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REVIEW ARTICLE

New trends in removing heavy metals from industrial wastewater

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Abstract Innovative processes for treating industrial wastewater containing heavy metals often involve technologies for reduction of toxicity in order to meet technology-based treatment standards. This article reviews the recent developments and technical applicability of various treatments for the removal of heavy metals from industrial wastewater. A particular focus is given to innovative physico-chemical removal processes such as; adsorption on new adsorbents, membrane filtration, electrodialysis, and photocatalysis. Their advantages and limitations in application are evaluated. The main operating conditions such as pH and treatment performance are presented. Published studies of 94 cited references (1999–2008) are reviewed.

It is evident from survey that new adsorbents and membrane filtration are the most frequently studied and widely applied for the treatment of metal-contaminated wastewater. However, in the near future, the most promising methods to treat such complex systems will be the photocatalytic ones which consume cheap photons from the UV-near visible region. They induce both degradation of organic pollutants and recovery of metals in one-pot systems. On the other hand, from the conventional processes, lime precipitation has been found as one of the most effective means to treat inorganic effluent with a metal concentration of >1000 mg/L. It is important to note that the overall treatment cost of metal-contaminated water varies, depending on the process employed and the local conditions. In general, the technical applicability, plant simplicity and cost-effectiveness are the key factors in selecting the most suitable treatment for inorganic effluent

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Contents

1. Introduction

Due to the discharge of large amounts of metal-contaminated wastewater, industries bearing heavy metals, such as Cd, Cr, Cu, Ni, As, Pb, and Zn, are the most hazardous among the chemical-intensive industries. Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders (Babel and Kurniawan, 2004). Therefore, it is necessary to treat metal-contaminated wastewater prior to its discharge to the environment. Heavy metal removal from inorganic effluent can be achieved by conventional treatment processes such as chemical precipitation, ion exchange, and electrochemical removal. These processes have significant disadvantages, which are, for instance, incomplete removal, high-energy requirements, and production of toxic sludge (Eccles, 1999).

Recently, numerous approaches have been studied for the development of cheaper and more effective technologies, both to decrease the amount of wastewater produced and to improve the quality of the treated effluent. Adsorption has become one of the alternative treatments, in recent years, the search for low-cost adsorbents that have metal-binding capacities has intensified (Leung et al., 2000). The adsorbents may be of mineral, organic or biological origin, zeolites, industrial by-products, agricultural wastes, biomass, and polymeric materials (Kurniawan et al., 2005). Membrane separation has been increasingly used recently for the treatment of inorganic effluent due to its convenient operation. There are different types of membrane filtration such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) Kurniawan et al., 2006. Electrotreatments such as electrodialysis (Pedersen, 2003) has also contributed to environmental protection. Photocatalytic process is an innovative and promising technique for efficient destruction of pollutants in water (Skubal et al., 2002). Although many techniques can be employed for the treatment of inorganic effluent, the ideal treatment should be not only suitable, appropriate and applicable to the local conditions, but also able to meet the maximum contaminant level (MCL) standards established. This article presents an overview of various innovative physico-chemical treatments for removal of heavy metals from industrial wastewater. Their advantages and limitations in application are evaluated. To highlight their removal performance, the main operating conditions such as pH and treatment efficiency are presented as well.

2. Heavy metals in industrial wastewater

2.1. Definition and toxicity

Heavy metals are generally considered to be those whose density exceeds 5 g per cubic centimeter. A large number of elements fall into this category, but the ones listed in Table 1 are those of relevance in the environmental context. Arsenic is usually regarded as a hazardous heavy metal even though it is actually a semi-metal. Heavy metals cause serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, nervous system, and damaging of the fetal brain. At higher doses, heavy metals can cause irreversible brain damage. Children may receive higher doses of metals from food than adults, since they consume more food for their body weight than adults. Wastewater regulations were established to minimize human and environmental exposure to hazardous chemicals. This includes limits on the types and concentration of heavy metals that may be present in the discharged wastewater. The MCL standards, for those heavy metals, established by USEPA (Babel and Kurniawan, 2003) are summarized in Table 1.

2.2. Industrial wastewater sources

Industrial wastewater streams containing heavy metals are produced from different industries. Electroplating and metal sur-

Table 1 The MCL standards for the most hazardous heavy metals (Babel and Kurniawan, 2003).

Heavy metal	Toxicities	MCL (mg/L)
Arsenic	Skin manifestations, visceral cancers, vascular disease	0.050
Cadmium	Kidney damage, renal disorder, human carcinogen	0.01
Chromium	Headache, diarrhea, nausea, vomiting, carcinogenic	0.05
Copper	Liver damage, Wilson disease, insomnia	0.25
Nickel	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20
Zinc	Depression, lethargy, neurological signs and increased thirst	0.80
Lead	Damage the fetal brain, diseases of the kidneys, circulatory system, and nervous system	0.006
Mercury	Rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system	0.00003

face treatment processes generate significant quantities of wastewaters containing heavy metals (such as cadmium, zinc, lead, chromium, nickel, copper, vanadium, platinum, silver, and titanium) from a variety of applications. These include electroplating, electroless depositions, conversion-coating, anodizing-cleaning, milling, and etching. Another significant source of heavy metals wastes result from printed circuit board (PCB) manufacturing. Tin, lead, and nickel solder plates are the most widely used resistant overplates. Other sources for the metal wastes include; the wood processing industry where a chromated copper-arsenate wood treatment produces arsenic-containing wastes; inorganic pigment manufacturing producing pigments that contain chromium compounds and cadmium sulfide; petroleum refining which generates conversion catalysts contaminated with nickel, vanadium, and chromium; and photographic operations producing film with high concentrations of silver and ferrocyanide. All of these generators produce a large quantity of wastewaters, residues, and sludges that can be categorized as hazardous wastes requiring extensive waste treatment (Sorme and Lagerkvist, 2002).

2.3. Conventional processes for removal

The conventional processes for removing heavy metals from wastewater include many processes such as chemical precipitation, flotation, adsorption, ion exchange, and electrochemical deposition. Chemical precipitation is the most widely used for heavy metal removal from inorganic effluent. The conceptual mechanism of heavy metal removal by chemical precipitation is presented in Eq. (1) Wang et al., 2004:

$$M^{2+} + 2(OH)^- \leftrightarrow M(OH)_2 \downarrow \quad (1)$$

where M^{2+} and OH^- represent the dissolved metal ions and the precipitant, respectively, while $M(OH)_2$ is the insoluble metal hydroxide. Adjustment of pH to the basic conditions (pH 9–11) is the major parameter that significantly improves heavy metal removal by chemical precipitation (Fig. 1). Lime and limestone are the most commonly employed precipitant agents due to their availability and low-cost in most countries (Mirbagherp and Hosseini, 2004; Aziz et al., 2008). Lime precipitation can be employed to effectively treat inorganic effluent with a metal concentration of higher than 1000 mg/L. Other advantages of using lime precipitation include the simplicity of the process, inexpensive equipment requirement, and convenient and safe operations. However, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge. Other drawbacks are its excessive sludge production that requires further treatment, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal (Aziz et al., 2008).

Ion exchange is another method used successfully in the industry for the removal of heavy metals from effluent. An ion exchanger is a solid capable of exchanging either cations or anions from the surrounding materials. Commonly used matrices for ion exchange are synthetic organic ion exchange resins. The disadvantage of this method is that it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater. Moreover ion exchange is nonselective and is highly sensitive to the pH of the solution. Electrolytic recovery or electro-winning is one of the many technologies used to remove metals from process water streams. This process uses electricity to pass a current through an aqueous metal-bearing solution containing a cathode plate and an insoluble anode. Positively charged metallic ions cling to the negatively charged cathodes leaving behind a metal deposit that is strippable and recoverable. A noticeable disadvantage was that corrosion could become a significant limiting factor, where electrodes would frequently have to be replaced (Kurniawan et al., 2006).

3. Adsorption on new adsorbents

Sorption is transfer of ions from water to the soil i.e. from solution phase to the solid phase. Sorption actually describes a group of processes, which includes adsorption and precipitation reactions. Recently, adsorption has become one of the alternative treatment techniques for wastewater laden with heavy metals. Basically, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions (Kurniawan and Babel, 2003). Various low-cost adsorbents, derived from agricultural waste, industrial by-product, natural material, or modified biopolymers, have been recently developed and applied for the removal of heavy metals from metal-contaminated wastewater. In general, there are three main steps involved in pollutant sorption onto solid sorbent: (i) the transport of the pollutant from the bulk solution to the sorbent surface; (ii) adsorption on the particle surface; and (iii) transport within the sorbent particle. Technical applicability and cost-effectiveness are the key factors that play major roles in the selection of the most suitable adsorbent to treat inorganic effluent.

3.1. Adsorption on modified natural materials

Natural zeolites gained a significant interest, mainly due to their valuable properties as ion exchange capability. Among the most frequently studied natural zeolites, clinoptilolite was

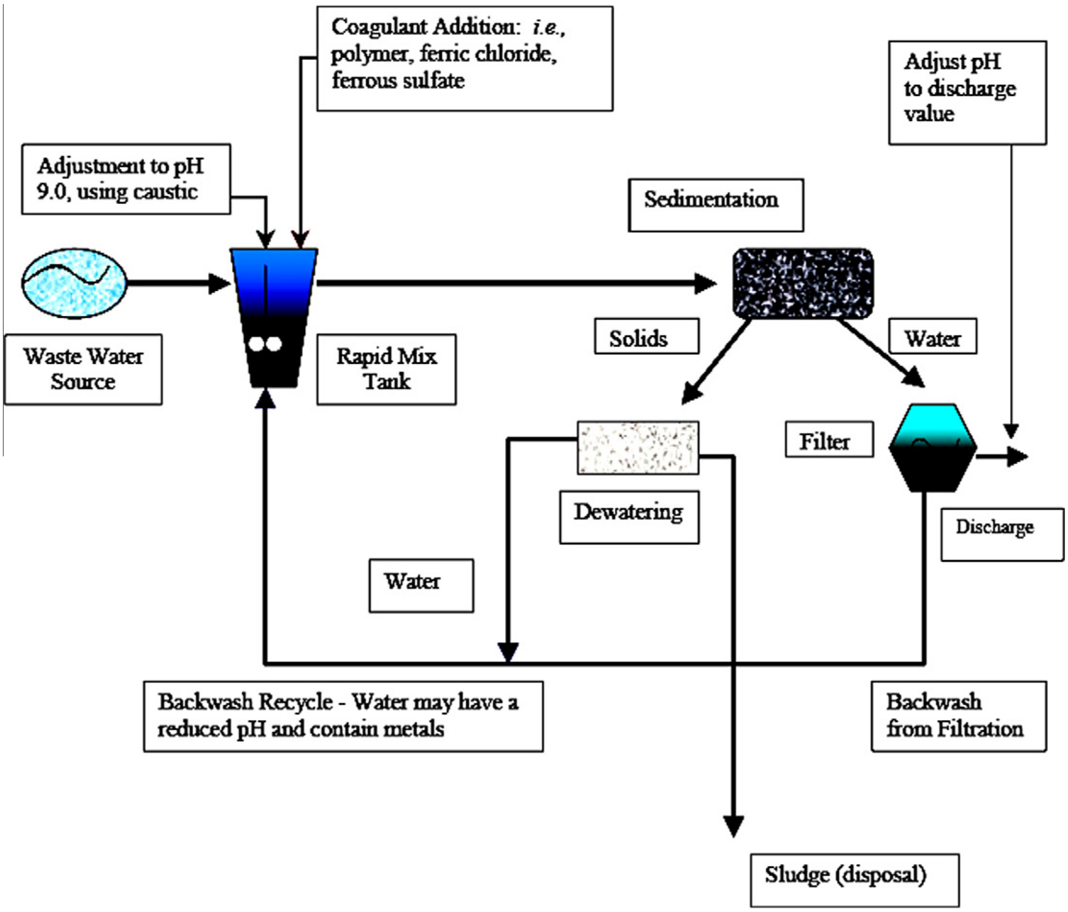

Figure 1 Processes of a conventional metals precipitation treatment plant (Wang et al., 2004).

shown to have high selectivity for certain heavy metal ions such as Pb(II), Cd(II), Zn(II), and Cu(II). It was demonstrated that the cation-exchange capability of clinoptilolite depends on the pre-treatment method and that conditioning improves its ion exchange ability and removal efficiency (Babel and Kurniawan, 2003; Bose et al., 2002). The ability of different types of synthetic zeolite for heavy metals removal was recently investigated. The role of pH is very important for the selective adsorption of different heavy metal ions (Basaldella et al., 2007; Ŕıos et al., 2008; Barakat, 2008a). Basaldella et al. (2007) used NaA zeolite for removal of Cr(III) at neutral pH, while Barakat (2008a) used 4A zeolite which was synthesized by dehydroxylation of low grade kaolin. Barakat reported that Cu(II) and Zn(II) were adsorbed at neutral and alkaline pH, Cr(VI) was adsorbed at acidic pH while the adsorption of Mn(IV) was achieved at high alkaline pH values. Nah et al. (2006) prepared synthetic zeolite magnetically modified with iron oxide (MMZ). MMZ showed high adsorption capacities for the Pb(II) ion and a good chemical resistance in a wide pH range 5–11. The natural clay minerals can be modified with a polymeric material in a manner that this significantly improves their capability to remove heavy metals from aqueous solutions. These kinds of adsorbents are called clay–polymer composites (Vengris et al., 2001; Sölenera et al., 2008; Abu-Eishah, 2008). Different phosphates such as; calcined phosphate at 900 °C, activated phosphate (with nitric acid), and zirconium phosphate have been employed as new adsorbents for removal of heavy metals from aqueous solution (Aklil et al., 2004; Moufliha et al., 2005; Pan et al., 2007). Fig. 2 shows the adsorption isotherm of Pb(II), Cu(II), and Zn(II) onto calcined phosphate at pH 5 (Aklil et al., 2004). Table 2 presents the highest reported metal adsorption capacities of low-cost adsorbents from various modified natural materials.

3.2. Adsorption on industrial by-products

Industrial by-products such as fly ash, waste iron, iron slags, hydrous titanium oxide, can be chemically modified to enhance its removal performance for metal removal from wastewater.

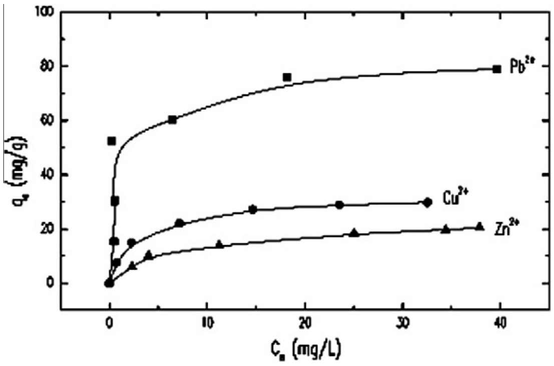

Figure 2 Adsorption isotherm of Pb(II), Cu(II), and Zn(II) onto calcined phosphate (Aklil et al., 2004).

Table 2 Adsorption capacities of modified natural materials for heavy metals.

Adsorbent	Adsorption capacity (mg/g)						References
	Pb^{2+}	Cd^{2+}	Zn^{2+}	Cu^{2+}	Cr^{6+}	Ni^{2+}	
Zeolite, clinoptilolite	1.6	2.4	0.5	1.64		0.4	Babel and Kurniawan (2003)
Modified zeolite, MMZ	123					8	Nah et al. (2006)
HCl-treated clay			63.2	83.3			Vengris et al. (2001)
Clay/poly(methoxyethyl)acrylamide	81.02		20.6	29.8		80.9	Sölenera et al. (2008)
	85.6						Aklil et al. (2004)
Calcined phosphate	155.0						Moufliha et al. (2005)
Activated phosphate	4						Pan et al. (2007)
Zirconium phosphate	398						

Several studies have been conducted; Lee et al. (2004) studied green sands, another by-product from the iron foundry industry, for Zn(II) removal. Feng et al. (2004) investigated Cu(II) and Pb(II) removal using iron slag. A pH range from 3.5 to 8.5 [for Cu(II)] and from 5.2 to 8.5 [for Pb(II)] was optimized. Fly ashes were also investigated as adsorbents for removal of toxic metals. Gupta et al. (2003) explored bagasse fly ash, a solid waste from sugar industry, for Cd(II) and Ni(II) removal from synthetic solution at pH ranging from 6.0 to 6.5. Alinnor (2007) used fly ash from coal-burning for removal of Cu(II) and Pb(II) ions. Sawdust treated with 1,5-disodium hydrogen phosphate was used for adsorption of Cr(VI) at pH 2 Uysal and Ar, 2007. Iron based sorbents such as ferrosorp plus (Genç-Fuhrman et al., 2008) and synthetic nanocrystalline akaganeite (Deliyanni et al., 2007) were recently used for simultaneous removal of heavy metals. Ghosh et al. (2003) and Barakat (2005) studied hydrous titanium oxide for adsorption of Cr(VI) and Cu(II), respectively. Barakat reported that, the adsorbed Cu(II) aqueous species can undergo surface hydrolysis reaction as pH rises. This yields a series of surface Cu(II) complexes such as $TiO–CuOH^{+}$, $TiO–Cu(OH)_2$, and $TiO–Cu(OH)_3^{-}$ species. The formation of surface metal complexes can also be depicted conceptually by the following scheme (Fig. 3).

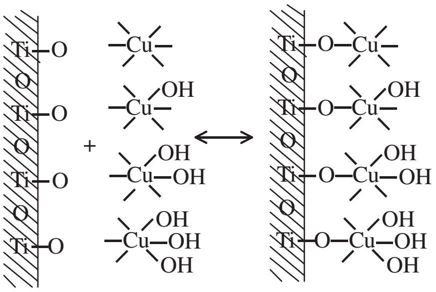

Figure 3 The adsorption mechanism of Cu(II) on hydrous TiO_2 (Barakat, 2005).

Zeta potential of TiO_2 and its adsorption behavior to Cu(II) in aqueous solution are shown in Fig. 4(a and b) Barakat, 2005. TiO_2 particles are negatively charged at pH ⩾6, and so complete Cu(II) adsorption was achieved at such pH range.

3.3. Adsorption on modified agriculture and biological wastes (bio-sorption)

Recently, a great deal of interest in the research for the removal of heavy metals from industrial effluent has been focused on the use of agricultural by-products as adsorbents. The use of agricultural by-products in bioremediation of heavy metal ions, is known as bio-sorption. This utilizes inactive (non-living) microbial biomass to bind and concentrate heavy metals from waste streams by purely physico-chemical pathways (mainly chelation and adsorption) of uptake (Igwe et al., 2005). New resources such as hazelnut shell, rice husk, pecan shells, jackfruit, maize cob or husk can be used as an adsorbent for heavy metal uptake after chemical modification or conversion by heating into activated carbon. Ajmal et al.

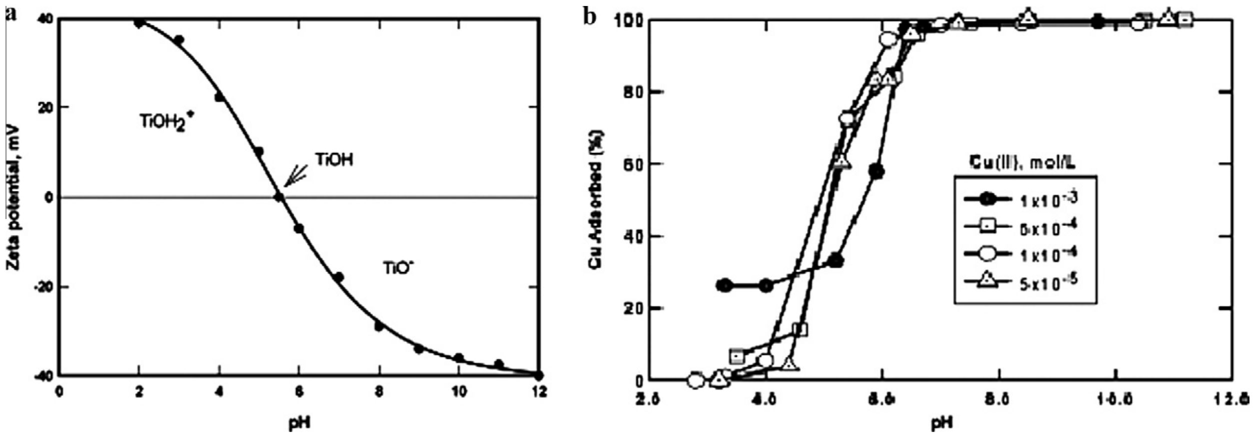

Figure 4 (a) Zeta potential of TiO_2 in aqueous solution. (b) Adsorption of Cu(II) on TiO_2.

Table 3 Adsorption capacities of some agricultural and biological wastes for heavy metals.

Adsorbent	Adsorption capacity (mg/g)						References
	Pb^{2+}	Cd^{2+}	Zn^{2+}	Cu^{2+}	Cr^{6+}	Ni^{2+}	
Maize cope and husk	456	493.7	495.9				Igwe et al. (2005)
Orange peel						158	Ajmal et al. (2000)
Coconut shell charcoal					3.65		Babel and Kurniawan (2004)
Pecan shells activated carbon			13.9	31.7			Bansode et al. (2003)
Rice husk		2.0			0.79		Bishnoi et al. (2003)
Modified rice hull					23.4		Tang et al. (2003)
Spirogyra (green alga)				133			Gupta et al. (2006)
Ecklonia maxima – marine alga	235			90			Fenga and Aldrich (2004)
Ulva lactuca					112.3		El-Sikaily et al. (2007)
Oedogonium species	145						Gupta and Rastogi (2008)
Nostoc species	93.5						Gupta and Rastogi (2008)
Bacillus – bacterial biomass	467	85.3	418	381	39.9		Ahluwalia and Goyal (2006)

(2000) employed orange peel for Ni(II) removal from simulated wastewater. They found that the maximum metal removal occurred at pH 6.0. The applicability of coconut shell charcoal (CSC) modified with oxidizing agents and/or chitosan for Cr(VI) removal was investigated by Babel and Kurniawan (2004). Cu(II) and Zn(II) removal from real wastewater were studied using pecan shells-activated carbon (Bansode et al., 2003) and potato peels charcoal (Amana et al., 2008). Bishnoi et al. (2003) conducted a study on Cr(VI) removal by rice husk-activated carbon from an aqueous solution. They found that the maximum metal removal by rice husk took place at pH 2.0. Rice hull, containing cellulose, lignin, carbohydrate and silica, was investigated for Cr(VI) removal from simulated solution (Tang et al., 2003). To enhance its metal removal, the adsorbent was modified with ethylenediamine. The maximum Cr(VI) adsorption of 23.4 mg/g was reported to take place at pH 2. Other type of biosorbents, such as the biomass of marine dried green alga (biological materials) (Gupta et al., 2006; Fenga and Aldrich, 2004; El-Sikaily et al., 2007; Gupta and Rastogi, 2008; Ahmady-Asbchin et al., 2008), were investigated for up-taking of some heavy metals from aqueous solution. Some of the used alga wastes were; *Spirogyra* species (Gupta et al., 2006), Ecklonia maxima (Fenga and Aldrich, 2004), *Ulva lactuca (El-Sikaily et al., 2007), Oedogonium* sp. and *Nostoc* sp. (Gupta and Rastogi, 2008), and brown alga *Fucus serratus* (Ahmady-Asbchin et al., 2008). On the whole, an acidic pH ranging 2–6 is effective for metal removal by adsorbents from biological wastes. The mechanism of up-taking heavy metal ions can take place by metabolism-independent metal-binding to the cell walls and external surfaces (Deliyanni et al., 2007). This involves adsorption processes such as ionic, chemical and physical adsorption. A variety of ligands located on the fungal walls are known to be involved in metal chelation. These include carboxyl, amine, hydroxyl, phosphate and sulfhydryl groups. Metal ions could be adsorbed by complexing with negatively charged reaction sites on the cell surface. Table 3 shows the adsorption capacities of different biosorbents.

3.4. Adsorption on modified biopolymers and hydrogels

Biopolymers are industrially attractive because they are, capable of lowering transition metal ion concentrations to sub-part per billion concentrations, widely available, and environmentally safe. Another attractive feature of biopolymers is that they posses a number of different functional groups, such as hydroxyls and amines, which increase the efficiency of metal ion uptake and the maximum chemical loading possibility. New polysaccharide-based-materials were described as modified biopolymer adsorbents (derived from chitin, chitosan, and starch) for the removal of heavy metals from the wastewater (Table 4). There are two main ways for preparation of sorbents containing polysaccharides: (a) crosslinking reactions, a reaction between the hydroxyl or amino groups of the chains with a coupling agent to form water-insoluble crosslinked networks (gels); (b) immobilization of polysaccharides on insoluble supports by coupling or grafting reactions in order to give hybrid or composite materials (Crini, 2005). Chitin is a naturally abundant mucopolysaccharide extracted from crustacean shells, which are waste products of seafood processing industries. Chitosan, which can be formed by deacetylation of chitin, is the most important derivative of chitin. Chitosan in partially converted crab shell waste is a powerful chelating agent and interacts very efficiently with transition metal ions (Pradhan, 2005). Recently other modified chitosan beads were proposed for diffusion of metal ions through crosslinked chitosan membranes (Lee et al., 2001). The excellent saturation sorption capacity for Cu(II) with the crosslinked chitosan beads was achieved at pH 5. Liu et al. (2003) prepared new hybrid materials that adsorb transition metal ions by immobilizing chitosan on the surface of non-porous glass beads. Column chromatography on the resulting glass beads revealed that they have strong affinities to Cu(II), Fe(III) and Cd(II). Yi et al. (2003) proposed the use of chitosan derivatives containing crown ether. The materials had high adsorption capacity for Pb(II), Cr(III), Cd(II) and Hg(II). The materials can be

Table 4 Adsorption capacities of modified biopolymers for heavy metals (Crini, 2005).

Adsorbent	Adsorption capacity (mg/g)					
	Pb^{2+}	Cd^{2+}	Zn^{2+}	Cu^{2+}	Cr^{6+}	As^{5+}
Crosslinked chitosan		150		164		230
Crosslinked starch gel	433			135		
Alumina/chitosan composite				200		

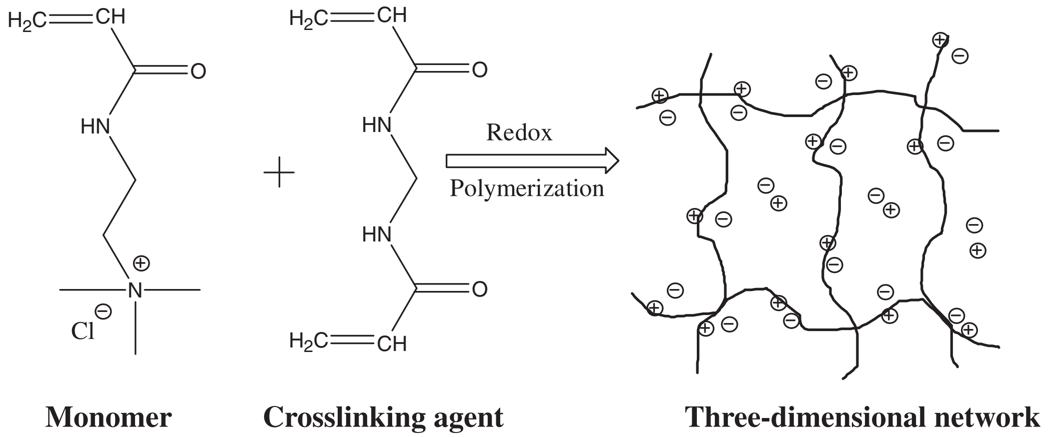

Figure 5 Three-dimensional network formation of cationic hydrogel (Barakat and Sahiner, 2008).

regenerated and their selectivity properties were better than crosslinked chitosan without crown ether. The sorption mechanism of polysaccharide-based-materials is different from those of other conventional adsorbents. These mechanisms are complicated because they implicate the presence of different interactions. Metal complexation by chitosan may thus involve two different mechanisms (chelation versus ion exchange) depending on the pH since this parameter may affect the protonation of the macromolecule (Crini, 2005). Chitosan is characterized by its high percentage of nitrogen, present in the form of amine groups that are responsible for metal ion binding through chelation mechanisms. Amine sites are the main reactive groups for metal ions though hydroxyl groups, especially in the C-3 position, and they may contribute to adsorption. However, chitosan is also a cationic polymer and its p*K*a ranges from 6.2 to 7. Thereby, in acidic solutions it is protonated and possesses electrostatic properties. Thus, it is also possible to sorb metal ions through anion exchange mechanisms. Sorbent materials containing immobilized thiacrown ethers were prepared by immobilizing the ligands into sol–gel matrix (Saad et al., 2006). The competitive sorption characteristics of a mixture of Zn(II), Cd(II), Co(II), Mn(II), Cu(II), Ni(II), and Ag(I) were studied. The results revealed that the thiacrown ethers exhibit highest selectivity toward Ag(I).

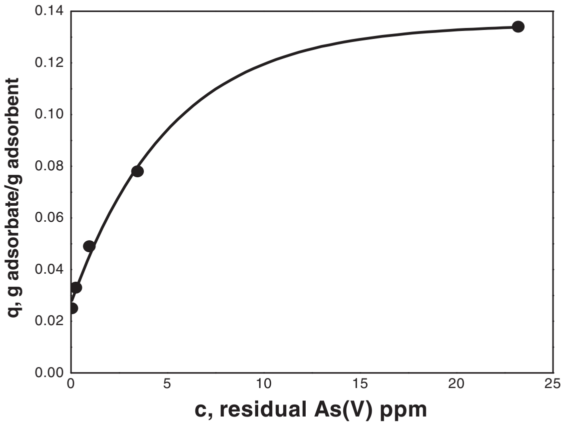

Figure 6 Adsorption isotherm of As(V) onto the hydrogel (Barakat and Sahiner, 2008).

Hydrogels, which are crosslinked hydrophilic polymers, are capable of expanding their volumes due to their high swelling in water. Accordingly they are widely used in the purification of wastewater. Various hydrogels were synthesized and their adsorption behavior for heavy metals was investigated. Kesenci et al. (2002) prepared poly(ethyleneglycol dimethacrylate-co-acrylamide) hydrogel beads with the following metals in the order Pb(II) > Cd(II) > Hg(II); Essawy and Ibrahim (2004) prepared poly(vinylpyrrolidone-co-methylacrylate) hydrogel with Cu(II) > Ni(II) > Cd(II); while Barakat and Sahiner (2008) prepared poly(3-acrylamidopropyl)trimethyl ammonium chloride hydrogels for As(V) removal. The removal is basically governed by the water diffusion into the hydrogel, carrying the heavy metals inside especially in the absence of strongly binding sites. Maximum binding capacity increases with pH increase to >6. Fig. 5 shows the schematic representation of polymerization/crosslinking reaction that results in three-dimensional network formation of cationic hydrogel, while the adsorption isotherm of As(V) onto the hydrogel is shown in Fig. 6.

4. Membrane filtration

Membrane filtration has received considerable attention for the treatment of inorganic effluent, since it is capable of removing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultrafiltration, nanofiltration and reverse osmosis can be employed for heavy metal removal from wastewater.

Ultrafiltration (UF) utilizes permeable membrane to separate heavy metals, macromolecules and suspended solids from inorganic solution on the basis of the pore size (5–20 nm) and molecular weight of the separating compounds (1000–100,000 Da). These unique specialties enable UF to allow the passage of water and low-molecular weight solutes, while retaining the macromolecules, which have a size larger than the pore size of the membrane (Vigneswaran et al., 2004). Some significant findings were reported by Juang and Shiau (2000), who studied the removal of Cu(II) and Zn(II) ions from synthetic wastewater using chitosan-enhanced membrane filtration. The amicon-generated cellulose YM10 was used as the ultrafilter. About 100% and 95% rejection were achieved at pH ranging from 8.5 to 9.5 for Cu(II) and Zn(II) ions, respectively. The results indicated that chitosan significantly enhanced metals removal by 6–10 times compared to using membrane alone. This could be attributed to the major role of the amino groups of chitosan chain, which served as coordination site for metal-binding. In acidic conditions, the amino groups of chitosan are protonated after reacting with H^+ ions as follows:

$$RNH_2 + H^+ \leftrightarrow RNH_3^+, \quad \log K_p = 6.3 \tag{2}$$

Having the unshared electron pair of the nitrogen atom as the sole electron donor, the non-protonated chitosan binds with the unsaturated transition metal cation through the formation of coordination bond. For most of the chelating adsorbent, the functional groups with the donor atoms are normally attached to the metal ions, thus leading to a donor–acceptor interaction between chitosan and the metal ions (Fei et al., 2005), as indicated by the Eq. (3):

$$M^{2+} + nRNH_2 \leftrightarrow M\text{–}(RNH_2)_n^{2+} \tag{3}$$

where M and RNH_2 represent metal and the amino group of chitosan, respectively, while n is the number of the unprotonated chitosan bound to the metal. Combination of Eqs. (2) and (3) gives the overall reaction as follows:

$$M^{2+} + nRNH_3^+ \leftrightarrow M\text{–}(RNH_2)_n^{2+} + nH^+ \tag{4}$$

Eq. (4) suggests that an increase in pH would enhance the formation of metal–chitosan complexes. To explore its potential to remove heavy metals, Saffaj et al. (2004) employed low-cost $ZnAl_2O_4$–TiO_2 UF membranes to remove Cd(II) and Cr(III) ions from synthetic solution. They reported that 93% Cd(II) rejection and 86% Cr(III) rejection were achieved. Such high rejection rates might be attributed to the strong interactions between the divalent cations and the positive charge of the membranes. These results indicate that the charge capacity of the UF membrane, the charge valencies of the ions and the ion concentration in the effluent, played major roles in determining the ion rejection rates by the UF membranes. Depending on the membrane characteristics, UF can achieve more than 90% of removal efficiency with a metal concentration ranging from 10 to 112 mg/L at pH ranging from 5 to 9.5 and at 2–5 bar of pressure. UF presents some advantages such as lower driving force and a smaller space requirement due to its high packing density. However, the decrease in UF performance due to membrane fouling has hindered it from a wider application in wastewater treatment. Fouling has many adverse effects on the membrane system such as flux decline, an increase in transmembrane pressure (TMP) and the biodegradation of the membrane materials (Kurniawan et al., 2006). These effects result in high operational costs for the membrane system.

The application of both reverse osmosis (RO) and nanofiltration (NF) technologies for the treatment of wastewater containing copper and cadmium ions was investigated (Abu Qdaisa and Moussab, 2004). The results showed that high removal efficiency of the heavy metals could be achieved by RO process (98% and 99% for copper and cadmium, respectively). NF, however, was capable of removing more than 90% of the copper ions existing in the feed water (Fig. 7).

Lv et al. (2008) investigated amphoteric polybenzimidazole nanofiltration hollow fiber membrane for both cations and anions removal NF membranes perform separation in between those of UF and RO ones. The molecular weight of the solute that is 90% rejected by NF membrane range from 200 to 1000 Da with pore diameters varying from 0.5 to 2 nm (Lv et al., 2008; Khedr, 2008). A multiple membrane process was developed for selective separation to reduce cost and mitigated the increasing heavy metal pollution. The process was divided into three stages: firstly, microfiltration (MF) and UF were used to separate the possible organic and suspended matters, secondly, electrodialysis (ED) was carried out for effective desalination, and thirdly, the concentrate from ED was treated by NF and RO separately to increase the recovery rate of water. Results showed that filtration characteristics of UF membrane here was not so good as is usually, even if compared with MF membrane. And RO performed better than NF in wastewater separation, especially in anti-compacting ability of membrane (Zuoa et al., 2008).

Polymer-supported ultrafiltration (PSU) technique has been shown recently to be a promising alternative for the removal of heavy metal ions from industrial effluent (Rether and Schuster, 2003). This method employs proprietary water-soluble polymeric ligands to bind metal ions of interest, and the ultrafiltration technique to concentrate the formed macromolecular complexes and produce an effluent, essentially free of the targeted metal ions (Fig. 8). Advantages of the PSU technology over ion exchange and solvent extraction are the low-energy requirements involved in ultrafiltration, the very fast reaction kinetics, all aqueous based processing and the high selectivity of separation if selective bonding agents are applied. Polyamidoamine dendrimers (PAMAM) have been surface modified, using a two-step process with benzoylthiou-

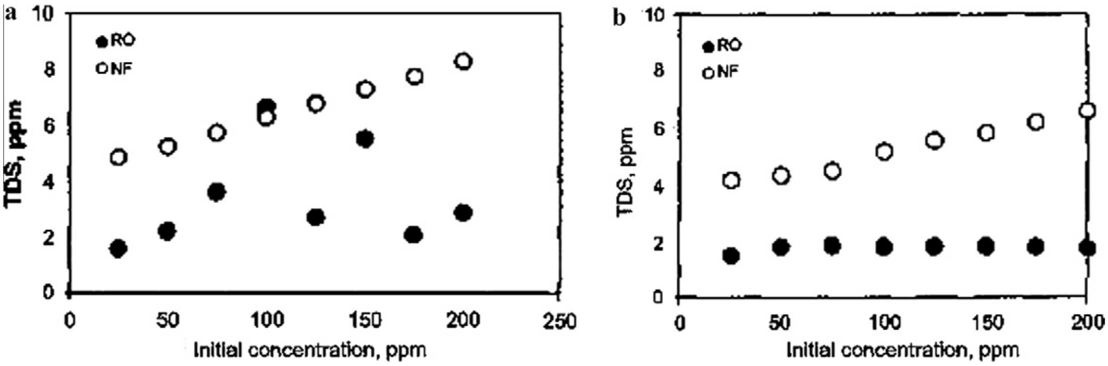

Figure 7 Concentration of (a) Cu(II) and (b) Cd(II) ions in the permeate from RO and NF (Abu Qdaisa and Moussab, 2004).

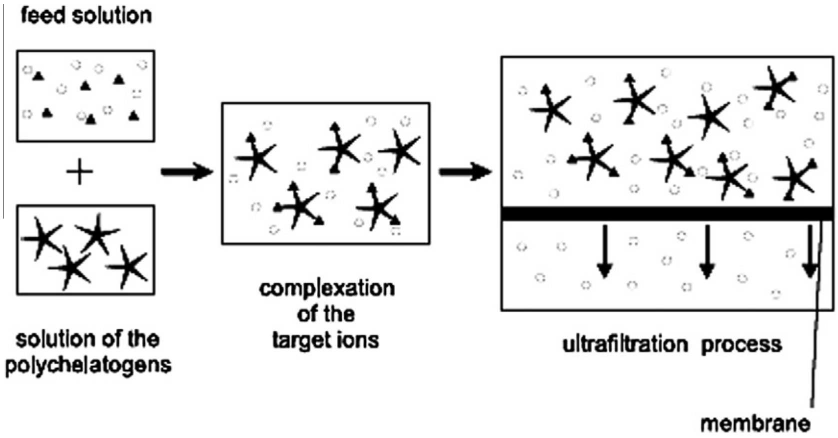

Figure 8 Principles of polymer-supported ultrafiltration (PSU) technique (Rether and Schuster, 2003).

rea groups to provide a new excellent water-soluble chelating ion exchange material with a distinct selectivity for toxic heavy metal ions. Studies on the complexation of Co(II), Cu(II), Ni(II), Pb(II) and Zn(II) by the dendrimer ligand were performed using the PSU method. The results show that all metal ions can be retained almost quantitatively at pH 9. Cu(II) form the most stable complexes with the benzoylthiourea modified PAMAM derivatives (can be completely retained at pH >4), and can be separated selectively from the other heavy metal ions investigated (Fig. 9).

Another similar technique, complexation–ultrafiltration, proves to be a promising alternative to technologies based on precipitation and ion exchange. The use of water-soluble metal-binding polymers in combination with ultrafiltration (UF) is a hybrid approach to concentrate selectively and to recover valuable elements as heavy metals. In the complexation – UF process cationic forms of heavy metals are first complexed by a macroligand in order to increase their molecular weight with a size larger than the pores of the selected membrane that can be retained whereas permeate water is then purified from the heavy metals (Petrov and Nenov, 2004; Barakat, 2008b; Trivunac and Stevanovic, 2006). The advantages of complexation–filtration process are the high separation selectivity due to the use of a selective binding and low-energy requirements involved in these processes. Water-soluble polymeric ligands have shown to be powerful substances to remove trace metals from aqueous solutions and industrial wastewater through membrane processes. Carboxyl methyl cellulose (CMC) Petrov and Nenov, 2004; Barakat, 2008b, diethylaminoethyl cellulose (Trivunac and Stevanovic, 2006), and polyethyleneimine (PEI) Aroua et al., 2007 were used as efficient water-soluble metal-binding polymers in combination with ultrafiltration (UF) for selective removal of heavy metals from water. Barakat (2008b) investigated the removal of Cu(II), Ni(II), and Cr(III) ions from synthetic wastewater solutions by using CMC and polyethersulfon ultrafiltration membrane. The efficiency of the metals rejection is shown in Table 5.

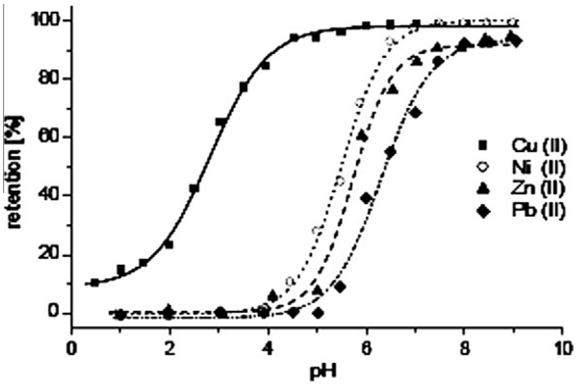

Figure 9 Selectivity of PSU polymer (Rether and Schuster, 2003).

Ferella et al. (2007) examined the performance of surfactants-enhanced ultrafiltration process for removal of lead and arsenic by using cationic (dodecylamine) and anionic (dodecylbenzenesulfonic acid) surfactants. The removal of lead ions was $>99\%$, while with arsenate ions it was 19%, in both the systems. Modified UF blend membranes based on cellulose acetate (CA) with polyether ketone (Arthanareeswaran et al., 2007), sulfonated polyetherimide (SPEI) Nagendran et al., 2008, and polycarbonate (Vijayalakshmi et al., 2008) were recently tested for heavy metals removal from water. It was found that CA/blend membranes displayed higher permeate flux and lower rejection compared to pure CA membranes.

A new integrated process combining adsorption, membrane separation and flotation was developed for the selective separation of heavy metals from wastewater (Mavrov et al., 2003). The process was divided into the following three stages: firstly, heavy metal bonding (adsorption) by a bonding agent, secondly, wastewater filtration to separate the loaded bonding agent by two variants: crossflow microfiltration for low-contaminated wastewater (Fig. 10), or a hybrid process combining flotation and submerged microfiltration for highly contaminated wastewater (Fig. 11), and thirdly, bonding agent regeneration. Synthetic zeolite R selected as a bonding agent, was

Table 5 Metal rejection in both individuals and simultaneous solutions (Barakat, 2008a) (pH 7, CMC = 1 g/L, metal ion concentration = 25 mg/L, *p* = 1 bar).

Metal ion	Ni(II) (%)	Cu(II) (%)	Cr(III) (%)
Metal rejection (independently) (wt.%)	95.1	98.6	99.1
Metal rejection (simultaneously) (wt.%)	94.4	98	98.3

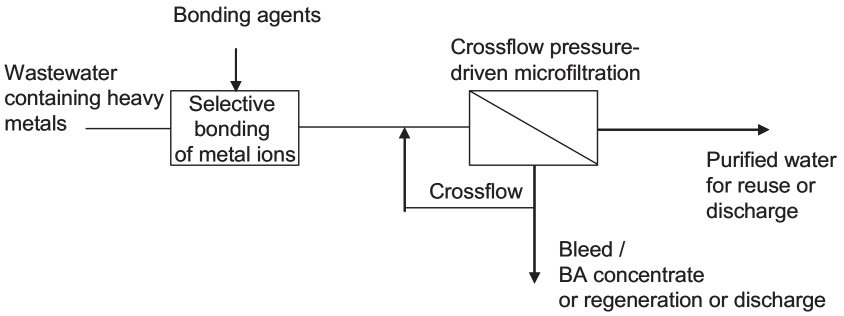

Figure 10 The integrated processes combining metal bonding and separation by cross flow membrane filtration (for low-contaminated wastewater) (Mavrov et al., 2003).

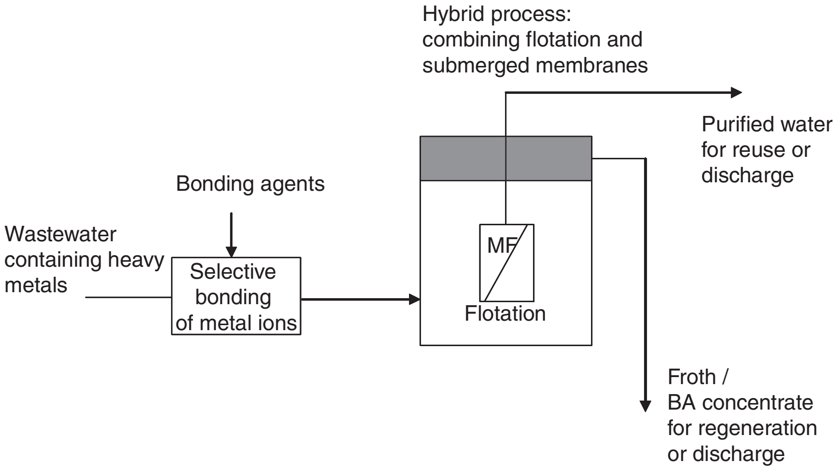

Figure 11 The integrated processes combining metal bonding and separation by a new hybrid process (for highly contaminated wastewater) (Mavrov et al., 2003).

characterized and used for the separation of the zeolite loaded with metal (Mavrov et al., 2003). Bloocher et al. (2003) and Nenov et al. (2008) developed a new hybrid process of flotation and membrane separation by integrating specially designed submerged microfiltration modules directly into a flotation reactor. This made it possible to combine the advantages of both flotation and membrane separation. The feasibility of this hybrid process was proven using powdered synthetic zeolites as bonding agents. The toxic metals, copper, nickel and zinc, were reduced from initial concentrations of 474, 3.3 and 167 mg/L, respectively, to below 0.05 mg/L, consistently meeting the discharge limits.

Another hybrid process, membrane contactor, is not only combined with an extraction or absorption process but both processes are fully integrated and incorporated into one piece of equipment in order to exploit the benefits of both technologies fully (Klaassen et al., 2008). It offers a flexible modular energy efficient device with a high specific surface area. It is important to note that the selection of the appropriate membrane depends on a number of factors such as the characteristics of the wastewater, the concentration of the heavy metals, pH and temperature. In addition, the membranes should be compatible with the feeding solution and cleaning agents to minimize surface fouling. It is observed that membranes with polyamide as their skin materials have a higher removal of heavy metals and can workin a wide range of temperature (5–45 °C). This may be attributed to the fact that polyamide membranes have a higher porosity and hydrophilicity than other materials such as cellulose acetate (Madaeni and Mansourpanah, 2003).

5. Electrodialysis

Electrodialysis (ED) is a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cations toward the cathode, crossing the anion exchange and cation-exchange membranes (Chen, 2004), Fig. 12 shows the principles of electrodialysis.

Some interesting results were reported by Tzanetakis et al. (2003), who evaluated the performance of the ion exchange membranes for the electrodialysis of Ni(II) and Co(II) ions from a synthetic solution. Two cation-exchange membranes, perfluorosulfonic Nafion 117 and sulfonated polyvinyldifluoride membrane (SPVDF), were compared under similar oper-

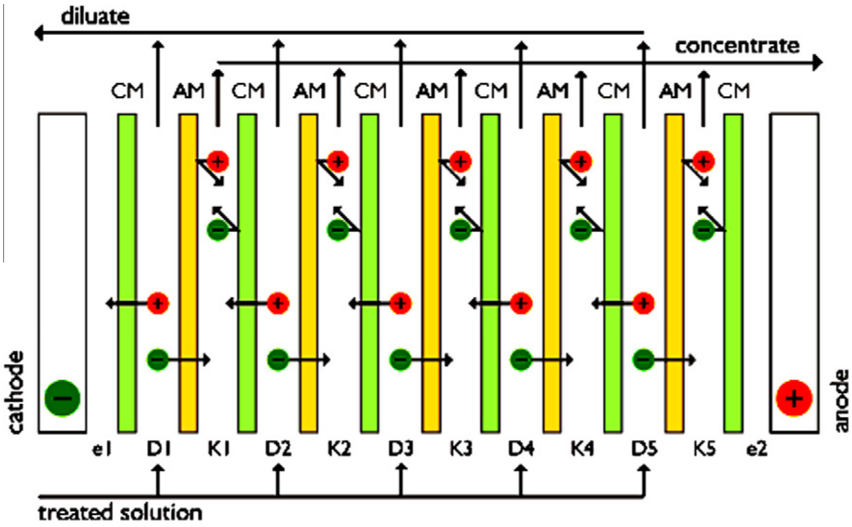

Figure 12 Electrodialysis principles (Chen, 2004). CM – cation-exchange membrane, D – diluate chamber, e1 and e2 – electrode chambers, AM – anion exchange membrane, and K – concentrate chamber.

ating conditions. By using perfluorosulfonic Nafion 117, the removal efficiency of Co(II) and Ni(II) were 90% and 69%, with initial metal concentrations of 0.84 and 11.72 mg/L, respectively. Effects of flow rate, temperature and voltage at different concentrations using two types of commercial membranes, using a laboratory ED cell, on lead removal were studied (Mohammadi et al., 2004). Results show that increasing voltage and temperature improved cell performance; however, the separation percentage decreased with an increasing flow rate. At concentrations of more than 500 ppm, dependence of separation percentage on concentration diminished. Using membranes with higher ion exchange capacity resulted in better cell performance. Electrodialytic removal of Cd(II) from wastewater sludge, was studied (Jakobsen et al., 2004). During the remediation a stirred suspension of wastewater sludge was exposed to an electric dc field. The liquid/solid (mL/g fresh sludge) ratio was between 1.4 and 2. Three experiments were performed where the sludge was suspended in distilled water, citric acid or HNO_3 (Fig. 13). The Cd(II) removal in the three experiments was 69%, 70% and 67%, respectively.

ED process was modeled based on basic electrochemistry rules and copper ion separation experimental data (Mohammadi et al., 2005). The experiments were performed for zinc, lead and chromium ions. It was found that performance of an ED cell is almost independent on the type of ions and only depends on the operating conditions and the cell structure. In spite of its limitation, ED offers advantages for the treatment of wastewater laden with heavy metals such as the ability to produce a highly concentrated stream for recovery and the rejection of undesirable impurities from water. Moreover, valuable metals such as Cr and Cu can be recovered. Since ED is a membrane process, it requires clean feed, careful operation, periodic maintenance to prevent any stack damages.

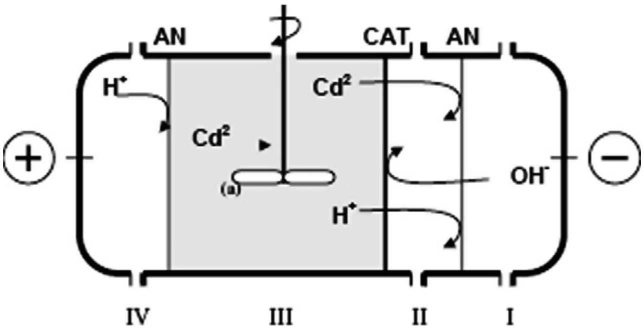

Figure 13 Electrodialytic remediation of cadmium from wastewater sludge (Jakobsen et al., 2004) (AN: anion exchange membrane, CAT: cation-exchange membrane, (a) stirrer).

6. Photocatalysis

In the recent years, photocatalytic process in aqueous suspension of semiconductor has received considerable attention in view of solar energy conversion. This photocatalytic process was achieved for rapid and efficient destruction of environmental pollutants. Upon illumination of semiconductor–electrolyte interface with light energy greater than the semiconductor band gap, electron–hole pairs (e^-/h^+) are formed in the conduction and the valence band of the semiconductor, respectively (Herrmann, 1999). These charge carriers,

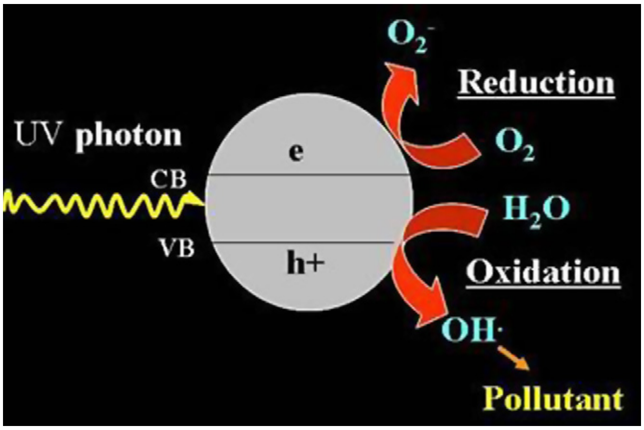

Figure 14 The conceptual reaction path of photocatalysis over TiO_2 (Herrmann, 1999).

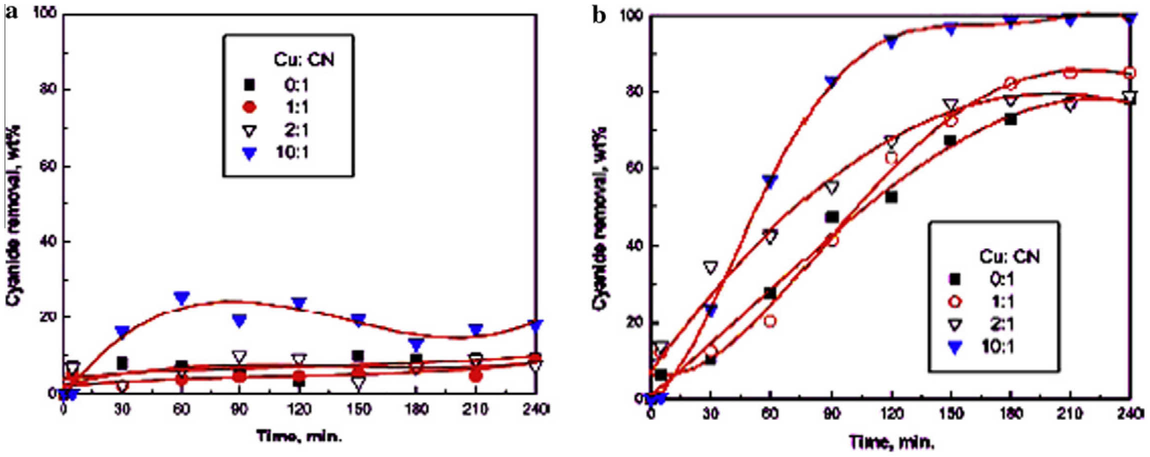

Figure 15 Cu(II) removal by UV illuminated TiO_2 at various Cu(II)/CN^- ratios Barakat et al., 2004. (a) Without UV-light and (b) with UV-light.

which migrate to the semiconductor surface, are capable of reducing or oxidizing species in solution having suitable redox potential. Various semiconductors have been used: TiO_2, ZnO, CeO_2, CdS, ZnS, etc. As generally observed, the best photocatalytic performances with maximum quantum yields are always obtained with titanium dioxide. Fig. 14 shows the conceptual reaction path of photocatalysis over titanium dioxide particle.

The mechanism of photocatalysis over titanium dioxide particle was reported (Zhang and Itoh, 2006). The generated electron–hole pairs must be trapped in order to avoid recombination. The hydroxyl ions (OH^-) are the likely traps for holes, leading to the formation of hydroxyl radicals which are strong oxidant agents, while the traps for electrons are adsorbed oxygen species, leading to the formation of superoxide species (O_2^{-}) which are unstable, reactive and may evolve in several ways.

$$TiO_2 + h\nu = TiO_2 + e^-_{CB} + h^+_{VB} \quad (5)$$

$$TiO_{2(substrate)}\text{–}OH^-_s + h^+ = TiO_{2(substrate)}\text{–}OH^{\bullet}_{(ads)} \quad (6)$$

$$O_{2(ads)} + e^- = O_2^{-(ads)} \quad (7)$$

Barakat et al. (2004) studied the photocatalytic degradation using UV-irradiated TiO_2 suspension for destroying complex cyanide with a con-current removal of copper. Results revealed that free copper (10^{-2} M) was completely removed in 3 h. The co-existence of Cu(II) and CN^- enhanced the removal efficiency of both CN^- and copper; the removal (%) increased with increase of Cu:CN^- molar ratio reaching a complete removal for both copper and cyanide at a ratio of 10:1 (Fig. 15).

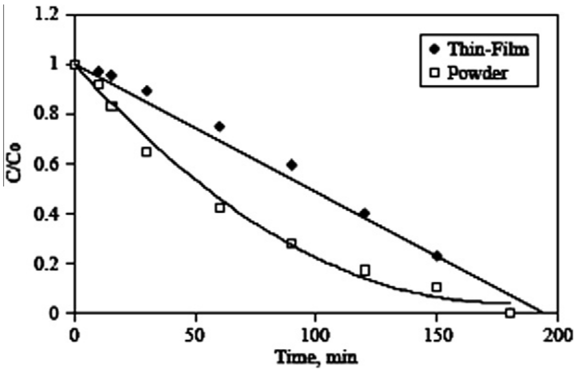

Figure 16 Comparison of photocatalytic reduction of Cr(VI) using thin film TiO_2 and Degussa P-25 (Kajitvichyanukula et al., 2005).

Several studies were reported for the photocatalytic reduction of Cr(VI), which is mobile and highly toxic, compared to Cr(III), which is immobile and less harmful. Various unmodified and modified semiconductors were synthesized and characterized as photocatalysts. TiO_2 thin films immobilized on glass plates and prepared by sol–gel technique wereinvestigated (Kajitvichyanukula et al., 2005). Cr(VI) was successfully removed, the photoactivity of the prepared TiO_2 thin films exhibited a comparable efficiency with TiO_2 powder, Degussa P-25 (Fig. 16). TiO_2 modified with sulfate (Mohapatra et al., 2005) and TiO_2 loading on zirconium phosphate (ZrP) and titanium phosphate (Dasa et al., 2006) were prepared and tested. Samples prepared at lower pH exhibit more surface area and higher reactivity than those prepared at higher pH (Fig. 17a and b). Polyoxometalates (POM) $PW_{12}O_{40}{}^{3-}$ or $SiW_{12}O_{40}{}^{4-}$ as photocatalyst and an organic substrate (salicylic acid or propan-2-ol) as electron donor were also investigated (Gkika et al., 2006). Increase of POM or salicylic acid (SA) concentration accelerated, till a saturation value, with both the reduction of metal and the oxidation of the organic compound. The method is suitable for a range of chromium concentration from 5 to 100 ppm achieving complete reduction of Cr(VI) to Cr(III).

Photocatalytic reduction of Cr(VI) over TiO_2 catalysts was investigated in both the absence and presence of organic compounds (Papadama et al., 2007; Wang et al., 2008). A marked synergistic effect between the photocatalytic reduction of Cr(VI) and organic compounds was observed over the photocatalyst with the largest specific surface area. These results demonstrated that the photocatalytic reduction of Cr(VI) alone was dependent on both the specific surface area and crystalline structure of the photocatalyst in the absence of any organic compounds, but was dominated by the specific surface area of the photocatalyst in the presence of organic compounds because of the synergistic effect between the photocatalytic reduction of Cr(IV) and the photocatalytic oxidation of organic compounds.

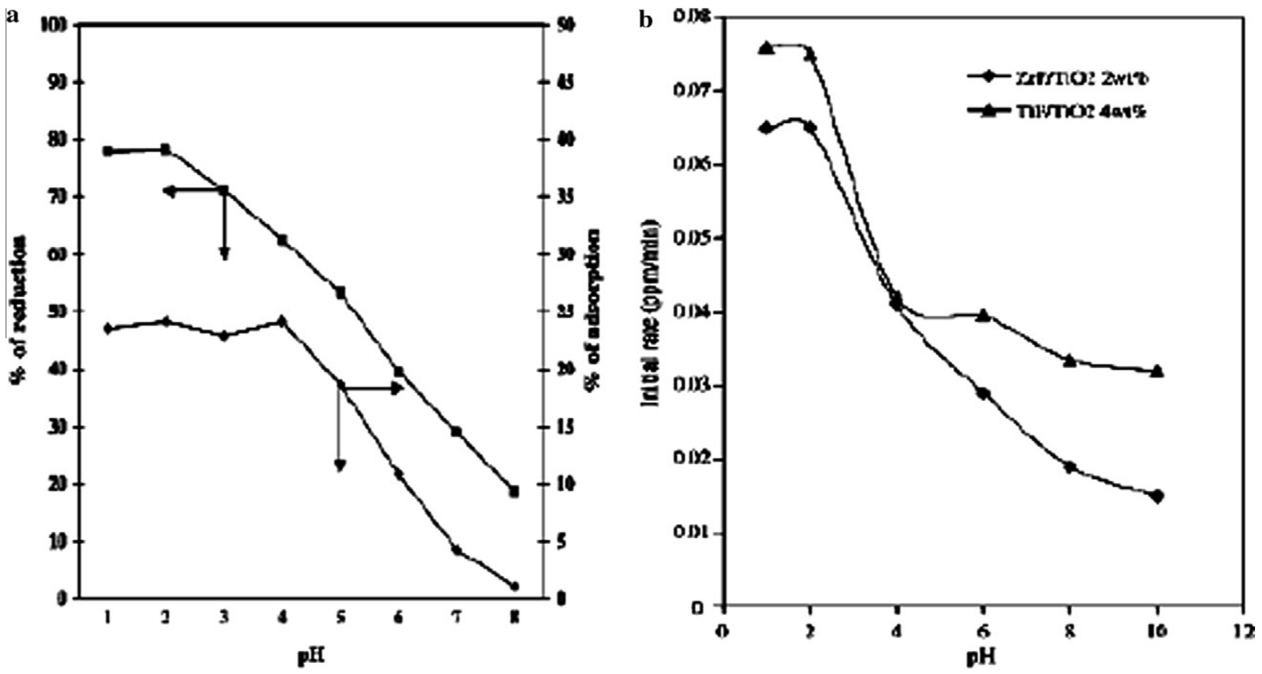

Figure 17 Effect of pH of the solution on the photocatalytic reduction of Cr(VI) over (a) TiO_2 modified with sulphate (Lv et al., 2008), (b) TiO_2 loading on zirconium phosphate (ZrP) and titanium phosphate (Dasa et al., 2006).

A novel photocatalyst, titanium dioxide (TiO_2) doped with neodymium (Nd), was prepared by the sol–gel method and used for the photocatalytic reduction of Cr(VI) under UV illumination (Rengaraj et al., 2007). The results indicated that the presence of Nd(III) in TiO_2 catalysts substantially enhances the photocatalytic reaction of Cr(VI) reduction. The neodymium ions deposited on the TiO_2 surface behave as sites at which electrons accumulate. The improved separation of electrons and holes on the modified TiO_2 surface allows more efficient channeling of the charge carriers into useful reduction and oxidation reactions rather than recombination reactions. The presence of sacrificial electron donors such as formic acid enhances the photocatalytic reduction. The Cr(VI) adsorbed on the surface of the TiO_2 particles was observed to be almost completely photoreduced to Cr(III). To overcome the limitation of powder TiO_2, a novel technique of immobilization based on anodization was applied and investigated (Yoona et al., 2009). Immobilized TiO_2 electrode was applied to reduce toxic Cr(VI) to non-toxic Cr(III) in aqueous solution under UV irradiation. The anodization was performed with 0.5% hydrofluoric acid, and then the anodized samples were annealed under oxygen stream in the range 450–850 °C. The photocatalytic Cr(VI) reduction was favorable in acidic conditions, with 98% of the Cr(VI) being reduced within 2 h at pH 3.

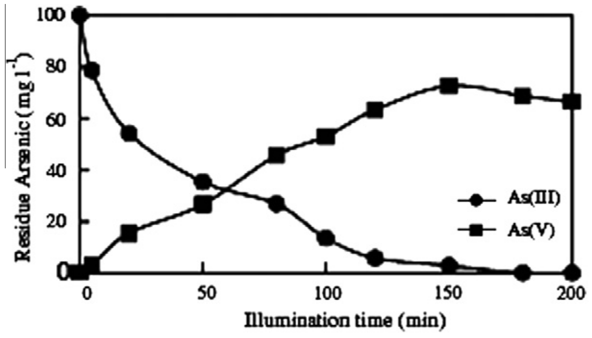

Figure 18 Effect of illumination time on the oxidation of arsenite to arsenate (Zhang and Itoh, 2006).

Heterogeneous photocatalytic oxidation of arsenite to arsenate in aqueous TiO_2 suspensions has also been proved recently to be an effective and environmentally acceptable technique for the remediation of arsenite contaminated water. The process was performed using an adsorbent developed by loading iron oxide and TiO_2 on municipal solid waste melted slag (Zhang and Itoh, 2006). A concentration of 100 mg/L arsenite could be entirely oxidized to arsenate within 3 h in the presence of the adsorbent and under UV-light irradiation (Fig. 18).

7. Evaluation of heavy metals removal processes

In general, physico-chemical treatments offer various advantages such as their rapid process, ease of operation and control, flexibility to change of temperature. Unlike in biological system, physico-chemical treatment can accommodate variable input loads and flow such as seasonal flows and complex discharge. Whenever it is required, chemical plants can be modified. In addition, the treatment system requires a lower space and installation cost. Their benefits, however, are outweighed by a number of drawbacks such as their high operational costs due to the chemicals used, high-energy consumption and handling costs for sludge disposal. However, with reduced chemical costs (such as utilizing of low-cost adsor-

Table 6 The main advantages and disadvantages of the various physico-chemical methods for treatment of heavy metal in wastewater.

#	Treatment method	Advantages	Disadvantages	References
1	Chemical precipitation	Low capital cost, simple operation	Sludge generation, extra operational cost for sludge disposal	Kurniawan et al. (2006)
2	Adsorption with new adsorbents	Low-cost, easy operating conditions, having wide pH range, high metal-binding capacities	Low selectivity, production of waste products	Babel and Kurniawan (2003); Aklil et al. (2004)
3	Membrane filtration	Small space requirement, low pressure, high separation selectivity	High operational cost due to membrane fouling	Kurniawan et al. (2006)
4	Electrodialysis	High separation selectivity	High operational cost due to membrane fouling and energy consumption	Mohammadi et al. (2005)
5	Photocatalysis	Removal of metals and organic pollutant simultaneously, less harmful by-products	Long duration time, limited applications	Barakat et al. (2004); Kajitvichyanukula et al. (2005)

bents) and a feasible sludge disposal, physico-chemical treatments have been found as one of the most suitable treatments for inorganic effluent (Kurniawan et al., 2006).

In wastewater systems containing heavy metals with other organic pollutants, the presence of one species usually impedes the removal of the other. For instance, hydrometallurgy, a classical process to recover metals, is inhibited by the presence of organic compounds and a pre-treatment step, to remove or destroy organics, is generally required, pyrometallurgy which is able to decontaminate systems from organic pollutants and recover metals suffers from lack of controllability, demanding extremely high temperatures. The most promising methods to treat such complex systems are the photocatalytic ones which consume cheap photons from the UV-near visible region. These photo catalysts serve as electron relays, from the organic substrates to metal ions. Thus, they induce both degradation of organic pollutants and recovery of metals in one-pot systems, operable at traces of the target compounds (less than ppm). Table 6 summarizes the main advantages and disadvantages of the various physico-chemical treatments presented in this study.

8. Conclusion

Over the past two decades, environmental regulations have become more stringent, requiring an improved quality of treated effluent. In recent years, a wide range of treatment technologies such as chemical precipitation, adsorption, membrane filtration, electrodialysis, and photocatalysis, have been developed for heavy metal removal from contaminated wastewater. It is evident from the literature survey of 94 articles (1999–2008) that: lime precipitation has been found as one of the most effective conventional means to treat inorganic effluent with a metal concentration higher than 1000 mg/L; new adsorbents and membrane filtration are the most frequently studied and widely applied for the treatment of the heavy metal-contaminated wastewater; photocatalysis is a promising innovative technique for a clean and efficient treatment.

Although many techniques can be employed for the treatment of wastewater laden with heavy metals, it is important to note that the selection of the most suitable treatment for metal-contaminated wastewater depends on some basic parameters such as pH, initial metal concentration, the overall treatment performance compared to other technologies, environmental impact as well as economics parameter such as the capital investment and operational costs. Finally, technical applicability, plant simplicity and cost-effectiveness are the key factors that play major roles in the selection of the most suitable treatment system for inorganic effluent. All the factors mentioned above should be taken into consideration in selecting the most effective and inexpensive treatment in order to protect the environment.

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