removal of cadmium from aqueous solutions by adsorption onto sugarcane bagasse. *American-Eurasian J. Agri. and Environ. Sci*., 1: 179–184.
22. Minamisawa, M., Nakajima, S., Minamisawa, H., Yoshida, S., and Takai, N. (2005) *Removal of Copper(II) and Cadmium(II) from Water using Coffee Roasted Beans*. Springer-Verlag: Berlin Heidelberg, Germany.

23. Jamali, A. A., Mahvi, A. H., and Nazmara, S. (2009) Removal of cadmium from aqueous solutions by hazel nut shell. *World Applied Sciences Journal* 5: 16–20.
24. Sen, T. K., and Sarzali, M. V. (2008) Removal of cadmium metal ion (Cd^{2+}) from its aqueous solution by aluminium oxide (Al_2O_3): A kinetic and equilibrium study. *Chemical Engineering Journal*, 142: 256–262.
25. Katsumata, H., Kaneco, S., Inomata, K., Itoh, K., Funasaka, K., Masuyama, K., Suzuki, T., and Ohta, K. (2003) Removal of heavy metals in rinsing wastewater from plating factory by adsorption with economical viable materials.*Journal of Environmental Management*, 69: 187–191.
26. Kalfa, O. M., Yalçinkaya Ö., and Türker, A. R. (2008) Synthesis of nano B_2O_3/TiO_2 composite material as a new solid phase extractor and its application to preconcentration and separation of cadmium. *Journal of Hazardous Materials*, 166: 455–461.
27. Ismail, A. A., El-Midany, A. A., Ibrahim, I. A., and Matsunaga, H. (2008) Heavy metal removal using SiO_2-TiO_2 binary oxide: Experimental design approach. *Adsorption-Journal of the International Adsorption Society*, 14: 21–29.
28. Aguado, J., Arsuaga, J. M., Arencibia, A., Lindo, M., and Gascón, V. (2008) Aqueous heavy metals removal by adsorption on amine-functionalized mesoporous silica. *J. Hazard. Mater*, 163: 213–221.
29. Liu, J. F., Zhao, Z. S., and Jiang, G. B. (2008) Coating Fe_3O_4 magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water. *Environmental Science and Technology*, 42: 6949–6954.
30. Sarı, A., and Tuzen, M. (2008) Kinetic and equilibrium studies of biosorption of Pb(II) and Cd(II) from aqueous solution by macrofungus (*Amanita rubescens*) biomass.*J. Hazardous Materials*, 164: 1004–1011.
31. Zhang, Q. R., Pan, B. C., Pan, B. J., Zhang, W. M., Jia, K., and Zhang, Q. X. (2008) Selective sorption of lead, cadmium and zinc ions by a polymeric cation exchanger containing nano-Zr(HPO_3S)(2). *Environmental Science and Technology*, 42: 4140–4145.
32. Bruggen, B., and Vandecasteele, C. (2003) Removal of pollutants from surface water and groundwater by nanofiltration: overview of possible applications in the drinking water industry. *Environmental Pollution*, 122: 435–445.
33. Bowen, W. R., Mohammad, A. W., and Hilal, N. (1997) Characterisation of nanofiltration membranes for predictive purposes — Use of salts, uncharged solutes and atomic force microscopy. *Journal of Membrane Science*, 126: 91–105.
34. Schäfer, A. I., Akanyeti, I., and Semião, A. J. C. (2010) Micropollutant sorption to membrane polymers: A review of mechanisms for estrogens. *Advances in Colloid and Interface Science, doi:10.1016/j.cis.2010.09.006*.
35. Diawara, C. K., Lo, S. M., Rumeau, M., Pontie, M., and Sarr, O. (2003) A phenomenological mass transfer approach in nanofiltration of halide ions for a selective defluorination of brackish drinking water. *Journal of Membrane Science*, 219: 103–112.
36. Diawara, C. K. (2008) Nanofiltration process efficiency in water desalination. *Separation and Purification Reviews*, 37: 303–325.
37. Linde, K. and Jonsson, A.S. (1995) Nanofiltration of salt solutions and landfill leachate. *Desalination*, 103: 223–232.

38. Pontie, M., Dach, H., Leparc, J., Hafsi, M., and Lhassani, A. (2008) Novel approach combining physico-chemical characterizations and mass transfer modelling of nanofiltration and low pressure reverse osmosis membranes for brackish water desalination intensification. *Desalination*, 221: 174–191.
39. Abu Qdais, H. and Moussa, H. (2004) Removal of heavy metals from wastewater by membrane processes: A comparative study, *Desalination*, 164: 105–110.
40. Kurniawan, T. A., Chan, G. Y. S., Lo, W. H., and Babel, S. (2006) Physico-chemical treatment techniques for wastewater laden with heavy metals. *Chemical Engineering Journal*, 118: 83–98.
41. Borah, D., Satokawa, S., Kato, S., and Kojima, T. (2009) Sorption of As(V) from aqueous solution using acid modified carbon black, *Journal of Hazardous Materials*, 162: 1269–1277.
42. Liptrot, G.F. (1992) *Modern Inorganic Chemistry*, Collins Educational.
43. Agency, U.S.E.P. (2010) *Arsenic rule*. [Accessed 11 June 2010].
44. Budinova, T., Savova, D., Tsyntsarski, B., Ania, C. O., Cabal, B., Parra, J.B., and Petrov, N. (2009) Biomass waste-derived activated carbon for the removal of arsenic and manganese ions from aqueous solutions. *Applied Surface Science*, 255: 4650–4657.
45. Pandey, P. K., Choubey, S., Verma, Y., Pandey, M., and Chandrashekhar, K. (2009) Biosorptive removal of arsenic from drinking water. *Bioresource Technology*, 100: 634–637.
46. Cornejo, L., Lienqueo, H., Arenas, M., Acarapi, J., Contreras, D., Yanez, J., and Mansilla, H.D. (2008) In field arsenic removal from natural water by zero-valent iron assisted by solar radiation. *Environmental Pollution*, 156: 827–831.
47. Murugesan, G. S., Sathishkumar, M., and Swaminathan, K. (2006) Arsenic removal from groundwater by pretreated waste tea fungal biomass. *Bioresource Technology*, 97: 483–487.
48. Amin, N., Kaneco, S., Kitagawa, T., Begum, A., Katsumata, H., Suzuki, T., and Ohta, K. (2006) Removal of arsenic in aqueous solutions by adsorption onto waste rice husk. *Ind. Eng. Chem. Res*, 45: 8105–8110.
49. Ghimire, K. N., Inoue, K., Makino, K., and Miyajima, T. (2002) Adsorptive removal of arsenic using orange juice residue. *Sep. Sci. Technol*., 37: 2785–2799.
50. Guo, H., Stüben, D., Berner, Z., and Yu, Q. (2008) Characteristics of arsenic adsorption from aqueous solution: Effect of arsenic species and natural adsorbents. *Applied Geochemistry*, 24: 657–663.
51. Raven, K. P., Jain, A., and Loeppert, R. H. (1998) Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes. *Environmental Science and Technology*, 32: 344–349.
52. Pena, M., Meng, X. G., Korfiatis, G. P., and Jing, C.Y. (2006) Adsorption mechanism of arsenic on nanocrystalline titanium dioxide. *Environmental Science and Technology*, 40: 1257–1262.
53. Gupta, K., and Ghosh, U. C. (2009) Arsenic removal using hydrous nanostructure iron(III)-titanium(IV) binary mixed oxide from aqueous solution, *Journal of Hazardous Materials*, 161: 884–892.

54. Pokhrel, D., and Viraraghavan, T. (2008) Organic arsenic removal from an aqueous solution by iron oxide-coated fungal biomass: An analysis of factors influencing adsorption. *Chemical Engineering Journal*, 140: 165–172.
55. Pokhrel, D., and Viraraghavan, T. (2006) Arsenic removal from an aqueous solution by a modified fungal biomass. *Water Research*, 40: 549–552.
56. White, B. R., Stackhouse, B. T., and Holcombe, J. A. (2009) Magnetic γ-Fe_2O_3 nanoparticles coated with poly-l-cysteine for chelation of As(III), Cu(II), Cd(II), Ni(II), Pb(II) and Zn(II). *Journal of Hazardous Materials*, 161: 848–853.
57. Choong, T. S. Y., Chuah, T. G., Robiah, Y., Koay, F. L. G., and Azni, I. (2007) Arsenic toxicity, health hazards and removal techniques from water: An overview. *Desalination*, 217: 139–166.
58. Duas, B., Wennrich, R., and Weiss, H. (2004) Sorption materials for arsenic removal from water: A comparative study. *Water Research*, 38: 2948–2954.
59. Borah, D., Satokawa, S., Kato, S., and Kojima, T. (2008) Surface modified carbon black for As(V) removal. *Journal of Colloid Interface Science*, 319: 53–68.
60. Chen, Y. N., Chai, L. Y., and Shu, Y. D. (2008) Study of arsenic(V) adsorption on bone char from aqueous solution. *Journal of Hazardous Materials*, 160: 168–172.
61. Guerra, D. L., Pinto, A. A., Airoldi, C., and Viana, R. R. (2008) Adsorption of arsenic(III) into modified lamellar Na-magadiite in aqueous medium—Thermodynamics of adsorption process. *Journal of Solid State Chemistry*, 181: 3374–3379.
62. Wang, S.-L., Liu, C. H., Wang, M. K., Chuang, Y. H., and Chiang, P. N. (2009) Arsenate adsorption by Mg/Al-NO3 layered double hydroxides with varying the Mg/Al ratio. *Applied Clay Science*, 43: 79–85.
63. Bhattacharyya, K. G., and Sen Gupta, S. (2008) Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review. *Advances in Colloid and Interface Science*, 140: 114–131.
64. Mondal, P., Majumder, C. B., and Mohanty, B. (2008) Treatment of arsenic contaminated water in a laboratory scale up-flow bio-column reactor. *Journal of Hazardous Materials*, 153: 136–145.
65. Rahman, M. A., Hasegawa, H., Ueda, K., Maki, T., and Rahman, M. M. (2008) Arsenic uptake by aquatic macrophyte Spirodela polyrhiza L.: Interactions with phosphate and iron. *Journal of Hazardous Materials*, 160: 356–361.
66. Chutia, P., Kato, S., Kojima, T., and Satokawa, S. (2009) Adsorption of As(V) on surfactant-modified natural zeolites. *Journal of Hazardous Materials*, 162: 204–211.
67. Yusof, A. M. and Malek, N. A. N. N. (2009) Removal of Cr(VI) and As(V) from aqueous solutions by HDTMA-modified zeolite Y. *Journal of Hazardous Materials*, 162: 1019–1024.
68. Yavuz, C. T., Mayo, J. T., Suchecki, C., Wang, J., Ellsworth, A. Z., D'Couto, H., Quevedo, E., Prakash, A., Gonzalez, L., Nguyen, C., Kelty, C., Colvin, V. L. (2000). Pollution magnet: Nano–magnetite for arsenic removal from drinking water. *Environmental Geochemistry and Health*, 32: 327–334.
69. Waypa, J. J., Elimelech, M., and Hering, J. G. (1997) Arsenic removal by RO and NF membranes. *Journal American Water Works Association*, 89: 102–114.

70. Urase, T., Oh, J., and Yamamoto, K. (1998) Effect of pH on rejection of different species of arsenic by nanofiltration. *Desalination*, 117: 11–18.
71. Brandhuber, P., and Amy, G. (1998) Alternative methods for membrane filtration of arsenic from drinking water. *Desalination*, 117: 1–10.
72. Seidel, A., Waypa, J. J., and Elimelech, M. (2001) Role of charge (Donnan) exclusion in removal of arsenic from water by a negatively charged porous nanofiltration membrane. *Environmental Engineering Science*, 18: 105–113.
73. Sato, Y., Kang, M., Kamei, T., and Magara, Y. (2002) Performance of nanofiltration for arsenic removal. *Water Research*, 36: 3371–3377.
74. Figoli, A., Cassano, A., Criscuoli, A., Mozumder, M. S. I., Uddin, M. T., Islam, M. A., and Drioli, E. (2010) Influence of operating parameters on the arsenic removal by nanofiltration. *Water Research*, 44: 97–104.
75. Bey, S., Criscuoli, A., Figoli, A., Leopold, A., Simone, S., Benamor, M., and Drioli, E. (2010) Removal of As(V) by PVDF hollow fibers membrane contactors using Aliquat-336 as extractant. *Desalination* 264: 193–200.
76. Assembly of Life Sciences, U.S. (1977) *Copper: Medical and Biological Effects Of Environmental Pollutants*, National Academy of Sciences: Washington, DC.
77. Sengil, I. A., Ozacar, M., and Turkmenler, H. (2009) Kinetic and isotherm studies of Cu(II) biosorption onto valonia tannin resin. *Journal of Hazardous Materials*, 162: 1046–1052.
78. Rao, M. M., Ramesh, A., Rao, G. P. C., and Seshaiah, K. (2006) Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls. *Journal of Hazardous Materials*, 129: 123–129.
79. Rao, M. M., Ramana, D. K., Seshaiah, K., Wang, M. C., and Chien, S. W. C. (2009) Removal of some metal ions by activated carbon prepared from Phaseolus aureus hulls. *Journal of Hazardous Materials*, 166: 1006–1013.
80. Mohan, S., and Sreelakshmi, G. (2008) Fixed bed column study for heavy metal removal using phosphate treated rice husk. *Journal of Hazardous Materials*, 153: 75–82.
81. Wong, K. K., Lee, C. K., Low, K. S., and Haron, M. J. (2002) Removal of Cu and Pb using tataric acid modified rice husks. *Chemospere*, 50: 23–28.
82. Wong, K. K., Lee, C. K., Low, K. S., and Haron, M. J. (2003) Removal of Cu and Pb from electroplating wastewater using tartaric acid modified rice husk. *Process Biochemistry*, 39: 437–445.
83. Zheng, W., Li, X. M., Wang, F., Yang, Q., Deng, P., and Zeng, G. M. (2008) Adsorption removal of cadmium and copper from aqueous solution by areca—A food waste. *Journal of Hazardous Materials*, 157: 490–495.
84. Amarasinghe, B., and Williams, R.A. (2007) Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chemical Engineering Journal*, 132: 299–309.
85. Sciban, M., Klasnja, M., and Skrbic, B. (2006) Modified softwood sawdust as adsorbent of heavy metal ions from water. *Journal of Hazardous Materials*, 136: 266–271.
86. Shukla, A., Zhang, Y.-H., Dubey, P., J.L., and Shukla, S.S. (2002) The role of saw dust in the removal of unwanted materials from water. *Journal of Hazardous Materials*, B95: 137–152.

87. Sun, G., and Shi, W. X. (1998) Sunflower stalks as adsorbents for the removal of metal ions from wastewater. *Industrial and Engineering Chemistry Research*, 37: 1324–1328.
88. Horsfall, M., Abia, A. A., and Spiff, A. I. (2003) Removal of Cu(II)and Zn(II) ions from waste water by cassava (Manihot esculenta Cranz) waste biomass. *African Journal of Biotechnology*, 2: 360–364.
89. Iftikhar, A. R., Bhatti, H. N., Hanif, M. A., and Nadeem, R. (2009) Kinetic and thermodynamic aspects of Cu(II) and Cr(III) removal from aqueous solutions using rose waste biomass. *Journal of Hazardous Materials*, 161: 941–947.
90. Liang, P., Qin, Y. C., Hu, B., Peng, T. Y., and Jiang, Z. C. (2001) Nanometer-size titanium dioxide microcolumn on-line preconcentration of trace metals and their determination by inductively coupled plasma atomic emission spectrometry in water. *Analytica Chimica Acta*, 440: 207–213.
91. Yavuz, O., Altunkaynak, Y., and Guzel, F. (2003) Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite. *Water Research*, 37: 948–952.
92. Liu, Y., Liang, P., and Guo, L. (2005) Nanometer titanium dioxide immobilized on silica gel as sorbent for preconcentration of metal ions prior to their determination by inductively coupled plasma atomic emission spectrometry. *Talanta*, 68: 25–30.
93. Huang, S. H., and Chen, D. H. (2009) Rapid removal of heavy metal cations and anions from aqueous solutions by an amino-functionalized magnetic nano-adsorbent. *Journal of Hazardous Materials*, 163: 174–179.
94. Zhou, Y. T., Nie, H. L., Branford-White, C., He, Z. Y., and Zhu, L. M. (2009) Removal of Cu2+ from aqueous solution by chitosan-coated magnetic nanoparticles modified with alpha-ketoglutaric acid. *Journal of Colloid and Interface Science*, 330: 29–37.
95. Xue, Y. J., Hou, H. B., and Zhu, S. J. (2009) Competitive adsorption of copper(II), cadmium(II), lead(II) and zinc(II) onto basic oxygen furnace slag. *Journal of Hazardous Materials*, 162: 391–401.
96. Tanninen, J., Platt, S., Weis, A., and Nystrom, M. (2004) Long-term acid resistance and selectivity of NF membranes in very acidic conditions. *Journal of Membrane Science*, 240: 11–18.
97. Chaabane, T., Taha, S., Ahmed, M. T., Maachi, R., and Dorange, G. (2006) Removal of copper from industrial effluent using a spiral wound module — Film theory and hydrodynamic approach. *Desalination*, 200: 403–405.
98. Castelblanque, J., and Salimbeni, F. (2004) NF and RO membranes for the recovery and reuse of water and concentrated metallic salts from waste water produced in the electroplating process. *Desalination*, 167: 65–73.
99. Tekerlekopoulou, A. G., Vasiliadou, I. A., and Vayenas, D. V. (2008) Biological manganese removal from potable water using trickling filters. *Biochemical Engineering Journal*, 38: 292–301.
100. Teng, Z., Huang, J.Y., Fujita, K., and Takizawa, S. (2001) Manganese removal by hollow fiber micro-filter. Membrane separation for drinking water. *Desalination*, 139: 411–418.

101. Howe, P., Malcolm, H., and Dobson, S. *Manganese and its compounds: Environmental aspects*, U.N.E. Programme, I.L. Organisation, and W.H. Organization, Editors. 2004, World Health Organization, Geneva.
102. Sigel, A., and Sigel, H. (2000) *Manganese and its Role in Biological Processes, Metal Ions in Biological Systems*. Marcel Dekker, Inc.: New York.
103. Guzel, F., Yakut, H., and Topal, G. (2008) Determination of kinetic and equilibrium parameters of the batch adsorption of Mn(II), Co(II), Ni(II) and Cu(II) from aqueous solution by black carrot (Daucus carota L.) residues. *Journal of Hazardous Materials*, 153: 1275–1287.
104. Gang, C., Zucheng, J., You, P. T., and Bin, H. (2003) Preparation of high-specific -surface-area nanometer-sized alumina by sol-gel method and study on adsorption behaviors of transition metal ions on the alumina powder with ICP-AES. *Acta Chimica Sinica*, 61: 100–103.
105. Vassileva, E., Varimezova, B., and Hadjiivanov, K. (1996) Column solid-phase extraction of heavy metal ions on a high surface area CeO2 as a preconcentration method for trace determination. *Analytica Chimica Acta*, 336: 141–150.
106. Garcia-Mendieta, A., Solache-Rios, M., and Olguin, M. T. (2009) Evaluation of the sorption properties of a Mexican clinoptilolite-rich tuff for iron, manganese and iron-manganese systems. *Microporous and Mesoporous Materials*, 118: 489–495.
107. Taffarel, S. R. and Rubio, J. (2009) On the removal of Mn^{2+} ions by adsorption onto natural and activated Chilean zeolites. *Minerals Engineering*, 22: 336–343.
108. Silva, R. M. P., Rodriguez, A. A., De Oca, J., and Moreno, D. C. (2009) Biosorption of chromium, copper, manganese and zinc by Pseudomonas aeruginosa AT18 isolated from a site contaminated with petroleum. *Bioresource Technology*, 100: 1533–1538.
109. Renman, A., Renman, G., Gustafsson, J. P., and Hylander, L. (2009) Metal removal by bed filter materials used in domestic wastewater treatment. *Journal of Hazardous Materials*, 166: 734–739.
110. Lipp, P., and Baldauf, G. (1996) Nanofiltration in combination with limestone filtration for treating a soft spring water containing high amounts of humic substances. *Acta Hydrochimica et Hydrobiologica*, 24: 267–276.
111. Ericsson, B., Hallberg, M., and Wachenfeldt, J. (1996) Nanofiltration of highly colored raw water for drinking water production. *Desalination*, 108: 129–141.
112. Soares, M. D. C. V., Bertrand, M. D. A., Lemos, F. D. A., and Masson, I. O. D. C. (2005) Removal of lead, cadmium and zinc from industrial effluent using nanofiltration and reverse osmosis membranes. In *International Conference on Heavy Metals in the Environment*, Rio de Janeiro Junho.
113. Guruswamy, S. (2000) *Engineering Properties and Application of Lead Alloys*, Marcel Dekker, Inc.
114. Nurchi, V. M., and Villaescusa, I. (2008) Agricultural biomasses as sorbents of some trace metals, *Coordination Chemistry Reviews*, 252: 1178–1188.
115. Bailey, S. E., Olin, T. J., Bricka, R. M., and Adrian, D. D. (1999) A review of potentially low-cost sorbents for heavy metals. *Water Research*, 33: 2469–2479.
116. Arslanoglu, H., Altundogan, H. S., and Tumen, F. (2008) Heavy metals binding properties of esterified lemon. *J. Hazardous Materials*, 164: 1406–1413.

117. Chaari, I., Fakhfakh, E., Chakroun, S., Bouzid, J., Boujelben, N., Feki, M., Rocha, F., and Jamoussi, F. (2008) Lead removal from aqueous solutions by a Tunisian smectitic clay. *Journal of Hazardous Materials*, 156: 545–551.
118. Adebowale, K. O., Unuabonah, E. I., and Olu-Owolabi, B. I. (2008) Kinetic and thermodynamic aspects of the adsorption of Pb^{2+} and Cd^{2+} ions on tripolyphosphate-modified kaolinite clay.*Chemical Engineering Journal*, 136: 99–107.
119. Eren, E., Afsin, B., and Onal, Y. (2009) Removal of lead ions by acid activated and manganese oxide-coated bentonite. *Journal of Hazardous Materials*, 161: 677–685.
120. Apiratikul, R., and Pavasant, P. (2008) Batch and column studies of biosorption of heavy metals by *Caulerpa lentillifera*. *Bioresource Technology*, 99: 2766–2777.
121. Elouear, Z., Bouzid, J., Boujelben, N., Feki, M., Jamoussi, F., and Montiel, A. (2008) Heavy metal removal from aqueous solutions by activated phosphate rock. *Journal of Hazardous Materials*, 156: 412–420.
122. Ozdes, D., Gundogdu, A., Kemer, B., Duran, C., Senturk, H. B., and Soylak, M. (2009) Removal of Pb(II) ions from aqueous solution by a waste mud from copper mine industry: Equilibrium, kinetic and thermodynamic study. *Journal of Hazardous Materials*, 166: 1480–1487.
123. Sayed, S., Tarek, S., Dijkstra, I., and Moerman, C. (2007) Optimum operation conditions of direct capillary nanofiltration for wastewater treatment. *Desalination*, 214: 215–226.
124. Vilar, V. J. P., Martins, R. J. E., Botelho, C. M. S., and Boaventura, R. A. R. (2009) Removal of Cu and Cr from an industrial effluent using a packed-bed column with algae Gelidium-derived material. *Hydrometallurgy*, 96: 42–46.