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Methods of Removing Heavy Metal Ions from Waste Waters; A Review

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ABSTRACT
One of the serious and persistent environmental problem globally is heavy metal pollution. Therefore, a special concern has been given on how to minimize, if not complete removal of their effect in environment. Since waste water is one of the major source of heavy metals, various studies have been conducted over the years on how to remove them from the waste water. This paper reviews some of the important methods that have been used to treat heavy metal waste water. These methods include chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation flocculation, flotation and electrochemical methods. Their Advantages and Limitations in applications are also evaluated.

I. Introduction

Heavy metals are elements having atomic weight between 63.5 and 200.6 and a specific gravity greater than 5.0 [5]. With the rapid development of industries such as; metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides etc., heavy metal waste water are directly or indirectly discharged into the environment increasingly, especially in developing countries. Unlike organic contaminants, heavy metals are not biodegradable and tend to accumulate in living organisms and many heavy metal ions are known to be toxic or carcinogenic. Toxic heavy metals of particular concern in treatment of industrial waste waters include zinc, copper nickel, mercury, cadmium, lead and chromium.

Zinc is a trace element that is essential for human health. It is important for the physiological functions of living tissue and regulates many biochemical processes. However, too much zinc can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia[6]..

Copper does essential work in animal metabolism. But the excessive ingestion of copper brings about serious toxicological concerns, such as vomiting cramps, convulsions or even death[14].

Nickel exceeding its critical level might bring about serious living and kidney problems aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis [13]. And it is known that nickel is human carcinogen.

Mercury is a neuro toxin that can cause damage to the central nervous system. High concentrations of mercury can cause impairment of pulmonary and kidney function, chest pain and dyspnoea [7]. The classical, exemple of mercury poising is minimata Bay. Cadmium has been classified by U.S. environmental protection agency as a probable human carcinogen. Cadmium exposes human health to severe risks. Chronic exposure of cadmium results in kidney dysfunction and high levels of exposure will result in death.

Lead can cause central nervous system damage. Lead can also damage kidney, liver and reproductive system basic cellular processes and brain functions. The toxic symptoms are anemia, insomnia, head ache, dizziness, irritability, weakness of muscles, hallucination and renal damages [11].

Chromium exist in the aquatic environment mainly in two states: cr(iii) and cr(vi). In general, cr(vi) is more toxic than cr(iii). Cr(vi) affects human physiology, accumulates in the food chain and causes severe health problems ranging from skin irritation to lung carcinoma[12].

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

II. Heavy Metal Waste Water Treatment methods

A. Chemical Precipitation

Chemical precipitation is effective and by far the most widely process in industry[8].because relatively simple and inexpensive to operate, in precipitation process, chemicals react with heavy metal ions to form insoluble precipitates. The forming precipitatecan be separated from the water by sedimentation or filtration. And the treated water is thendecanted and appropriately discharged or reused. The conventional chemical precipitation processes include hydroxide precipitation and sulfide precipitation.

B. Hydroxide Precipitation

The most widely used chemical precipitation technique is hydroxide precipitation due its relative simplicity, low cost and ease of PH control [9]. The solubilities of the various metal hydroxides are minimize in the PH range of 8.0-11.0. The metal hydroxides can be removed by flocculation and sedimentation. A variety of hydroxides have been used to

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precipitate metal from waste water based on the low cost and ease of handling lime is the preferred choice of base used in hydroxide precipitation at industrial settings[10].

Hydroxide precipitation process using $Ca(OH)_2$and NaoH in removing Cu(II) and Cr(VI) ions from waste water was evaluated by [15]. 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 concentration of chromate was reduced from 30mg/L to 0.01mg/L. the cupro-ammonia was reduced by aeration and the optimum PH for maximum copper precipitation was about 12.0 for both $Ca(OH)_2$ and NaoHand the concentration of copper was reduced from 48.51 mg/L to 0.694m/L. To enhance lime precipitation fly ash was used as a seed material [16]. The fly ash lime carbonation treatment increased the partule size of the precipitate and significantly improved the efficiency of heavy metal removal. The concentrations of cr, cu, pb, and zn in effluents can be reduced from initial concentration of 100.0mg/L to 0.08, 0.14, 0.03 and 0.45 mg/L respectively.

In hydroxide precipitation process the addition of coagulatants such as alum, iron salts, and organic polymers can enhance the removal of heavy metals from waste water.

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 [19]. 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 waste water, they will inhibit metal hydroxide precipitation.

C. Sulfide precipitation

Sulfide precipitation is also an effective process for the treatment of toxic heavy metals ions. One of the primary advantages of using sulphides is that the solubilities of the metal sulphide precipitate are dramatically lower than hydroxide precipitates and sulphide precipitates are not amphoteric, and hence, the sulphide precipitates process can achieve a high degree of metal removal over abroad PH range compared with hydroxide precipitation. Metal sulphide sludges also exhibit better thickening and dewatering characteristics than the corresponding metal hydroxide sludges, [20],investigated pyrite and synthetic iron sulfide to remove Cu2+, Cd2+, and Pb2+.

However, there are potential dangers in the use of sulphide precepitate process. As we know, heavy metal ions often in acid conditions and sulfide precipitants in acidic conditions can result in the evolution of toxic H2S fumes. It is essential that this precipitation process can be performed in a neutral or basic medium. Moreover, metal sulfide precipitation tends to form colloidal precipitates that cause some separation problems in either settling or filtration processes.

D. Ion exchange

Ion exchange processes have been widely used to remove heavy metals from waste water due to their many advantages, such as high treatment capacity high removal efficiency and fast kinetics[24]. Ion exchange resin, either synthetic or natural solid resin, has the specific ability to exchange its cations with the metals in the waste water. Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they are effective to nearly remove the heavy from the solution[25].

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

nR-SO3H + Mn+ ----> (R-SO3-)n Mn++ nH+(1)

nR-COOH+ Mn+ ----> (R-COO-)n Mn+ + nH+(2)

The uptake of the heavy metal ions by ion-exchange resins is rather affected by certain variable such as PH, temperature, initial metal concentration and contact time[23]. Ionic charge also plays an important role in ion-exchange process. The influence of ionic charge on the removal of Ce^{4+}, $Fe^{3+}$and $Pb^{2+}$from aqueous systems by cation-exchange resin purolie C100 was tested by Abo-Farha et al. (2009). They found that the metal ions adsorption sequence can be given as $Ce^{4+}>Fe^{3+}> Pb^{2+}$. Similar results for Co^{2+}, Ni^{2+} and Cr^{3+} on Amberlite IRN-77 cation exchange resin were previously obtained by[15].

E. Adsorption

Adsorption is now recognized as an effective and economic method for heavy metal waste water 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.

F. Bioadsorbents

Biosorption of heavy metals from aqueous solution is a relatively new process that has been confirmed a very promising process in the removal of heavy metal contaminants. The major advantages of biosorption are its high effectiveness in reducing the heavy metal ions and the use of inexpensive biosorbents. Biosorption processes are particularly suitable to treat dilute heavy metal waste water. Typical biosorbents can be derived from the sources as follows:(1) non-living biomass such as bark, liguin, shrimop, krill, squid, crab shell etc. (2) algal biomass (3) microbial biomass, eg bacteria fungi and yeast.[12].

Different form if inexpensive, non-living plant material such as potato peels, sawdust,eggshell, seedshell and coffee husk etc have been widely investigated as potential biosorbent for heavy metals[18].

Algae, a renewable natural biomass proliferates ubiquitously and abundantly in the littoral zones of world has attracted the attention of many investigations as organisms to be tested and used a new adsorbents to adsorb metal ions. Several advantages in applying algae as biosorbent include the wide availability, low cost, high metal sorption capacity and reasonably regular quality[27]. There are a large number of research works on the metal biosorption using algal biomass.

Examples of recent reports include the biosorption of $Cu^{2t}$and Zn^{2t}using dried marine chaetomorpha linum, the biosorption of Cu^{2t}, Cd^{2t},Pb^{2t} and Pb^{2t} usin^{g} dried marine green macroalga caulerpalentillifara, the biosorption of chromium from waste water using green alga ulvalaetuca [24].

Microbial removal of metal ions from waste water has been indicated as being highly effective. Biosorption of heavy metals in aqueous solutions by bacteria includes Bacillus cereus, Escherichia Coli, Pseudomonas aeruginosa etc[26].

Biosorbents were charactersistics of braod sources, low-cost and rapid adsorption.

G. Membrane Filtration

Membrane filtration technologies with different types of membrane show great promise for heavy metal removal for their high efficiency, easy operation and space saving. The membrane processes used to remove metal from the waste water are ultra filtration, reverse osmosis, nanofiltration and electrodialysis Ultrafiltration (UF) is a membrane technique working at low transmembrane pressure for the removal of dissolved metal ions in the form of hydrated ions or as low molecular weight complexes; these ions would pass easily through UF membranes. To obtain high removal efficiency of metal ions, the micellar enhanced ultrafiltration (MEUF) and polyular enhanced ultrafiltration (PEUF) was proposed MEUF was first introduced by Scamehorn et al, in the 1980s for the removal of dissolve organic compounds and multivalent metal ions from aqueous steams [17] MEUF has been proven to be an effective separation technique to remove metal ions from waste water. This separation technique is based on the addition of surfactants in aqueous solutions is beyond the critical micelle concentration (CMC) the surfactant molecules will aggregate into micelles that can bind metal ions to form large metal surfactant structures. The micelles containing metal ions can be retained by a UF membrane with pore sizes smaller that micelle sizes, where the UF membrane. To obtain the highest retentions, surfactants of electric charge opposite to that of the ions to be removed have to be used sodium dodecyl sulfate (SDS), an anionic surfactant, is often selected for the effective removal of heavy metal ions in MEU

The reverse osmosis (RO) process use a semi-permeable membrane, allowing the fluid that is being purified to pass through it, while rejecting the contaminants. RO is one of the techniques able to remove a wide range of dissolved species from water. It accounts for more than 20% of the world's desalination capacity [16]. Ro is and increasing popular waste water treatment option in high chemical and environmental engineering. Using appropriate RO systems to remove heavy metal have been investigated, but these have yet to be widely applied.

CU^{2+} and Ni^{+2}ions were successfully removed by the RO process and the ejection efficiency of the two ions increased up to 99.5% by using Na_2 EDTA [15].

The major drawback of RO is the high power consumption due to the pumping pressures and the restoration of the membrane.

H. Nanofiltration

.Nanofiltration (NF) is the intermediate process between UF and RO, NF is a promising technology for rejection of heavy metal ions such as nickel, chromium, copper [17] from waste waters.NF process benefits from ease of operation,reliability and comparatively low energy consumption as well ashigh efficiencyof pollutant removal.

I. Coagulation and flocculation

Coagulation and flocculation followed by sedimentation and filtration is also employed to remove heavy metals from waste waters. Coagulation is the destabilization of colloids by neutralizing the forces that keep them a parts. Many coagulant are widely used in the conventional waste water treatment processes such as aluminum, ferrous sulphate ferric chloride, resulting in the effective removal of waste water particulates and impurities by charge neutralization of particles and by enmeshment of the impurities on the formed amorphous metal hydroxide precipitates [24]. Investigate the removal of heavy metal by coagulation of combined sewer overflow with two commercial coagulants, ferric chloride solution and a polyaluminiumchloride (PAC). They found excellent heavy metal elimination was achieved with a narrow range of coagulant around optimum coagulant concentrations.

Coagulation is one of the most important method for waste water treatment, but the main objects of coagulation are only hydrophobic colloids and suspended particles. In order to remove both soluble heavy metal and insoluble substances efficiently by coagulation. Sodium xanthogenate group was grafted to polyethyleneimine [2].

Flocculation is the action of polymers to form bridges between the flocs and bind the particles into large agglomerates or clumps. Once suspended particles are flocculated into larger particles, they areusually removed or separated by filtration, straining or floatation. Today many kinds of flocculants, such as PAC, polyferic sulphate (PFS) and polyacrylamide (PAM), are widely used in the treatment of waste water, however, it is nearly impracticable to remove heavy metals very well from waste water directly by these current flocculant.

Generally, coagulation-flocculation cannot treat heavy metal waste water completely [2]. Therefore, coagulation-flocculation must be followed by the treatment techniques. [13] employed precipitation, coagulation and flocculation processes using ferric chloride to removal turgsten from industrial waste water. Tungsten removal was found to be most efficient (98-99%) in acidic conditions (PH<6)

J. 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 waste water technologies involve relatively large capital investment and the expensive electricity supply, so they have not been widely applied. However, with the stringent environmental regulations regarding the waste water discharge, worldwide during the past two decades [6] some of the established technologies are electrocoagulation, electroflotation and electrodeposition.

Electrocoagulation (EC) involves the generation of coagulants in situ by dissolving electrically either aluminum or iron ions from aluminum or iron electrodes (Chen, 2004). The metal ion generation takes place at the anode, and hydrogen gas is released from the cathode. The hydrogen gas can help to float the flocculated particles out of the water [1].

III. Evaluation of the various Methods

Despite the fact that all the heavy metal waste water treatment techniques can be employed to remove heavy metals, they have their inherent advantages and limitations.

Heavy metals removal from aqueous solutions has been traditionally carried out by chemical precipitation for its simplicity process and inexpensive capital cost. However, this method is usually adopted to treat high concentration waste water containing heavy metal ions and it 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 waste water. 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.

Adsorption is a recognized method for the removal of heavy metals from low concentration waste water containing heavy metal. The high cost of AC limits its use in adsorption. Adsorption efficiency depends on the adsorbent.

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

The technique of coagulation-flocculation in heavy metal waste water treatment involves chemical consumption and increased sludge volume generation. Flotation offers several advantages over the more conventional methods, such as high selectivity, high removal efficiency, high over flow rates low detention periods, low operating cost and production of more concentrated sludge. [19]. But the disadvantages involves high capital cost, high maintenance and high operational costs.

Conclusion

Although, all the above techniques can be employed for the treatment of heavy metal waste water, it is important to mention that the selection of most suitable treatment techniques depends on the initial metal concentration, the component of the waste water, capital investment and operation cost, plant flexibility and reliability and environmental impact, etc[28].

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