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Advanced Techniques for Wastewater Treatment: A Review

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Review Article
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Abstract

Freshwater in lake and pond are often found to be polluted by heavy metals such as As, Zn, or Pb which are toxic in nature and non-biodegradable. Heavy metals are readily consumed by both aquatic flora and fauna present in the freshwater environment. It also polluted the air, water, and soil. Thus, they have adverse impact on the entire ecosystem. These heavy metals also enter the human systems through food consumed. This review discusses the methods and their mechanism used to reduce the amount of such heavy metals The methods which are in practice are Electrochemical Treatment (Electrocoagulation, Electro-Floatation, and Electro-Deposition), Physicochemical Process (Chemical Precipitation, Ion-Exchange, and Adsorption), Membrane Filtration (Nanofiltration, Reverse Osmosis, Microfiltration, Ultrafiltration, and Electro-Dialysis),and Photo-Catalysis and Nanotechnology Treatment.

Keywords: Wastewater Treatment; Membrane Filtration; Heavy Metals Removal

Introduction

Fresh clean water is a necessity for all living organisms and often there is scarcity due to draughts, industrialization, and growing population. The treated wastewater can be used to fill this scarcity by treating them through certain processes in order to eliminate the toxic heavy metals as well as other pollutants to make it safe for domestic or industrial reuse. Some of the common toxic heavy metals present in waste water are Co, Cu, Ni, As, Cr, Pb, Zn and Hg [1-3]. In higher concentration, heavy metals are fatal when consumed by humans through foods and drinks. In fact, water is the apex origin of all diseases caused by pathogens [4-6]. There are many treatments available to purify the wastewater from its toxic elements but the most preferred are the ones which are Economical, Environment friendly, and feature no alternative pollutants. The two main types of methods for treatment include biological methods and physical/chemical methods; however, biological methods are not as applicable as chemical method for eliminating heavy metals. This article will discuss the physical and chemical treatment methods for eliminating heavy metals from wastewater as well as analyze their procedures, applications, advantages, and disadvantages.

Current Methods for Treating Wastewater

The different options for eliminating heavy metals effectively are Electrochemical Treatment (electrocoagulation, electroflotation, and electro-deposition), Physicochemical Process (chemical precipitation, ion-exchange, and adsorption), Membrane Filtration (nanofiltration, reverse osmosis, microfiltration and ultrafiltration, and electro-dialysis), Photo-Catalysis and Nanotechnology Treatment. The methods, their limitations, and scope for their improvement are discussed below.

Electrochemical Treatment

Electrochemical treatments are the least studied methods as they are the most expensive ones. However, electrochemical treatment offers better efficiency and required less space than all other treatments [7-10]. The electrochemical treatments to be known are Electrocoagulation (EC), Electroflotation (EF), and Electro-Deposition (ED).

Electro-Floatation (EF): Recently Electroflotation (EF) method has gained attraction in wastewater treatment to remove heavy metal pollutants as the other methods were not as efficient with dilute solutions [11-13]. EF was used for the first time in 1904 to remove mineral ores. It gained widespread usage due to its adaptability, low expense, and ease of operation. EF is currently used in the industries such as food processing for wastewater treatment [14]. EF dissociates pollutants by floating them to the top of the liquid and all this occur in 3 phases. First, the pollutants were drawn to a cell that has 2 electrodes and a power supply. The reaction for this phase is:

The heavy metals stick to O_2 and H_2 molecules and are destabilized to form flocs. The second step is the separation by settling or flotation of generated foam and settled flocs. The third step is removing collected pollutants by filtration method. Pollutant removal efficiency depends upon the size of the bubbles created during electrolysis. The energy consumed depends on the cell design, electrode materials, and operating conditions. It is common practice in wastewater treatment to combine EC and EF in order to decrease the limitations mentioned above. Combining the two method leads to higher efficiency than using them isolated [15].

Electrocoagulation (EC): EC is a straightforward method that is generally considered unreliable; however, due to improved technology, many pollutants are now eliminated with this method [16-19]. EC works by supplying low electric current to the wastewater and thereby the electrical charge keeps the heavy metals together are negative charged and the metals are coagulated from the aqueous phase to come together in the mass (called the sludge or floc). The floc developed by EC is more stable, larger, and can be easily taken out by normal physical filtration system [20-22]. EC is usually conducted with Al or Fe electrodes. The main reaction for Al electrodes is:

$$Al^{3+} + 3OH^{-} \rightarrow Al(OH)_3$$

The $Al(OH)_3$ formed becomes a substance that can trap the heavy metal ions and separated them from the rest. Experimental results indicated as an optimum removal efficiency of 98.2% was achieved by using the Al anode at current density of 0.2 Adm^{-2}. Previous studies had demonstrated the removal efficiency of 97.2% with current density of 0.5 Adm^{-2} and pH value 7 using 2 mg/l of Mg [23,24]. In an earlier study, 30 iron and stainless-steel rods of 50 mm length and 5 mm diameter were utilized. Results from this experiment indicated that at the current densities of 6 and 8 $mAcm^{-3}$ the Pb amount is reduced by 96.7% and 95.2% respectively. These results demonstrate that how removal efficiency is directly proportional to the current density used as a result of increase in the rate of formation of hydroxide and steel flocs [25]. EC is also an ecofriendly method for removing waste since it utilizes electrons instead of adding additional chemicals. However, EC cannot remove particles that are infinitely soluble.

Electro deposition (ED): Electro-deposition (ED) is a convenient and economical method for removing the heavy metals present in wastewater. This method is better because no other reagents are needed, and no sludge is formed during the whole process. ED works by changing dissolved metal ions from liquid state to solid state by depositing on ionic conductor in order to protect them from decay. ED reduces and oxidizes the heavy metal ions in a single step in a cell that includes one anode, one cathode, one electrolyte cell, and a current source [15,26-31]. The metal reduced, and electroplated on the cathode. The ultimate size of electrodeposite depends upon the nucleation of deposits, and their growth. Anodes must be insoluble in water in order to avoid disrupting the process. Competing reactions do occur during the process; which includes hydrogen turning into a gaseous state.

The productivity of the ED method depends upon the heavy metal's concentration in the initial waste product solution, temperature, pH level, and the presence of any complex and chelating agents [26,27]. This method is of great advantage due to its ability to be used with non-aqueous solutions or those containing chelating agents. ED can be used with aqueous solution as well and it often contains chelating agents such as EDTA, NTA, and citrate [32-34]. Chelating agents are very helpful since they bind with heavy metal cations to decrease the formation of insoluble salts thereby improving removal efficiency very effectively.

Physicochemical Processes

Ion-Exchange: The ion-exchange method was established on a reversible interchange of ions between solid and liquid state. The process starts with ion-exchange reaction followed by the physical absorption of heavy metal ions, which produces the complex by the counter-ion and the functional group. Finally, hydration occurs at the surface of the solution or pores of the adsorbent. The ion exchange method is affected by numerous variables including: pH, anion concentration, temperature, initial concentration of adsorbent and sorbate, and the contact time [35-38]. This technique utilizes a resin which removes the ions from the electrolytic solution to release other ions with similar electrical charges. During the metal ions capture, the following interaction occurs:

$$nRSO_3^- - H^+ + Mn^+ \rightleftharpoons \quad nRSO^{3-} - Mn^+ + nH^+$$

n is a constant connected to the oxidation state of metal ions. Ion-exchange method is more preferred to methods such as chemical precipitation as it offers many advantages like limited cost, high metal recovery levels, high selectivity, and increased efficiency. The resins that are favored for the use in ion-exchange processes are synthetic polymers such as styrene-divinyl-benzene or other gel options such as macropore. Gel option offers the benefit on cost efficiency and stability [35,39-41].

Adsorption: Adsorption is a common technique to remove heavy metals from wastewater that has had significant result in reducing the amount of heavy metals. Adsorption is a transfer between the liquid phase and solid phase (adsorbent). Adsorption comprises of three stages 42-45]. First, the pollutant is penetrated from the bulk solution onto the adsorbent surface. Then, the pollutant is adsorbed on the adsorbent surface. Lastly, the penetration in the adsorbent structure. Adsorbent provides a high surface area and high adsorption ability. Adsorbents can easily be found in agricultural waste, industrial by-products, or other materials found in nature. Commonly used adsorbents include activated carbon, carbon nanotubes, and [44].

- **Activated Carbon**

When potassium carbonate (K_2CO_3) is used, the activated carbon (AC) is produced from agricultural by-products. Their surface area ranges from 1266-3256 m^2g^{-1}. AC is commonly used for adsorption methods to take out the toxic metal from wastewater [43,46,47]. Previous research indicates that activated carbon prepared at 900 ºC is highly efficient at eliminating Ni from a liquid solution with an adsorbent concentration of 0.25g. pH values may also affect adsorption method and adsorption is best when the pH level is between 2 and 5 [43,48,49].

- **Carbon Nanotubes**

Carbon nanotubes (CNTs) are known for having properties which make absorbent extremely effective in taking out heavy metals from wastewater [50-52]. However, CNTs are immobilized by calcium alginate to limit the risks created when CNTs are discharged into water. Previous studies show that a pH of 5 is optimal for using CNTs to eliminate heavy metals.

- **Wood Sawdust**

Wood sawdust is a waste product that is produced after mechanical wood processing in plant and can be utilized as a cheap adsorbent for heavy metals removal. Sawdust can be used due to its lignocellulosic composition. Sawdust is made up of cellulose and lignin which both display the ability to bind metal cations. Recently, this interest has arisen to search for more environment friendly techniques to eliminate heavy metals from wastewater and sawdust is one such good option [53,54]. In addition, modified cotton, waste wool, tree barks, and nuts waste are all good alternatives for heavy metals adsorption. Previous studies have shown that sawdust is more effective in removing Cu, Zn, and Cd through adsorption method [55-57].

Chemical Precipitation: Chemical precipitation is a straightforward and an easy treatment method for removing heavy metals from wastewater [58-60]. Chemical precipitation requires a significant amount of chemicals in order to decrease heavy metal ions to an adequate limit for safe disposal. However, it may fail to reach that point and chemicals added may themselves pose a pollution threat. In this process, chemical agents react with metal ions and transform them into insoluble particles. The solid phase is then separated from the solution by sedimentation or filtration. pH is significant to this process with basic condition (pH=11) favored to improve the removal of heavy metals. After creating the ideal pH levels, the soluble metal ions are transformed to the dissolved solid by reacting with a precipitant agent [61].

- **Sulfide Precipitation**

Sulfide precipitation is similar to hydroxide precipitation, since both soluble and insoluble can be used to precipitate metal ions. Sulfide is utilized to precipitate the heavy metal ions as metal sulfides and the resultant sludge formed can be taken out of the solution by gravity settling or filtration [38,62,63]. Sulfide precipitation requires pre& post treatment, and proper control of reagent additions because of the toxicity of the sulfide ions and H_2S. The precipitation methods are performed by adjusting the composition and other parameters so that the ionic elements of the metals can be removed by differentiated from a soluble phase to a solid phase [64-66]. Heavy metal ions generally precipitate in the form of hydroxide:

$$M^{2+} + 2OH^- \rightleftharpoons M(OH)_2$$

M^{2+} and OH^- are the metal ions and the precipitant respectively. The ones most often utilized are lime (CaO) and $Ca(OH)_2$, both are commonly available. CaO requires a significant dosage as well as offers low metal removal efficiency due to inadequate settling and dissolution of precipitates. Past research indicates that sulfide precipitation was successful in eliminating Cu, Zn, Cr, and Pb from wastewater [65,67,68].

- **Hydroxide Precipitation**

Hydroxide precipitation integrates coagulant such as iron salts, alum, and polymers that may improve the heavy metal separation from wastewater. Soluble metals can be precipitated as hydroxide by using filtration or sedimentation process. Alkaline agents can be used to increase the pH of the wastewater. Alkaline agents reduce the solubility of metal ions and precipitate out from the solvent [37,38,41 69]. The reaction for hydroxide precipitation is;

$$M^{2+} + OH^- + nR \rightleftharpoons M(R)_n(OH)^+$$

Membrane Filtration Process

Membrane Filtration process was developed during the 1970s and 1980s in order to increase efficiency with no pollution and less energy consumption than the other prevailing methods of that time period. Membrane filtration process is highly utilized for removing heavy metals from wastewater due to its simplicity of the method [70-72]. The procedure starts with a separation occurring through a semipermeable membrane. There are many different membranes used and they vary in terms of type of nature, fabrication, and structure. In practice, three different types of membranes are used for separation processes. Thsee membranes can be called as liquid, pressure driven, and hybrid membranes. A membrane is defined as a layer with a porous or nonporous structure that is used to produce contact between two homogenous phases in order to separate pollutants of different sizes. Membrane performance can be affected by materials used, its pore size, and composition. Materials should be selected more judiciously as it helps to produce membranes with more chemical resistance and less structural imperfections. The different materials, typically used to produce membranes are metallic, ceramic, composite, nano based, reactive or catalytic, and biologically modified materials [73-76]. Composite materials like polymers, Polymers are often selected for membrane production due to their porous structures and affordability. Polymers can be used with many filtration processes including microfiltration and reverse osmosis. Polymer membrane materials are cellulose acetate, polyvinylidene fluoride, polyacrylonitrile, polypropylene, polyethersulfone, and polysulfone. Ceramic materials are often optimal and better than polymer materials due to their narrow pore size and high mechanic, thermal, and chemical stability [70,77-79]. Ceramic membranes are formed out of alumina, zirconia, silica, titania, oxide mixtures, and sintered metals. The different methods of membrane filtration are nanofiltration, reverse osmosis, microfiltration and ultrafiltration, and electro-dialysis.

Nano filtration: Nanofiltration (NF) is a recent technology and was developed to make separation of large molecules using small spores possible. NF is environment friendly and energy efficient and is often used to remove pollutants found in groundwater, surface water, and wastewater. This process is referred to as a liquid phase filtration since it separates a large range of organic and inorganic particles from their [80-82]. The separation is dependent upon the molecular weight cut off. NF requires a three-step procedure: pretreatment, treatment, and post treatment. Firstly, the water needs to be treated before going into the system in order to reduce more pollution. This step includes pre filtration, coagulation, adsorption, ion exchange, and chemical conditioning. Secondly, the actual membrane separation process occurs and finally the post treatment is carried out. NF is successful in eliminating heavy metals found in water especially in cleaning water contaminated by strong pollutants such as Pb and Cd [75,83-85].

Microfiltration and Ultrafiltration: Microfiltration (MF) and Ultrafiltration (UF) are one topic as mentioned due to their many similarities. Both MF and UF are pressure driven with a shared area of usage and are based on molecular sieving with porous membranes. Both have remarkably similar separation procedure. However the key difference between MF and UF, is that the solutes eliminated by MF are bigger than those eliminated by UF [86-88]. Both MF and UF have wide applications such as water purification, removing particles, and clarifying different solutions. The toughest part of a MF and UF method is selecting the appropriate membrane unless this may lead to have an impact on the efficiency of heavy metals removal. Membranes vary accordingly to their porosity, structure, and material [80,89,90]. UF and MF both use membrane that must be porous; however, membranes can be symmetric or asymmetric. Symmetric membranes are characterized by structures which do not change over the membrane cross section. MF membranes are usually symmetric while UF membranes are typically asymmetric. Hydrophilic membranes, hydrophobic membranes and crystalline polymers are commonly used as MF and UF membranes [91,92]. The two filtration methods are dead-end and cross-flow methods. Dead end is used when feed flow perpendicular to the membrane surface while cross-flow method is used when the flow is parallel. Cross-flow requires more complex utilities; however, it does result in higher flux rates and membrane lifetimes.

Electro dialysis: Electrodialysis (ED) research and developement starts during the 1950s. ED is a helpful method for removing pollutants and is now used by many industries. ED works by an ion selective exchange membrane (IEMs). IEMs do not transport cations and anions at the same time; however, the ion transportation occurs only due to electrical potential or the concentration gradient [93-95]. If the ED electrodes polarity is reversed, then the method is referred to as electrodialysis reversal (EDR) which may be preferred over ED. EDR has a larger water recovery rate than ED but requires more plumbing and electrical controls.

Reverse Osmosis: Reverse Osmosis (RO) was initially researched in the 1920s; however, it did not become widely used until around the 1950s. RO is used by a variety of industries including food, biotechnology, pharmaceuticals, and water processing. RO is a pressure driven membrane technique. RO operates under hydraulic operating pressure and utilizes a semipermeable membrane with no distinct pores in order for the particles to flow through. Therefore, the transition must occur by diffusion [96-100]. For RO to occur first the water from a concentrated solution of heavy metal ions absorbs onto the surface of the membrane. Next, the particles diffuse through the membrane due to a concentration gradient. After the separation is complete there is a concentrated heavy metal solution one side and a treated solution on the other side.

Nanotechnology

Nanotechnology is commonly used for treating wastewater because to its large surface area and high adsorption efficiency. However, the use of nanotechnology also increases the chance of nano-pollutants being released into the environment. Nanotechnology has been the main focus of many researchers due to its pervasive use in chemistry, biology, medicine, and marketing products [101]. There are two methods used for removing heavy metals from wastewater by nanotechnology which are *in- situ* and *ex-situ*. *In-situ* is used if the wastewater is being treated in a place of contamination. *Ex-situ* is used for the treatment done after transferring wastewater to a preferred area. *In-situ* treatments are favored over *ex-situ* due to higher removal rates and economic benefit 102-104]. The three different types of nanoparticles used are adsorptive, reactive, and hybrid magnetic particles. Nano magnetic oxides (NMOs) are adsorptive and used often due to their high surface area, stability, and mesoporous shape. Nano zero-valent iron (nZVI) is a nanoparticle used to clean the wastewater and remove heavy metals through reactive technologies [104,105]. *In-situ* use of nZVI starts with injecting it into the wastewater solution thereby increasing the pH and thus reducing the redox potential. The final type of nanoparticles is hybrid magnetic nanoparticles (MNP's) which include two or more nanometer components upon which one of them is magnetic. MNP's are used because of their low toxicity, cost efficiency, ease, and high removal rates. Many materials can be applied to coat the MNP's including polymers. Past research has shown that different kinds of MNP's can be used to remove heavy metal in an efficient and economical manner [106,107].

Photo catalysis Process

Photocatalysis is a type of advanced oxidation process that used as recent advance technology for air and water purification. This technique uses non-toxic semiconductors and light with an appropriate wavelength as opposed to a chemical compound. This technique favored over chemical processes due to the absence of toxic materials, simplicity, affordability, increased stability, and increased efficiency [108,109]. Photocatalytic systems consist of five steps to separate the pollutants. First, the pollutants are transferred to the surface. Next, the pollutants are absorbed by the semiconductors. Thirdly, the photocatalytic reactions occur. Fourthly, the products are decomposed. Finally, the decomposed products are taken out of the area [110]. The third step is the vital step for the succession of reaction. This method required light to act as an activator which made thermal activation unnecessary. The first step also includes a photon excitation in the semiconductors. When a visible light with energy equal or more than the energy of the semiconductor excitation is used, the valence electrons get elevated to the conduction band [109]. This creates an electron hole pair so the light absorption process can take place. While this is occurring, the pollutants are reduced and oxidized by the transferring of photo holes and photoelectrons.

After the transformation is completed, heavy metals are recovered by mechanical and thermal procedures. Common semiconductors used in photocatalysis are oxides such as TiO_2, ZnO_2, CeO_2, WO_2, and sulfides such as CdS, ZnS, WS_2 [111-113]. Limitation to this method includes recombination of electron or hole, unwanted by-products formed, and errors in visible light absorption.

Conclusions

Heavy metals are detrimental to both environment as well as human beings. These metals are often found in wastewater and must be removed. This paper discusses the most common methods which are currently used to clean wastewater. The methods discussed are Electrochemical, Physicochemical, Membrane Filtration, Photocatalytic, and Nanotechnology. Each treatment has its own advantages, limitations and removal efficiencies under different specific circumstances. However, despite unique optimal conditions for each treatment, these are all found to be an effective way of removing heavy metals, pollutants from wastewater.

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