Review

Removal of heavy metal ions from wastewaters: A review

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ABSTRACT

Heavy metal pollution has become one of the most serious environmental problems today. The treatment of heavy metals is of special concern due to their recalcitrance and persistence in the environment. In recent years, various methods for heavy metal removal from wastewater have been extensively studied. This paper reviews the current methods that have been used to treat heavy metal wastewater and evaluates these techniques. These technologies include chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation–flocculation, flotation and electrochemical methods. About 185 published studies (1988–2010) are reviewed in this paper. It is evident from the literature survey articles that ion-exchange, adsorption and membrane filtration are the most frequently studied for the treatment of heavy metal wastewater.

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1. Introduction

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0 (Srivastava and Majumder, 2008). With the rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides, etc., heavy metals wastewaters are directly or indirectly discharged into the environment increasingly, especially in developing countries. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. Toxic heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium.

Zinc is a trace element that is essential for human health. It is important for the physiological functions of living tissue and regulates many biochemical processes. However, too much zinc can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia (Oyaro et al., 2007). Copper does essential work in animal metabolism. But the excessive ingestion of copper brings about serious toxicological concerns, such as vomiting, cramps, convulsions, or even death (Paulino et al., 2006).

Nickel exceeding its critical level might bring about serious lung and kidney problems aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis (Borba et al., 2006). And it is known that nickel is human carcinogen. Mercury is a neurotoxin

that can cause damage to the central nervous system. High concentrations of mercury cause impairment of pulmonary and kidney function, chest pain and dyspnoea (Namasivayam and Kadirvelu, 1999). The classic example of mercury poisoning is Minamata Bay. Cadmium has been classified by U.S. Environmental Protection Agency as a probable human carcinogen. Cadmium exposes human health to severe risks. Chronic exposure of cadmium results in kidney dysfunction and high levels of exposure will result in death.

Lead can cause central nervous system damage. Lead can also damage the kidney, liver and reproductive system, basic cellular processes and brain functions. The toxic symptoms are anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damages (Naseem and Tahir, 2001). Chromium exits in the aquatic environment mainly in two states: Cr(III) and Cr(VI). In general, Cr(VI) is more toxic than Cr(III). Cr(VI) affects human physiology, accumulates in the food chain and causes severe health problems ranging from simple skin irritation to lung carcinoma (Khezami and Capart, 2005).

Faced with more and more stringent regulations, nowadays heavy metals are the environmental priority pollutants and are becoming one of the most serious environmental problems. So these toxic heavy metals should be removed from the wastewater to protect the people and the environment. Many methods that are being used to remove heavy metal ions include chemical precipitation, ion-exchange, adsorption, membrane filtration, electrochemical treatment technologies, etc. The present review article deals with the current techniques for the removal of heavy metal ions from wastewater. Their advantages and limitations in application are also evaluated.

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2. Heavy metal wastewater treatment techniques

2.1. Chemical precipitation

Chemical precipitation is effective and by far the most widely used process in industry (Ku and Jung, 2001) because it is relatively simple and inexpensive to operate. In precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates. The forming precipitates can be separated from the water by sedimentation or filtration. And the treated water is then decanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation and sulfide precipitation.

2.1.1. Hydroxide precipitation

The most widely used chemical precipitation technique is hydroxide precipitation due to its relative simplicity, low cost and ease of pH control (Huisman et al., 2006). The solubilities of the various metal hydroxides are minimized in the pH range of 8.0–11.0. The metal hydroxides can be removed by flocculation and sedimentation. A variety of hydroxides has been used to precipitate metals from wastewater, based on the low cost and ease of handling, lime is the preferred choice of base used in hydroxide precipitation at industrial settings (Baltpurvins et al., 1997) (Table 1).

Hydroxide precipitation process using $Ca(OH)_2$ and NaOH in removing Cu(II) and Cr(VI) ions from wastewater was evaluated by Mirbagheri and Hosseini (2005). The Cr(VI) was converted to Cr(III) using ferrous sulfate. Maximum precipitation of Cr(III) occurred at pH 8.7 with the addition of $Ca(OH)_2$ and the concentration of chromate was reduced from 30 mg/L to 0.01 mg/L. The cupro-ammonia was reduced by aeration and the optimum pH for maximum copper precipitation was about 12.0 for both $Ca(OH)_2$ and NaOH and the concentration of copper was reduced from 48.51 mg/L to 0.694 mg/L. To enhance lime precipitation, fly ash was used as a seed material (Chen et al., 2009b). The fly ash–lime-carbonation treatment increased the particle size of the precipitate and significantly improved the efficiency of heavy metal removal. The concentrations of chromium, copper, lead and zinc in effluents can be reduced from initial concentration of 100.0 mg/L to 0.08, 0.14, 0.03 and 0.45 mg/L, respectively.

In hydroxide precipitation process, the addition of coagulants such as alum, iron salts, and organic polymers can enhance the removal of heavy metals from wastewater. Charerntanyarak (1999) employed chemical coagulation and precipitation by lime to treat synthetic wastewater consisting of Zn, Cd, Mn and Mg at the concentration of 450, 150, 1085 and 3154 mg/L, respectively. He found that the optimum pH was more than 9.5 and the treated wastewater could meet the Wastewater Standard of the Ministry of Industry. Moreover, if coagulant was added, the residual concentration of heavy metal can be decreased further.
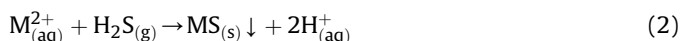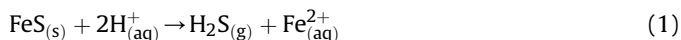
Although widely used, hydroxide precipitation also has some limitations. Firstly, hydroxide precipitation generates large volumes of relatively low density sludge, which can present dewatering and disposal problems (Kongsricharoern and Polprasert, 1995). Secondly, some metal hydroxides are amphoteric, and the

mixed metals create a problem using hydroxide precipitation since the ideal pH for one metal may put another metal back into solution. Thirdly, when complexing agents are in the wastewater, they will inhibit metal hydroxide precipitation.

2.1.2. Sulfide precipitation

Sulfide precipitation is also an effective process for the treatment of toxic heavy metals ions. One of the primary advantages of using sulfides is that the solubilities of the metal sulfide precipitates are dramatically lower than hydroxide precipitates and sulfide precipitates are not amphoteric. And hence, the sulfide precipitation process can achieve a high degree of metal removal over a broad pH range compared with hydroxide precipitation. Metal sulfide sludges also exhibit better thickening and dewatering characteristics than the corresponding metal hydroxide sludges.

Özverdi and Erdem (2006) investigated pyrite and synthetic iron sulfide to remove Cu^{2+}, Cd^{2+} and Pb^{2+}. The mechanism governing the metal removal processes was determined as chemical precipitation at low pH (<3) due to H_2S generation (Eqs. (1) and (2)) and adsorption at high pH (in the range of 3–6)

$$FeS_{(s)} + 2H^+_{(aq)} \rightarrow H_2S_{(g)} + Fe^{2+}_{(aq)} \tag{1}$$

$$M^{2+}_{(aq)} + H_2S_{(g)} \rightarrow MS_{(s)} \downarrow + 2H^+_{(aq)} \tag{2}$$

Recently, new sulfide precipitation process has been developed based on sulfate-reducing bacteria (SRB). SRB oxidize simple organic compounds under anaerobic conditions and the SRB transform the sulfates into hydrogen sulfide

$$3SO_4^{2-} + 2CH_3CH(OH)COOH \rightarrow 3H_2S + 6HCO_3^- \tag{3}$$
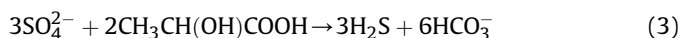
where $CH_3CH(OH)COOH$ stands for simple organic compounds. Hydrogen sulfide reacts with divalent soluble metals to form insoluble metal sulfides (Eq. (2)).

Some attractive findings were reported by Kousi et al. (2007) who developed an upflow fixed-bed SRB to monitor for the treatment of zinc-bearing wastewater. They found that the reactor has a considerable capacity of completely reducing sulfates for initial concentrations up to 6000 mg/L, completely removing soluble zinc for initial concentrations up to 400 mg/L and completely removing TOC for initial concentrations up to 1500 mg/L. The possibility of using SRB for the treatment of an acid mine drainage was also studied (Alvarez et al., 2007).

However, there are potential dangers in the use of sulfide precipitation process. As we know, heavy metal ions often in acid conditions and sulfide precipitants in acidic conditions can result in the evolution of toxic H_2S fumes. It is essential that this precipitation process be performed in a neutral or basic medium. Moreover, metal sulfide precipitation tends to form colloidal precipitates that cause some separation problems in either settling or filtration processes.

2.1.3. Chemical precipitation combined with other methods

Chemical precipitation has been shown to be successful in combination with other methods. González-Muñoz et al. (2006)

Table 1
Heavy metal removal using chemical precipitation.

Species	Initial metal conc.	Precipitant	Optimum pH	Removal efficiency (%)	Ref.
Zn^{2+}	32 mg/L	CaO	9–10	99–99.3	Ghosh et al., in press
Cu^{2+}, Zn^{2+}, Cr^{3+}, Pb^{2+}	100 mg/L	CaO	7–11	99.37–99.6	Chen et al., 2009b
Cu^{2+}, Zn^{2+}, Pb^{2+}	0.018, 1.34, 2.3 mM	H_2S	3.0	100, >94, >92	Alvarez et al., 2007
Cr^{3+}	5363 mg/L	CaO and MgO	8.0	>99	Guo et al., 2006
Hg^{2+}	65.6, 188 µg/L	1,3-benzenediamidoethanethiolate	4.7 and 6.4	>99.9	Blue et al., 2008
CuEDTA	25, 50,100 mg/L	1,3,5-hexahydrotriazinedithiocarbamate	3.0	99.0, 99.3, 99.6	Fu et al., 2007

reported sulfide precipitation to reuse and recover heavy metal ions and employed nanofiltration as a second step. Results indicated sulfide precipitation was successful in reducing the metal content and nanofiltration yielded solutions capable to being directly reused in the plant. Ghosh et al. (in press) used electro-Fenton process and chemical precipitation to treat rayon industry wastewater to reduce its COD (2400 mg/L) and Zn^{2+} (32 mg/L). Results revealed that approximately 88% COD was reduced using electro-Fenton method and zinc removal (99–99.3%) was attained in the range of pH 9–10 using lime precipitation.

There are some reports on chemical precipitation in combination with ion-exchange treatments. Papadopoulos et al. (2004) reported using ion-exchange processes individually and then combining with chemical precipitation in removing nickel from wastewater streams from a rinse bath of aluminum parts. They found that the individual application of ion exchange led to the removal of nickel up to 74.8%, while using the combination of ion-exchange and precipitation processes, higher removal from 94.2% to 98.3% was obtained. Besides, treating acid mine water by the precipitation of heavy metals with lime and sulfides, followed by ion exchange was also reported (Feng et al., 2000).

2.1.4. Heavy metal chelating precipitation

As is known, conventional chemical precipitation processes have many limitations and it is difficult to meet the increasingly stringent environmental regulations by application of conventional precipitation processes to treat the heavy metal wastewaters especially containing coordinated agents. As an alternative, many companies use chelating precipitants to precipitate heavy metals from aqueous systems. Matlock et al. (2002a) reviewed and examined the effectiveness of three widely used commercial heavy metal precipitants, trimercaptotriazine, potassium/sodiumthiocarbonate and sodiumdimethyldithiocarbamate. Since commercial heavy metal precipitants today either lack the necessary binding sites or pose too many environmental risks to be safely utilized, there is a definite need for new and more effective precipitants to be synthesized to meet the discharged requirements.

Matlock et al. (2002b,c) designed and synthesized a new thiol-based compound, 1,3-benzenediamidoethanethiol ($BDET^{2-}$) dianion. $BDET^{2-}$ can effectively precipitate mercury in the leachate solution and heavy metals from acid mine drainage. Fu et al. (2006, 2007) employed dithiocarbamate-type supramolecular heavy metal precipitants, N,N′-bis-(dithiocarboxy)piperazine (BDP) and 1,3,5-hexahydrotriazinedithiocarbamate (HTDC) in treating complex heavy metal wastewater. Results indicated that both BDP and HTDC could effectively reduce heavy metal ions in wastewater to much lower than 0.5 mg/L. The xanthate process has also been shown to be an effective method for heavy metal removal from contaminated water. Potassium ethyl xanthate was employed to remove copper ions from wastewater (Chang et al., 2002) and results showed that ethyl xanthate was suitable for the treatment of copper-containing wastewater over a wide copper concentration range (50, 100, 500 and 1000 mg/L) to the level that meets the Taiwan EPA's effluent regulations (3 mg/L).
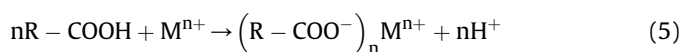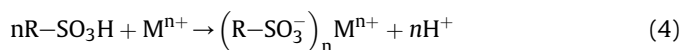
Xu and Zhang (2006) developed a new organic heavy metal chelator—dipropyl dithiophosphate. The chelator can remove the concentration of lead, cadmium, copper and mercury being 200 mg/L at pH 3–6 up to over 99.9% and the heavy metal concentrations in the wastewater after treatment are less than 1, 0.1, 0.5 and 0.05 mg/L, respectively.

2.2. Ion exchange

Ion-exchange processes have been widely used to remove heavy metals from wastewater due to their many advantages, such as high treatment capacity, high removal efficiency and fast kinetics (Kang et al., 2004). Ion-exchange resin, either synthetic or natural solid resin, has the specific ability to exchange its cations with the metals in the wastewater. Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they are effective to nearly remove the heavy metals from the solution (Alyüz and Veli, 2009).

The most common cation exchangers are strongly acidic resins with sulfonic acid groups ($-SO_3H$) and weakly acid resins with carboxylic acid groups ($-COOH$). Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cations. As the solution containing heavy metal passes through the cations column, metal ions are exchanged for the hydrogen ions on the resin with the following ion-exchange process:

$$nR-SO_3H + M^{n+} \rightarrow \left(R-SO_3^-\right)_n M^{n+} + nH^+ \tag{4}$$

$$nR-COOH + M^{n+} \rightarrow \left(R-COO^-\right)_n M^{n+} + nH^+ \tag{5}$$

The uptake of heavy metal ions by ion-exchange resins is rather affected by certain variables such as pH, temperature, initial metal concentration and contact time (Gode and Pehlivan, 2006). Ionic charge also plays an important role in ion-exchange process. The influence of ionic charge on the removal of Ce^{4+}, Fe^{3+} and Pb^{2+} from aqueous systems by cation-exchange resin purolite C100 was tested by Abo-Farha et al. (2009). They found that the metal ions adsorption sequence can be given as $Ce^{4+} > Fe^{3+} > Pb^{2+}$. Similar results for Co^{2+}, Ni^{2+} and Cr^{3+} on an Amberlite IRN-77 cation-exchange resin were previously obtained by Kang et al. (2004).

Besides synthetic resins, natural zeolites, naturally occurring silicate minerals, have been widely used to remove heavy metal from aqueous solutions due to their low cost and high abundance. Many researchers have demonstrated that zeolites exhibit good cation-exchange capacities for heavy metal ions under different experimental conditions (Motsi et al., 2009; Ostroski et al., 2009; Taffarel and Rubio, 2009). Clinoptilolite is one of the most frequently studied natural zeolites that have received extensive attention due to its selectivity for heavy metals. Table 2 shows the efficiency of clinoptilolite for removing heavy metal ions.

Recently, some researchers reported that the surface of clinoptilolite loaded with amorphous Fe-oxide species would significantly improve the exchange capacity of clinoptilolite (Doula and Dimirkou, 2008; Doula, 2009). Doula (2009) employed clinoptilolite—Fe system to simultaneously remove Cu, Mn and Zn from drinking water. He found that the system has very large metal adsorption capacity and for most of the cases the treated water samples were suitable for human consumption or agricultural use.

Though there are many reports on the use of zeolites and montmorillonites as ion-exchange resin to remove heavy metal, they are limited at present compared with the synthetic resins. And the application of zeolites is on the laboratory experiments scale. More work is needed for the application of zeolites at an industrial scale.

2.3. Adsorption

Adsorption is now recognized as an effective and economic method for heavy metal wastewater treatment. The adsorption process offers flexibility in design and operation and in many cases will produce high-quality treated effluent. In addition, because adsorption is sometimes reversible, adsorbents can be regenerated by suitable desorption process.

Table 2
Selective heavy metal uptake using clinoptilolite ion-exchange resin.

Species	Operation styles	Initial metal conc. (mg/L)	Optimum pH	Adsorption capacity (meq/g)	Removal efficiency (%)	Clinoptilolite (g/L)	Ref.
Pb^{2+}	Fixed-bed and batch operation	2072	4.0	0.21–1	NA	20–40	Inglezakis and Grigoropoulou, 2003
Pb^{2+}	Batch experiments	1036	4.0	NA	55	20	Inglezakis et al., 2007
Ni^{2+}	Fluidized bed process	2900	NA	0.5–1.77	NA	50	Rodríguez-Iznaga et al., 2002
Ni^{2+}	Batch experiments	25	7.0	0.11	93.6	15	Argun, 2008
Zn^{2+}	Batch experiments	65.4–654	5.0	2.237 ± 0.15	100	25	Athanasiadis and Helmreich, 2005
Pb^{2+}	Batch experiments	162.65–400	4.0	1.361, 1.372	NA	0.52–4.17	Berber-Mendoza et al., 2006

NA: not available.

2.3.1. Activated carbon adsorbents

Activated carbon (AC) adsorbents are widely used in the removal of heavy metal contaminants. Its usefulness derives mainly from its large micropore and mesopore volumes and the resulting high surface area. A large number of researchers are studying the use of AC for removing heavy metals (Jusoh et al., 2007; Kang et al., 2008).

Nowadays, the depleted source of commercial coal-based AC results in the increase of price. To make progress in heavy metals adsorption to AC without the expense of decline in the pollutants adsorption, additives and AC composite could be an option. Additives of alginate (Park et al., 2007), tannic acid (Üçer et al., 2006), magnesium (Yanagisawa et al., 2010), surfactants (Ahn et al., 2009) and AC composite could be effective adsorbents for heavy metals.

And searching for alternative AC from abundant and inexpensive sources is of concern. Converting carbonaceous materials into AC for heavy metals remediation have been reported. Dias et al. (2007) reviewed the waste materials for AC preparation. Kongsuwan et al. (2009) explored the use of AC from eucalyptus bark in the binary component sorption of Cu^{2+} and Pb^{2+}. The maximum sorption capacities for Cu^{2+} and Pb^{2+} were 0.45 and 0.53 mmol/g. A major mechanism for the uptake of both heavy metals was proven to be adsorption. Poultry litter to manufacture AC for treating heavy metal-contaminated water was explored by Guo et al. (2010). They revealed that poultry litter-based AC possessed significantly higher adsorption affinity and capacity for heavy metals than commercial AC derived from bituminous coal and coconut shell.

2.3.2. Carbon nanotubes adsorbents

Carbon nanotubes (CNTs) discovered by Iijima (1991) in 1991, have been widely studied for their excellent properties and applications. As relatively new adsorbents, CNTs have been proven to possess great potential for removing heavy metal ions such as lead (Wang et al., 2007a; Kabbashi et al., 2009), cadmium (Kuo and Lin, 2009), chromium (Pillay et al., 2009), copper (Li et al., 2010), and nickel (Kandah and Meunier, 2007) from wastewater. The results of these studies show that CNTs are promising candidates for adsorption of heavy metal (Table 3).

CNTs are divided into two types: (1) single-walled CNTs (SWCNTs) and (2) multi-walled CNTs (MWCNTs) (Odom et al., 1998). The mechanisms by which the metal ions are sorbed onto CNTs are very complicated and appear attributable to electrostatic attraction, sorption–precipitation and chemical interaction between the metal ions and the surface functional groups of CNTs (Rao et al., 2007).

The sorption capacities of metal ions by raw CNTs are very low but significantly increase after oxidized by HNO_3, NaClO and $KMnO_4$ solutions. Wang et al. (2007a) reported the adsorption of Pb (II) using acidified MWCNTs and found the oxygenous functional groups on MWCNTs play an important role in Pb(II) adsorption to form chemical complex adsorption, which accounts for 75.3% of all the Pb(II) adsorption capacity. Pillay et al. (2009) investigated the adsorption capabilities for the removal of parts per billion levels (ppb) of Cr(VI) by three adsorbents, namely AC, functionalised MWCNTs and unfunctionalised MWCNTs. The unfunctionalised MWCNTs showed the highest adsorption capability with up to 98% of a 100 ppb Cr(VI) solution being adsorbed. Both functionalised and non-functionalised MWCNTs showed a superior adsorption capability to that of AC. Widespread usage of CNTs will eventually be discharged to the water environment and poses a risk to humans. To resolve this problem, an environmental friendly adsorbent, CNTs immobilized by calcium alginate (CNTs/CA) was prepared and tested to remove copper (Li et al., 2010). The copper adsorption capacity by CNTs/CA can attain 67.9 mg/g at copper equilibrium concentration of 5 mg/L.

2.3.3. Low-cost adsorbents

AC has been the most used adsorbent, nevertheless it is relatively expensive. Searching for low-cost and easily available adsorbents to remove heavy metal ions have become a main research focus. To date, hundreds of studies on the use of low-cost adsorbents have been published. Agricultural wastes, industrial by-products and wastes and natural substances have been studied as adsorbents for the heavy metal wastewater treatment. Several reviews are available that discuss the use of low-cost adsorbents for the treatment of heavy metals wastewater. Bhattacharyya and

Table 3
Maximum sorption capacities of metal ions on CNTs.

CNTs	Heavy metal	Q_m (mg/g)	Conditions	Ref.
Acidified MWCNTs	Pb^{2+}	85	$[Pb^{2+}]_{initial}$ = 50 mg/L with 6 h acidified MWCNTs	Wang et al., 2007a
MWCNTs/iron oxide	Ni^{2+}, Sr^{2+}	Ni^{2+}: 9.18 Sr^{2+}: NA	$[Ni^{2+}]_{initial}$ = 6.0 mg/L, m/V = 0.75 g/L	Chen et al., 2009a
CNTs	Pb^{2+}	102.04	pH 5, 40 mg/L of CNTs, contact time 80 min, agitation speed 50 r/min	Kabbashi et al., 2009
Oxidized MWCNTs	Cd^{2+}	25.7	Ultrasonically 45 min at 45 °C	Vuković et al., 2010
Oxidized MWCNTs	Cr(VI)	4.262	m/V = 1.0 g/L, $T = 20 \pm 2$ °C, pH = 2.05, contact time = 165 h	Hu et al., 2009
CNTs immobilized by calcium alginate	Cu^{2+}	67.9	Dose of adsorbents 0.05 g, pH = 5.0, $T = 25$ °C	Li et al., 2010
MWCNTs/oxidized CNTs	Ni^{2+}	MWCNTs: 18.08, Oxidized CNTs: 49.26	m/V = 0.2 g/L, pH 6	Kandah and Meunier, 2007

NA: not available.

Gupta (2008) reviewed the adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite. Sud et al. (2008) reviewed agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions. Wan Ngah and Hanafiah (2008) reviewed the removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents. Babel and Kurniawan (2003) reviewed the use of low-cost adsorbents for heavy metals uptake from contaminated water.

Researchers investigated industrial by-products such as lignin (Betancur et al., 2009; Reyes et al., 2009), diatomite (Sheng et al., 2009), clino-pyrrhotite (Lu et al., 2006), lignite (Mohan and Chander, 2006), aragonite shells (Kohler et al., 2007), natural zeolites (Apiratikul and Pavasant, 2008a), clay (Al-Jlil and Alsewailem, 2009), kaolinite (Gu and Evans, 2008) and peat (Liu et al., 2008a), etc.

Jiang et al. (2010) investigated the kaolinite clay obtained from Longyan, China to remove heavy metal ions Pb(II), Cd(II), Ni(II) and Cu(II) from wastewater. The uptake is rapid with maximum adsorption being observed within 30 min. And kaolinite clay was used for removing metal ions from real wastewater containing Pb (II), where its concentration was reduced from 160.00 mg/L to 8.00 mg/L. Agoubordea and Navia (2009) reported zinc and copper removal from aqueous solutions using brine sediments, sawdust and the mixture of both materials. The maximum adsorption capacity was found to be 4.85, 2.58 and 5.59 mg/g for zinc and 4.69, 2.31 and 4.33 mg/g for copper, respectively, using an adsorbent/solution ratio of 1/40.

2.3.4. Bioadsorbents

Biosorption of heavy metals from aqueous solutions is a relatively new process that has been confirmed a very promising process in the removal of heavy metal contaminants. The major advantages of biosorption are its high effectiveness in reducing the heavy metal ions and the use of inexpensive biosorbents. Biosorption processes are particularly suitable to treat dilute heavy metal wastewater. Typical biosorbents can be derived from three sources as follows (Apiratikul and Pavasant, 2008b): (1) non-living biomass such as bark, lignin, shrimp, krill, squid, crab shell, etc.; (2) algal biomass; (3) microbial biomass, e.g. bacteria, fungi and yeast.

Different forms of inexpensive, non-living plant material such as potato peels (Aman et al., 2008), sawdust (Kaczala et al., 2009), black gram husk (Saeed et al., 2005), eggshell (Jai et al., 2007), seed shells (Amudaa et al., 2009), coffee husks (Oliveira et al., 2008), sugar-beet pectin gels (Mata et al., 2009) and citrus peels (Schiewer and Patil, 2008), etc., have been widely investigated as potential biosorbents for heavy metals.

Algae, a renewable natural biomass proliferates ubiquitously and abundantly in the littoral zones of world has attracted the attention of many investigators as organisms to be tested and used as new adsorbents to adsorb metal ions. Several advantages in applying algae as biosorbent include the wide availability, low cost, high metal sorption capacity and reasonably regular quality (Apiratikul and Pavasant, 2008b). There are a large number of research works on the metal biosorption using algal biomass. Examples of recent reports include the biosorption of Cu^{2+} and Zn^{2+} using dried marine green macroalga *Chaetomorpha linum* (Ajjabi and Chouba, 2009), the biosorption of Cu^{2+}, Cd^{2+}, Pb^{2+}, and Zn^{2+} using dried marine green macroalga *Caulerpa lentillifera* (Pavasant et al., 2006), the biosorption of chromium from wastewater using green alga *Ulva lactuca* (El-Sikaily et al., 2007), and the biosorption of lead (II) from wastewater by green algae *Cladophora fascicularis* (Deng et al., 2007). The biosorption of Cu^{2+} and Zn^{2+} by dried marine green macroalga (*C. linum*) was investigated by Ajjabi and Chouba (2009). At the optimum particle size (100–315 mm), biosorbent dosage (20 g/L) and initial solution pH 5, the dried alga

produced maximum Cu^{2+} and Zn^{2+} uptake values of 1.46 and 1.97 mmol/g, respectively.

Microbial removal of metal ions from wastewater has been indicated as being highly effective. Biosorption of heavy metals in aqueous solutions by bacteria includes *Bacillus cereus* (Pan et al., 2007), *Escherichia coli* (Souiri et al., 2009; Quintelas et al., 2009), *Pseudomonas aeruginosa* (Gabr et al., 2008; Tuzen et al., 2008), etc.

Fungi and yeasts are easy to grow, produce high yields of biomass and at the same time can be manipulated genetically and morphologically. Fungi biosorbents include *Aspergillus niger* (Amini et al., 2009; Tsekova et al., 2010), *Rhizopus arrhizus* (Aksu and Balibek, 2007; Bahadir et al., 2007), *Saccharomyces cerevisiae* (Chen and Wang, 2008; Cojocaru et al., 2009), *Lentinus edodes* (Bayramoğlu and Arıca, 2008), etc. There are a number of reports involving removal of heavy metals using *Rhizopus* biomass. Bhainsa and D'Souza (2008) investigated the removal of copper ion using NaOH treated *Rhizopus* oryzae biomass in a batch reactor. The maximum copper loading capacity of the viable and pretreated biomass was 19.4 and 43.7 mg/g, respectively.

Biosorbents were characteristic of broad sources, low-cost and rapid adsorption. Unfavorably, these researches were still in the theoretic and experimental phase. Moreover, the separation of biosorbents would be difficult after adsorption.

2.4. Membrane filtration

Membrane filtration technologies with different types of membranes show great promise for heavy metal removal for their high efficiency, easy operation and space saving. The membrane processes used to remove metals from the wastewater are ultra-filtration, reverse osmosis, nanofiltration and electrodialysis.

2.4.1. Ultrafiltration

Ultrafiltration (UF) is a membrane technique working at low transmembrane pressures for the removal of dissolved and colloidal material. Since the pore sizes of UF membranes are larger than dissolved metal ions in the form of hydrated ions or as low molecular weight complexes, these ions would pass easily through UF membranes. To obtain high removal efficiency of metal ions, the micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) was proposed.

MEUF was first introduced by Scamehorn et al. in the 1980s for the removal of dissolved organic compounds and multivalent metal ions from aqueous streams (Landaburu-Aguirre et al., 2009). MEUF has been proven to be an effective separation technique to remove metal ions from wastewater (Table 4). This separation technique is based on the addition of surfactants to wastewater. When the concentration of surfactants in aqueous solutions is beyond the critical micelle concentration (CMC), the surfactant molecules will aggregate into micelles that can bind metal ions to form large metal-surfactant structures. The micelles containing metal ions can be retained by a UF membrane with pore sizes smaller than micelle sizes, whereas the untrapped species readily pass through the UF membrane. To obtain the highest retentions, surfactants of electric charge opposite to that of the ions to be removed have to be used. Sodium dodecyl sulfate (SDS), an anionic surfactant, is often selected for the effective removal of heavy metal ions in MEUF.

Metal removal efficiency by MEUF depends on the characteristics and concentrations of the metals and surfactants, solution pH, ionic strength, and parameters related to membrane operation. Landaburu-Aguirre et al. (2009) investigated the removal of zinc from synthetic wastewater by MEUF using SDS. They found that rejection coefficients up to 99% were achieved when the surfactant to metal molar ratio (S/M) was above 5. Sampera et al. (2009) used MEUF to remove Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} from synthetic

Table 4
Heavy metal removal by MEUF and PEUF.

UF type	Membrane	Surfactant/complexing agent	Heavy metal	Initial conc.	Optimum pH	Removal efficiency (%)	Ref.
MEUF	Ceramic	Dodecylbenzenesulfonic acid, dodecylamine	Pb^{2+}, AsO_4^-	4.4–7.6 mg/L	7.47	Pb: >99%, As: 19%	Ferella et al., 2007
MEUF	Polysulfone	SDS	Cd^{2+}, Zn^{2+}	50 mg/L	NA	92–98	Huang et al., 2010
MEUF	Amicon regenerated cellulose	SDS	Cd^{2+}, Zn^{2+}	0.5 mM	NA	99	Landaburu-Aguirre et al., 2010
MEUF	Polycarbonate	Sodium lauryl ether sulfate	Ni^{2+}	0.2 mM	7	98.6	Danisa and Aydiner, 2009
PEUF	Polyethersulfone	PEI	Cu^{2+}, Ni^{2+}	50 mg/L	pH > 6.0, pH > 8.0	94, 100	Molinari et al., 2008
PEUF	Polyethersulfone	Carboxy methyl cellulose	Cu^{2+}, Cr^{3+}, Ni^{2+}	10 mg/L	7.0	97.6, 99.5, 99.1	Barakat and Schmidt, 2010
PEUF	AMICON 8400	Sodium polyacrylate, PEI	Cr(III), Cr(VI)	5, 50 mg/L	6–7, 5–6	82–100	Korus and Loska, 2009
PEUF	Ceramic	Poly(acrylic acid) sodium	Cu^{2+}	160 mg/L	5.5	99.5	Camarilloa et al., 2010
PEUF	Polysulfone	Poly(ammonium acrylate)	Cd(II)	112.4 mg/L	6.32	99	Ennigrou et al., 2009

NA: not available.

water using two anionic surfactants: SDS and linear alkylbenzene sulfonate (LAS) in a lab-scale membrane system. The molar concentration ratio of the surfactant to metal is higher than 5 in all the experiments. When the initial SDS concentration was below the CMC, metal retention higher than 90% was unexpectedly obtained, except for Ni^{2+}. Moreover, it was shown that complete removal of metal ions, except for Ni^{2+}, could be achieved at an LAS concentration below CMC.

The retentate is the concentrated solution of surfactants and heavy metals retained by membrane. Since the surfactant may account for a large portion of operating costs, it is essential to recover and reuse the surfactant as economically as feasible. And if the surfactant and heavy metals are not disposed, they will cause secondary pollution. Li et al. (2009) tested chelation followed by UF and acidification followed by UF for the separation of Cd^{2+} or Zn^{2+} from SDS micelles in simulated retentate solution of MEUF and the reuse of SDS. In the method using chelating agents, EDTA at pH 4.4 was the best for separating heavy metal ions (90.1% for Cd^{2+}, 87.1% for Zn^{2+}) and recovering SDS (65.5% for Cd^{2+}, 68.5% for Zn^{2+}). With the reclaimed SDS in MEUF, the removal efficiencies of heavy metal ions were 90.3% for Cd^{2+}, 89.6% for Zn^{2+}. In the method using acid agents, H_2SO_4 at pH 1.0 was the best for separating heavy metal ions (98.0% for Cd^{2+}, 96.1% for Zn^{2+}) and recovering SDS (58.1% for Cd^{2+}, 54.3% for Zn^{2+}). The efficiencies of reclaimed SDS were 88.1% for removing Cd^{2+} and 87.8% for removing Zn^{2+} in MEUF.

PEUF has also been proposed as a feasible method to separate a great variety of metal ions from aqueous streams (Table 4). PEUF uses water-soluble polymer to complex metallic ions and form a macromolecular, having a higher molecular weight than the molecular weight cut off of the membrane. The macromolecular will be retained when they are pumped through UF membrane. After that, retentate can be treated in order to recover metallic ions and to reuse polymeric agent. The main concern of the previous PEUF studies was to find suitable polymers to achieve complexation

with metal ions. Complexing agents such as polyacrylic acid (PAA) (Labanda et al., 2009), polyethyleneimine (PEI) (Aroua et al., 2007; Molinari et al., 2008), diethylaminoethyl cellulose (Trivunac and Stevanovic, 2006) and humic acid (Kim et al., 2005), etc., have been proven to achieve selective separation and recovery of heavy metals with low energy requirements.

The main parameters affecting PEUF are metal and polymer type, the ratio of metal to polymer, pH and existence of other metal ions in the solution. Molinari et al. (2008) used PEI as a polymer to study the complexation–ultrafiltration process in the selective removal of Cu(II) from Ni(II) contained in aqueous media. Preliminary tests showed that optimal chemical conditions for Cu(II) and Ni(II) complexation by the PEI were pH > 6.0 and 8.0, respectively, and polymer/metal weight ratio of 3.0 and 6.0, respectively. Aroua et al. (2007) investigated the removal of chromium species from aqueous dilute solutions using PEUF process by three water-soluble polymers, namely chitosan, PEI and pectin. High rejections approaching 100% for Cr(III) were obtained at pH higher than 7 for the three tested polymers.

The advantages of PEUF include high removal efficiency, high binding selectivity and highly concentrated metal concentrates for reuse, etc. There are a lot of publications in this topic, but it has not spread wide in the industry yet.

2.4.2. Reverse osmosis

The reverse osmosis (RO) process uses a semi-permeable membrane, allowing the fluid that is being purified to pass through it, while rejecting the contaminants. RO is one of the techniques able to remove a wide range of dissolved species from water. It accounts for more than 20% of the world's desalination capacity (Shahalam et al., 2002). RO is an increasingly popular wastewater treatment option in chemical and environmental engineering. Using appropriate RO systems to remove heavy metals have been investigated (Table 5), but these have yet to be widely applied.

Table 5
A list of some selected examples of heavy metal removal by RO, NF and NF + RO.

Membrane	Heavy metal	Initial metal Conc.	Removal efficiency (%)	Conditions	Ref.
RO	Cu^{2+}, Ni^{2+}	500 mg/L	99.5	Operation pressure 5 atm	Mohsen-Nia et al., 2007
RO	Cu^{2+}	20–100 mg/L	70–95	Low pressure reverse osmosis combined with electrowinning	Zhang et al., 2009
RO	As	<500 µg/L	As(V) 91–99, As(III) 20–55	NA	Chan and Dudeney, 2008
RO	Ni^{2+}, Zn^{2+}	Ni^{2+}: 44–169 Zn^{2+}: 64–170 mg/L	99.3 98.9	Operational pressure 1100 kPa	Ipek, 2005
NF	Cu^{2+}	10 mM	47–66	Transmembrane pressure (1–3 bar)	Chaabane et al., 2006
NF	Cr(VI)	NA	99.5	Surfactants enhanced NF	Muthukrishnan and Guha, 2008
NF	Cu^{2+}	0.47 M	96–98	Flat-heet NF membranes at 20 bar	Tanninen et al., 2006
RO + NF	Cu^{2+}	2 g/L	>95	Operating pressures 35 bar	Cséfalvay et al., 2009
RO + NF	Cu^{2+}	15 mg/L	95–99	Combination of flotation and membrane filtration, 3.8 bar	Sudilovskiy et al., 2008

NA: not available.

Cu^{2+} and Ni^{2+} ions were successfully removed by the RO process and the rejection efficiency of the two ions increased up to 99.5% by using Na_2EDTA (Mohsen-Nia et al., 2007). Dialynas and Diamadopoulos (2009) applied a pilot-scale membrane bioreactor system in combination with RO and they found heavy metal removal efficiencies were very high. The major drawback of RO is the high power consumption due to the pumping pressures, and the restoration of the membranes.

2.4.3. Nanofiltration

Nanofiltration (NF) is the intermediate process between UF and RO. NF is a promising technology for the rejection of heavy metal ions such as nickel (Murthy and Chaudhari, 2008), chromium (Muthukrishnan and Guha, 2008), copper (Cséfalvay et al., 2009; Ahmad and Ooi, 2010) and arsenic (Nguyen et al., 2009; Figoli et al., 2010) from wastewater. NF process benefits from ease of operation, reliability and comparatively low energy consumption as well as high efficiency of pollutant removal (Erikson, 1988).

Figoli et al. (2010) studied the removal of pentavalent arsenic from synthetic water by two commercial NF membrane (NF90 and N30F). They found that an increase of pH and a decrease of operating temperature and As feed concentration led to higher As removal for both membranes. Among the parameters affecting the As rejection, feed concentration plays a key role for the production of a permeate stream. In recent years, Murthy and Chaudhari devoted a lot in the removal of heavy metal ions using NF membrane. They reported the application of a thin-film composite polyamide NF membrane for the rejection of nickel ions from aqueous wastewater (Murthy and Chaudhari, 2008). The maximum observed rejection of nickel is found to be 98% and 92% for an initial feed concentration of 5 and 250 mg/L, respectively. And they investigated the binary heavy metals (cadmium and nickel) separation capability of a commercial NF membrane from aqueous solutions (Murthy and Chaudhari, 2009). The maximum observed solute rejection of nickel and cadmium ions is 98.94% and 82.69%, respectively, for an initial feed concentration of 5 mg/L.

There are many reports on the removal of heavy metal by NF and RO membrane. Cséfalvay et al. (2009) used NF and RO to recover copper from process wastes. Liu et al. (2008b) studied the performance of different NF and RO membranes in treating the toxic metal effluent from metallurgical industry. They reported that the product water by both NF and RO desalination satisfied the State Reutilization Qualification, but NF would be more suitable for large-scale industrial practice. Koseoglu and Kitis (2009) investigated the recovery of silver from mining wastewaters using NF or RO after the silver is taken into solution as AgCN employing re-cyanidation and subsequent sedimentation and/or pre-filtration of wastewaters. Silver recoveries achieved by hybrid cyanidation and membrane separation were 29–59% and 54–62% for NF and RO membranes, respectively.

2.4.4. Electrodialysis

Electrodialysis (ED) is another membrane process for the separation of ions across charged membranes from one solution to another using an electric field as the driving force. In most ED processes, ion-exchange membranes are used. The membranes are actually of two basic types: cation-exchange and anion-exchange membranes. This process has been widely used for the production of drinking and process water from brackish water and seawater, treatment of industrial effluents, recovery of useful materials from effluents and salt production (Sadrzadeha et al., 2009). ED has also proven a promising method in heavy metal wastewater treatment.

Nataraj et al. (2007) performed a new working system to investigate the removal of hexavalent chromium ions using a built ED pilot plant comprising a set of ion-exchange membranes. Results were satisfactory in meeting the maximum contamination level of 0.1 mg/L for chromium. The effectiveness of ED for the separation of Cu and Fe and water recovery from solutions in copper electrowinning operations was studied by Cifuentes et al. (2009). They found that ED proved very effective in the removal of Cu and Fe from the working solution. Lambert et al. (2006) studied the separation of Cr(III) from sodium ion by ED using modified cation-exchange membranes. Mohammadi et al. (2004) investigated the effect of operating parameters on Pb^{2+} separation from wastewater using ED. The results showed that increasing voltage and temperature improved cell performance; however, the separation percentage decreased with an increasing flow rate. At concentrations of more than 500 mg/L, dependence of separation percentage on concentration diminished.

2.5. Coagulation and flocculation

Coagulation and flocculation followed by sedimentation and filtration is also employed to remove heavy metal from wastewaters. Coagulation is the destabilization of colloids by neutralizing the forces that keep them apart. Many coagulants are widely used in the conventional wastewater treatment processes such as aluminium, ferrous sulfate and ferric chloride, resulting in the effective removal of wastewater particulates and impurities by charge neutralization of particles and by enmeshment of the impurities on the formed amorphous metal hydroxide precipitates. El Samrani et al. (2008) investigated the removal of heavy metal by coagulation of combined sewer overflow with two commercial coagulants, a ferric chloride solution and a polyaluminium chloride (PAC). They found excellent heavy metal elimination was achieved within a narrow range of coagulant around optimum coagulant concentrations.

Coagulation is one of the most important methods for wastewater treatment, but the main objects of coagulation are only the hydrophobic colloids and suspended particles. In order to remove both soluble heavy metal and insoluble substances efficiently by coagulation, sodium xanthogenate group was grafted to polyethyleneimine (Chang and Wang, 2007). This new kind of coagulant was an amphoteric polyelectrolyte. When the pH of water sample is lower, the colloidal substances with negative charges can be coagulated by it, but the cationic Ni^{2+} ion cannot be removed very well. When the pH of water sample is higher, the turbidity removal decreases, and the Ni^{2+} removal increases.

Flocculation is the action of polymers to form bridges between the flocs and bind the particles into large agglomerates or clumps. Once suspended particles are flocculated into larger particles, they can usually be removed or separated by filtration, straining or floatation. Today many kinds of flocculants, such as PAC, polyferric sulfate (PFS) and polyacrylamide (PAM), are widely used in the treatment of wastewater, however, it is nearly impracticable to remove heavy metal very well from wastewater directly by these current flocculants. Macromolecule heavy metal flocculants is a new kind of flocculant. Chang et al. (2009b) prepared a macromolecule heavy metal flocculant mercaptoacetyl chitosan by reacting chitosan with mercaptoacetic acid. They reported that this new flocculant could not only remove turbidity, but also remove heavy metals in wastewater. Flocculants of Konjac-graft-poly (acrylamide)-co-sodium xanthate (Duan et al., 2010) and polyampholyte chitosan derivatives – N-carboxyethylated chitosans (Bratskaya et al., 2009) were also used to remove heavy metals.

The research on flocculation by humic acid (HA) binding heavy metal is also investigated. The enhanced removal of heavy metal ions from solution, such as Pb^{2+} and Zn^{2+}, was studied by binding the ions to HA and then coagulating–flocculating with the cationic polyelectrolyte polydiallyldimethylammonium chloride (Poly-DADMAC) (Hankins et al., 2006). The removal of bound metal ions

was found to increase with the extent of coagulation–flocculation of the HA by PolyDADMAC. Generally, metal–HA complexes are removed from a solution by polyelectrolyte flocculation, followed by centrifugation or filtration. Recently, Tokuyama et al. (2010) proposed a flocculation technique using a thermosensitive polymer to remove undesirable heavy metals and humic substances, and this technique is free from centrifugation and filtration. Besides, a new commercial tannin-based flocculant has been reported to remove Zn^{2+}, Ni^{2+} and Cu^{2+} by coagulation–flocculation process (Heredia and Martín, 2009).

Generally, coagulation–flocculation can't treat the heavy metal wastewater completely (Chang and Wang, 2007). Therefore, coagulation–flocculation must be followed by other treatment techniques. Plattes et al. (2007) employed precipitation, coagulation and flocculation processes using ferric chloride to remove tungsten from industrial wastewater. Tungsten removal was found to be most efficient (98–99%) in acidic conditions (pH < 6). Bojic et al. (2009) explored spontaneous reduction–coagulation process using micro-alloyed aluminium composite in a laboratory semi-flow system to treat model heavy metal wastewater. The residual concentrations of metals were at admissible levels after only 20 min of treatment.

2.6. Flotation

Flotation has nowadays found extensive use in wastewater treatment. Flotation has been employed to separate heavy metal from a liquid phase using bubble attachment, originated in mineral processing. Dissolved air flotation (DAF), ion flotation and precipitation flotation are the main flotation processes for the removal of metal ions from solution.

DAF is to allow micro-bubbles of air to attach to the suspended particles in the water, developing agglomerates with lower density than water, causing the flocs to rise through the water and accumulating at the surface where they can be removed as sludge (Lundh et al., 2000). DAF had been widely studied to remove heavy metal in 1990s (Waters, 1990; Tassel et al., 1997; Tessele et al., 1998).

Ion flotation has been shown a promising method for the removal of heavy metal ions from wastewaters. The process of ion flotation is based on imparting the ionic metal species in wastewaters hydrophobic by use of surfactants and subsequent removal of these hydrophobic species by air bubbles (Polat and Erdogan, 2007). Yuan et al. (2008) investigated the potential of ion flotation to remove cadmium, lead and copper from dilute aqueous solution with a plant-derived biosurfactant tea saponin. The maximum removal of Pb^{2+}, Cu^{2+} and Cd^{2+} can reach 89.95%, 81.13% and 71.17%, respectively, when the ratio of collector to metal was 3:1. Polat and Erdogan (2007) implemented ion flotation to remove Cu^{2+}, Zn^{2+}, Cr^{3+} and Ag^+ from wastewaters. SDS and hexadecyltrimethyl ammonium bromide were used as collectors. Ethanol and methyl isobutyl carbinol were used as frothers. Metal removal reached about 74% under optimum conditions at low pH. At basic pH it became as high as 90%, probably due to the contribution from the flotation of metal precipitates.

Precipitate flotation process is another alternative of flotation method, based on the formation of precipitate and subsequent removal by attachment to air bubbles. Depending on the concentration of the metal solution, the precipitation may proceed via metal hydroxide formation or as a salt with a specific anion (sulfide, carbonate, etc.) (Capponi et al., 2006). The removal of Cr(III) by precipitate flotation from dilute aqueous solutions, using SDS as anionic collector and ethanol as frother was investigated at laboratory scale (Medina et al., 2005). The results showed that a 96.2% maximum removal was achieved at pH around 8.0.

2.7. Electrochemical treatment

Electrochemical methods involve the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state. Electrochemical wastewater technologies involve relatively large capital investment and the expensive electricity supply, so they haven't been widely applied. However, with the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide during the past two decades (Wang et al., 2007b). In this paper, the established technologies, electrocoagulation, electroflotation, and electrodeposition were examined.

Electrocoagulation (EC) involves the generation of coagulants in situ by dissolving electrically either aluminum or iron ions from aluminum or iron electrodes (Chen, 2004). The metal ion generation takes place at the anode, and hydrogen gas is released from the cathode. The hydrogen gas can help to float the flocculated particles out of the water (Chen, 2004). Heidmann and Calmano (2008) studied the performance of an EC system with aluminium electrodes for removing Zn^{2+}, Cu^{2+}, Ni^{2+}, Ag^+ and $Cr_2O_7^{2-}$. Initial concentrations from 50 mg/L to 5000 mg/L Zn, Cu, Ni and Ag did not influence the removal rates, whereas higher initial concentrations caused higher removal rates of Cr, Zn, Cu, Ni and Ag ions are hydrolyzed and co-precipitated as hydroxides. Cr(VI) was proposed to be reduced first to Cr(III) at the cathode before precipitating as hydroxide. Kabdaşlı et al. (2009) experimentally investigated the treatability of a metal plating wastewater containing complexed metals originating from the nickel and zinc plating process by EC using stainless steel electrodes. Their study demonstrated that the highest TOC abatement (66%) as well as nickel and zinc removals (100%) were achieved with an applied current density of 9 mA/cm² at the original electrolyte (chloride) concentration and original pH of the composite sample used. EC was also used to evaluate the treatment of synthetic solutions containing Hg^{2+} of concentration 2×10^{-5} M by Nanseu-Njiki et al. (2009). The removal efficiency was above 99.9% when the distance between the electrodes was 3 cm, the current density ranging from 2.5 Adm^{-2} to 3.125 Adm^{-2} and pH of the Hg^{2+} solutions from 3 to 7. Ölmez (2009) studied the performance of EC to remove hexavalent chromium having a high Cr(VI) concentration of 1470 mg/L. The optimum conditions for 100% Cr(VI) removal were established as 7.4 A applied electric current, 33.6 mM electrolyte (NaCl) concentration and 70 min application time. Besides, EC has been employed to remove Mn^{2+}, As(V), Mn^{2+}, and Ni^{2+}, etc. (Table 6)

Table 6
Heavy metal removal by electrochemical methods.

Method	Heavy metal	Current density	Initial conc. (mg/L)	Optimum pH	Removal efficiency (%)	Ref.
EC	Mn^{2+}	6.25 mA/cm²	100	7.0	78.2	Shafaei et al., 2010
EC	Ni^{2+}, Zn^{2+}	9 mA/cm²	248, 270, 282; 217, 232, 236	6.0	100	Kabdaşlı et al., 2009
EC	As(III), As(V)	3.7–4.6 mA/cm²	2.24	8.30	>99	Parga et al., 2005
EC	Cr(VI)	Current 7.4 A	1470	1.84	100	Ölmez, 2009
EF	Zn^{2+}	8 mA/cm²	20	7.0	96	Casqueira et al., 2006
EF	Ni^{2+}, Cu^{2+}	Current 0.3 A	100	6	98–99	Khelifa et al., 2005

Electroflotation (EF) is a solid/liquid separation process that floats pollutants to the surface of a water body by tiny bubbles of hydrogen and oxygen gases generated from water electrolysis. EF has wide range applications in heavy metals removal from industrial wastewater. Belkacem et al. (2008) studied the clarification of wastewater using the EF technique with aluminum electrodes. The application of the optimized parameters on the separation of some heavy metal ions such as iron, nickel, copper, zinc, lead and cadmium was studied. Their study demonstrated that the metal removal rate reached 99%. EF with iron electrodes hybrid with filter paper, micro- and ultra- filtration bench scale tests were performed to obtain high removal efficiency of nickel with and without the introduction of external oxygen (Sun et al., 2009). Research results indicated that with the hybridization of EF without aeration followed by microfiltration, and aeration-enhanced EF followed by settling and mechanical filtration, the residual nickel and iron could meet the discharge standard of metal finishing industry.

Electrodeposition has been usually applied for the recovery of metals from wastewater. It is a "clean" technology with no presence of the permanent residues for the separation of heavy metals (Issabayeva et al., 2006). Oztekin and Yazicigil (2006) found that electrodeposition is an applicable method for the recovery of metals under appropriate conditions. They investigated the electrolytic recovery of metals from aqueous solutions containing complexing chelating agents such as EDTA, nitrilotriacetic acid and citrate in a two-chamber cell separating with a commercial cation-exchange membrane. The results showed that least value of recovery of metal was approximately 40% and this value increased due to the type of the experiments up to 90% for copper. Chang et al. (2009a) used electrodeposition in conjunction with ultrasound to reclaim EDTA–copper wastewater. They found that the technique can effectively remove copper (95.6%) and decompose EDTA (84% COD removal) from wastewater. Issabayeva et al. (2006) presented on the electrodeposition of copper and lead ions onto palm shell AC electrodes. Besides, recovery of Cd and Ni by electrodeposition was investigated (Yang, 2003).

3. Remarks of heavy metal treatment methods

Although all the heavy metal wastewater treatment techniques can be employed to remove heavy metals, they have their inherent advantages and limitations.

Heavy metals removal from aqueous solutions has been traditionally carried out by chemical precipitation for its simplicity process and inexpensive capital cost. However, chemical precipitation is usually adapted to treat high concentration wastewater containing heavy metal ions and it is ineffective when metal ion concentration is low. And chemical precipitation is not economical and can produce large amount of sludge to be treated with great difficulties.

Ion exchange has been widely applied for the removal of heavy metal from wastewater. However, ion-exchange resins must be regenerated by chemical reagents when they are exhausted and the regeneration can cause serious secondary pollution. And it is expensive, especially when treating a large amount of wastewater containing heavy metal in low concentration, so they cannot be used at large scale.

Adsorption is a recognized method for the removal of heavy metals from low concentration wastewater containing heavy metal. The high cost of AC limits its use in adsorption. Many varieties of low-cost adsorbents have been developed and tested to remove heavy metal ions. However, the adsorption efficiency depends on the type of adsorbents. Biosorption of heavy metals from aqueous solutions is a relatively new process that has proven very promising for the removal of heavy metal from wastewater.

Membrane filtration technology can remove heavy metal ions with high efficiency, but its problems such as high cost, process complexity, membrane fouling and low permeate flux have limited their use in heavy metal removal.

Using coagulation–flocculation heavy metal wastewater treatment technique, the produced sludge has good sludge settling and dewatering characteristics. But this method involves chemical consumption and increased sludge volume generation.

Flotation offers several advantages over the more conventional methods, such as high metal selectivity, high removal efficiency, high overflow rates, low detention periods, low operating cost and production of more concentrated sludge (Rubio et al., 2002). But the disadvantages involve high initial capital cost, high maintenance and operation costs.

Electrochemical heavy metal wastewater treatment techniques are regarded as rapid and well-controlled that require fewer chemicals, provide good reduction yields and produce less sludge. However, electrochemical technologies involving high initial capital investment and the expensive electricity supply, this restricts its development.

Although all above techniques can be employed for the treatment of heavy metal wastewater, it is important to mention that the selection of the most suitable treatment techniques depends on the initial metal concentration, the component of the wastewater, capital investment and operational cost, plant flexibility and reliability and environmental impact, etc. (Kurniawan et al., 2006).

4. Conclusions

Hazardous heavy metal pollution of wastewater is one of the most important environmental problems throughout the world. To meet the increased more and more stringent environmental regulations, a wide range of treatment technologies such as chemical precipitation, coagulation–flocculation, flotation, ion-exchange and membrane filtration, have been developed for heavy metal removal from wastewater. It is evident from the literature survey of 185 articles that ion-exchange, adsorption and membrane filtration are the most frequently studied for the treatment of heavy metal wastewater. Ion-exchange processes have been widely used to remove metals from wastewater. Adsorption by low-cost adsorbents and biosorbents is recognized as an effective and economic method for low concentration heavy metal wastewater treatment as an alternative AC. Membrane filtration technology can remove heavy metal ions with high efficiency.

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