

Revive Paper - Removal of Toxic Heavy Metal Ions on Bentonite and Kaolinite clay from Wastewater

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Abstract

Scattered literature is harnessed to critically review the possible source, chemistry, potential biohazards and best available remedial strategies for a number of toxic heavy metals lead, chromium, copper, aluminium and selenium commonly found in wastewater. The environmental pollution is caused by a variety of pollutants in water, air and soil. One of the major concerned pollutants of living environment is “Hazardous Metals” also termed as “Trace Elements”. This term is used in geochemical and biochemical literature to refer to a group of otherwise unrelated chemical elements which are found in nature at very low concentrations. Their concentrations in different natural environments vary widely. (Gueguen M. et al. 2011). Heavy metal cause a number of disease e.g. lead cause’s mental relation, chromium is responsible for bronchial asthma, Since heavy metals are not eliminated from the aquatic ecosystem in nature process and retain there for longer time therefore it is more dangerous for the mankind and environment. In recent past a variant of treatment techniques for the removal of different type of pollution from water and waste water have been developed such as biological methods, physical methods, chemical methods and integrate methods chemical methods consist of reduction, precipitation, coagulation, ion exchange and adsorption. Among all the methods described above the adsorption methods is specially preferred as an advance technique for the treatment of water and wastewater due to its high efficiency, easy handling and less expensive.

Keywords: Revive Paper, Adsorption Capacity of Bentonite clay, Adsorption Capacity of Kaolinite clay Removal of metal ion, Thermodynamic studies.

1. Introduction

Heavy metal pollution has become one of the most serious environmental problems today. The environmental pollution is caused by a variety of pollutants in water, air and soil. One of the major concerned pollutants of living environment is “Hazardous Metals” also termed as “Trace Elements”. This term is used in geochemical and biochemical literature to refer to a group of otherwise unrelated chemical elements which are found in nature at very low concentrations. Their concentrations in different natural environments vary widely. (Gueguen M. et al. 2011).

Exponential growth of human population coupled with ways to attain high standard of living through technology advancement which has resulted in widespread contamination of the environmental at the global level. During the past few decades’ rapid industrialization wanton exploitation of natural resources and excessive use of environmentally abhorrent material have resulted in discernible environmental disruption threatening the life support system. Several kind of substances cause water pollution e.g. Heavy metal, organic and inorganic pollutants, oreano metallic compounds, sewage, detergent, petroleum waste and pesticides, etc. (Mahvi. A. H. et al. 2005).

Unlike organic pollutants heavy metals are indestructible poisons even a small concentration is capable of disrupting the body’s normal metabolic functions. Heavy metal pollution can remain dormant for a long time and then surface with vengeance. The main sources of water pollutant are domestic sewage, sewage and industrial effluents and thermal power plants. According to national environmental engineering research institute Nagpur (NEERI Nagpur) more than 70% of inland water in India is not fit for drinking purpose. All major rivers contain toxic metals such as lead, Zinc, Cadmium, Chromium, Mercury, Nickel, Iron and manganese in excess of the preserved link. (Mamtani R. et al. 2011, Jaishankar M. et al. 2014).

Source of pollution generally mining processes, discharge of industrial effluents containing metallic solutions, dumping of solid wastes which contain metal salts and some agricultural practices such as the use of mercury based biocides introduce toxic metals to water. Battery manufacturing industries, paint manufacturing industries, electroplating industries, viscous-rayon manufacturing industries, copper picking industries and galvanizing & rubber processing industries are some of the important industries the effluents of

which contain considerable amounts of heavy metals. The primary metals considered to be toxic are lead, Mercury, copper, cadmium, mercury and nickel. Contamination of River water with toxic metals prevents the further use of water for industrial and drinking purposes. Mercury and Lead particularly make the water dangerous for drink. These toxic metals are reported to cause chromosome damage and thus interfere with the process of heredity (Srigowthem S. et al. 2011).

Heavy metal cause a number of disease e.g. lead cause's mental relation, chromium is responsible for bronchial asthma, cadmium for fragile bones, Nickel for dermatitis, pneumonia and so on. Since heavy metals are not eliminated from the aquatic ecosystem in nature process and retain there for longer time therefore it is more dangerous for the mankind and environment. In recent past a variant of treatment techniques for the removal of different type of pollution from water and waste water have been developed such as biological methods, physical methods, chemical methods and integrate methods chemical methods consist of reduction, precipitation, coagulation, ion exchange and adsorption. Among all the methods described above the adsorption methods is specially preferred as an advance technique for the treatment of water and wastewater due to its high efficiency, easy handling and less expensive.

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 it is simple and inexpensive to operate. In precipitation process, 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, ease of pH control (Huisman et al., 2006). The solubility of the various metal hydroxides is minimized in the pH range of 8.0-11.0. The metal hydroxides can be removed by sedimentation and flocculation. A variety of hydroxides has been used to precipitates metals from wastewater, based on the ease of handling, lime is the preferred choice of base used in hydroxide precipitation at industrial settings (Baltpurvins et al., 1997).

Hydroxide precipitation process using Ca(OH)_2 and NaOH in removing Pb(II), Cu(II), Al(III), Se(IV) 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 25 mg/L to 0.01 mg/L. The cuproammonia 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.

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.

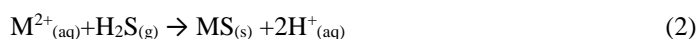
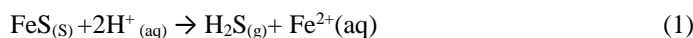
Table 1 Removal of Heavy metal ion by Chemical Precipitation

Metal ion	Initial metal ion Concentration	Precipitant	pH	% Removal	Reference
Zn(II)	32 mgL ⁻¹	CaO	09	99 .00	Ghose et.al.in press
Cu(II)	100 mgL ⁻¹	CaO	7.2	99.37	Chen et.al.2009b
Cr(II)	100 mgL ⁻¹	CaO	8.3	99.43	Chen et.al.2009b
Pb(II)	100 mgL ⁻¹	CaO	7.8	99.11	Chen et.al.2009b
Zn(II)	100 mgL ⁻¹	CaO	9.5	99.60	Chen et.al.2009b
Cu(II)	0.018 mM	H ₂ S	3.0	100.0	Alvarez et.al.2006
Pb(II)	1.34 mM	H ₂ S	3.0	94.00	Alvarez et.al.2006
Zn(II)	2.30mM	H ₂ S	3.0	92.00	Alvarez et.al.2006
Cr(III)	5363 mgL ⁻¹	MgO	8.0	99.00	Guo et.al2006
Hg(II)	188 ugL ⁻¹	CaO	6.4	99.39	Blue et.al.2007

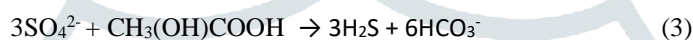
2.1.2. Sulfide precipitation

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 solubility 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.

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



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



Where $\text{CH}_3(\text{OH})\text{COOH}$ stands for simple organic compounds. Hydrogen sulfide react with divalent soluble metals to form insoluble metal sulfide (Eq.(2)).

Some attractive findings were reported by Kousi et al. (2007) who developed an up flow fixed-bed SRB to monitor for the treatment of zinc-bearing wastewater. They found that the reactor has considerable capacity of completely reducing sulfates for initial concentrations up to 6000 mg/L, completely removing soluble zinc for initial concentration up to 400 mg/L. and completely removing TOC for initial concentration 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 ion 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 process.

2.1.3. Chemical precipitation combined with other methods

Chemical precipitation has been shown to be successful in combination with other methods. Gonzalez-munoz et al. (2006) reported sulfide precipitation to reuse and recover heavy metal ion and employed nano filtration as a second step. Results indicated sulfide precipitation was successful in reducing the metal content and nano filtration yielded solution 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 85% COD was reduced using electro-Fenton method and zinc removal (99%) was attained in the range of pH 9 using lime precipitation.

There are some reports on chemical precipitation in combination with ion-exchange treatments. Papadopoulos et al. (2004) reported using ion-exchange process 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 process, 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 process has many limitations and it is difficult to meet the increasingly stringent environmental regulations by application of conventional precipitation process to treat the heavy metal wastewater 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, trimmer captotriazine, potassium/ sodiumthiocarbonate precipitants, and/ sodiumthiocarbonate. 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 safely utilized, there is a definite need for new and more effective precipitants to be synthesized to meet the discharged requirements.

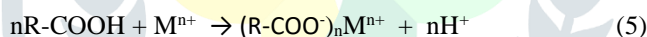
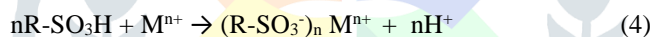
Matlock et al. (2002b,c) designed and synthesized a new thiol-based compound, 1,3-benzenediamidoethanethiol (BDET) dianion. BDET²⁻ can effectively precipitate mercury in the leachate solution and heavy metals from acid mine drainage. Fu et al. (2006, 2007) employed dithiocarbamate-type supramolecular 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 ion 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 concentrations 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 cation with the metals in the wastewater. Among the materials used in ion-exchange process, synthetic resins are commonly preferred as they are effective to nearly remove the heavy metals from the solutions (Alyuz and Veli, 2009).

The most common cation exchangers are strongly acidic resins with sulfonic acid groups (-SO₃H) and weakly acid resins with carboxylic acid (-COOH). Hydrogen ions in the sulfonic group or carboxylic group of the resin can serve as exchangeable ions with metal cation. As the solution containing heavy metal passes through the cation column, metal ions are exchanged for the hydrogen ions on the following ion-exchange process;



The uptake of heavy metals 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, Fe³⁺ and Pb²⁺ from aqueous systems by cation-exchange resin purolite C100 was adsorption sequence can be given as Ce⁴⁺ > Fe³⁺ > Pb²⁺. Similar results for Co²⁺, Ni²⁺ and Cr³⁺ 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 capacities (Motsi et al., 2009; Ostroski et al., 2009; Taffarel and Rudio, 2009). Clinoptilolite is one of the most frequently studied natural zeolites that have received extensive attentions due to its selectivity for heavy metals.

Table 2 shows the efficiency of clinoptilolite for removing heavy metals ions

Metal ion	Initial metal ion Concentration	Clinoptilolite (g/L)	pH	Adsorption Capacity	% Removal	Reference
Zn(II)	65.4 mg/L	25	5.0	2.258	99.00	Athanasiadis and Helmreich, 2005
Ni(II)	2900 mg/L	50	8.7	0.9	NA	Rodrigues-Izanga et al. 2002
Ni(II)	25 mg/L	15	7.0	0.11	93.4	Argun 2008
Pb(II)	400 mg/L	4	4.0	1.25	78.2	Berber-Mendoza et al. 2006
Pb(II)	1036 mg/L	20	4.0	NA	55	Inglezakis et al. 2007
Pb(II)	2072 mg/L	30	4.0	1	NA	Inglezakis and Grigoropoulou. 2003

2.3 Electrodialysis

Electrodialysis (ED) is another membrane process of the separation of ions across charged membranes from one solution to another using an electric field as the driving force. In most ED process, 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 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 solution in copper electro winning operations was studied by Cifuennets 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 concentration of more than 500 mg/L, dependence of separation percentages on concentration diminished.

2.4 Coagulation

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 force that keeps them apart. Many coagulation are widely used in the conventional wastewater treatment process such as aluminum, ferrous sulfate and ferric chloride, resulting in the effective removal of wastewater particulates and impurities by charge neutralization of colloids 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 (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 colloidal and suspended particles. In order to remove both soluble heavy metal and insoluble substance efficiently by coagulation, sodium xanthogenate group was granted to polyethyleneimine (Chang and Wang, 2007). This new kind in coagulant was an amphoteric polyelectrolyte. When the pH of water sample is lower, the colloidal substance with negative charge 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.

2.5 Flocculation

Flocculation is the action of polymers to form bridges between the flocs and bind the particles are 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 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 flocculants. Chang et al. (2009b) prepared a macromolecule heavy metal flocculent mercaptoacetyl Chitosan by reacting Chitosan with mercaptoacetic acid.

They reported that this new flocculent 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.

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 metals 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).

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 solution, 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, electro coagulation, electro flotation, and electro deposition were examined.

Electro coagulation (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 aluminum 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 concentration caused higher removal rates 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. Kabdash 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 $9mA/cm^2$ at the original electrolyte concentration and original pH of the composite sample used. EC was also used to evaluate the treatment of synthetic solution containing Hg^{2+} of concentration $2 \times 10^{-5} M$ by Nansu-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. Olmez (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^{5+} and Ni^{2+} etc.

Table 2 shows the efficiency of clinoptilolite for removing heavy metals ions

Metal ion	Initial metal ion Concentration	pH	% Removal	Reference
Zn(II)	270 mgL ⁻¹	6.0	100	Kabdash et al. 2009
Zn(II)	20 mgL ⁻¹	7.0	96	Chsqueira et al. 2006
Ni(II)	270 mgL ⁻¹	6.0	99	Kabdash et al. 2009
Ni(II)	100 mgL ⁻¹	6.0	98	Khelifa et al. 2005
Cu(II)	100 mgL ⁻¹	6.0	99	Khelifa et al. 2005
Cr(VI)	1470 mgL ⁻¹	2.0	100	Olmez. 2009

2.8 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.

2.8.1. 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 (Dhanesh Singh et al., 2003;). Nowadays, the depleted source of commercial coal-based AC results in the increase of price. To make progress in heavy metals adsorption, additives and AC composite could be an option. Additives of alginate (Park et al., 2007), tannic acid (Ucer 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 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 m.mol/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 Gue 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.

2.8.2. 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 Meuneir, 2007) from wastewater. The results of these studies show that CNTs are promising candidates for adsorption of heavy metal ions. 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 , NaCl and KMnO_4 solutions. Wang et al., (2007a) reported the adsorption of Pb (II) using acidified MWCNTs and found the oxygen 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, functionalized MWCNTs and unfunctionalized MWCNTs. The unfunctionalized MWCNTs showed the highest adsorption capability with up to 98% of a 100 ppb Cr (VI) solution being adsorbed. Both functionalized and non-functionalized MWCNTs showed a superior adsorption capability to that of AC. Widespread usage of CNTs will eventually be discharged to the water environment. Friendly adsorption, 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.

2.8.3. 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 byproducts 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 Gupta (2008) reviewed the adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite. Sujata Kumar et al., (2014) reviewed agricultural waste material as potential adsorbents 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 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-Jilil and Alsewailem, 2009), kaolinite (Gu and Evans, 2008) and peat (Liu et al., 2008a), etc.

Ali A et al., (2019) investigated the Halloysite clay obtained from wastewater Halloysite to remove heavy metal ions Cr (VI) from wastewater. The uptake is related with maximum adsorption being observed within 160 min. And Halloysite clay was used for removing metal ion from real wastewater containing Cr(VI), where its concentration was reduced from 100.00 mg/L to 12.05 mg/L.

Kumar Sujata and Singh D. (2014) reported cadmium and copper removal from aqueous solutions using brine sediments, sawdust and the mixture of both materials. The maximum adsorption capacity was found to be 1.94, 2.77, 3.47 and 4.12 mg/g for zinc and 1.98, 2.78, 3.61 and 4.38 mg/g for copper, respectively.

2.8.4. Bioadsorbents

Biosorption of heavy metals from aqueous is a relative 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, 2008): (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 (Amudda et al., 2009), coffee husks (Olilveira 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 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 macro alga *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 algae *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 1.97mmol/g, respectively.

Microbial removal of metal ions from wastewater has been indicated as being highly effective. Biosorption of heavy metals in aqueous solution by bacteria includes *Bacillus cereus* (Pan et al. 2007), *Escherichia coli* (Souiri et al., 2009; Qunitelas 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; Cojocararu et al., 2009), *Lentinus edodes* (Byramoglu and Arica, 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.

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 metal 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 ion and it is ineffective 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 wastewater containing heavy metal in low concentration, so they cannot be used at large scale.

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 disadvantage involves 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.

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 solution is a relative new process that has proven very promising for the removal of heavy metal from wastewater.

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 capital investment and operation cost, plant flexibility and reliability and environmental impact, etc. (Kuriawan 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 have been developed for heavy metal removal from wastewater. It is evident from the literature survey of 150 articles that ion-exchange, adsorption and membrane filtration are the most frequently studied for treatment of heavy metal wastewater. Ion-exchange process has been widely used to remove metal 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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