Review of Methods of Removal of Heavy Metals from Wastewater

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ABSTRACT: Heavy metals like copper, cadmium, chromium, nickel, zinc, lead, arsenic, and mercury are most common pollutants of water owing to their poisonous, persistent nature and non-biodegradable. The expansion of industry is the greatest source of heavy metals. These pollutants spread in different sections of the environment including air, water, soil, fish, vegetables. Human may easily absorb these metals from food and water, because they are very soluble in aquatic media. Different techniques have been developed and applied for wastewater treatment to remove heavy metals from the surrounding environment. These methods include membrane filtration, ion-exchange, adsorption, chemical precipitation, nanotechnology treatments, electrochemical and advanced oxidation processes. In this review, some of the methods are discussed. The different types of water treatment methods were mentioned and surveyed. In addition, the hazardous effect of different metals were mentioned. Advantages and disadvantages of the methods were discussed. Conclusions of the survey were added. Many important references were summarized.

Keywords: Heavy metals; water treatment; adsorption; wastewater, electrochemical

INTRODUCTION

Environmental contamination is causing more controversy in both human and ecological systems. Water contamination, in particular, is rising quickly as a result of industrial wastewater discharge. Reusing the recycled wastewater is the only method to discover new water sources. Several technologies for cleanup are used. It is convenient to reuse the reclaimed wastewater when it is accessible. Because of their toxicity, heavy metals like Zn, Cu, Pb, Ni, Cd, and Hg contribute to a variety of environmental issues (Carolina et al, 2017). Different materials have been proposed for removing of the heavy metals from wastewater (Meligi et al, 2008). Heavy metals pollution is a loading place of toxic metals such as copper, chromium, lead, cadmium, nickel into the environment. Common sources of these heavy metals are petroleum products, industrial waste, and soil leaching. The heavy metal pollutants in the aqueous environment are due to releasing from the industrial (Rojas et al, 2017) wastewater. The continuous exposing of heavy metal on the human body can cause multiple and dangerous health damages (Merzouk et al, 2011). For example, heavy metals are act as a reason for cancer in the human (Grimm et al, 1998; Kurniawan et al, 2006). The greatest danger of Pb lies in the development of the brain, where irreversible damage can occur. High levels can damage the kidneys and nervous system in both children and adults. Extremely high lead levels can also cause seizures, loss of consciousness, and death. Copper, like other rare metals, can become toxic if its rate is more than enough, and its abundance leads to: diarrhea - eczema - high blood pressure - kidney disease - nausea - sickle cell anemia - infectious pain - weakness and severe damage to the central nervous system - as well Its high levels, like the toxic metal lead, are associated with mental disorders (De Zuane, 1990; Kurniawan et al, 2006). High levels of Zn cause too much problems like skin irritations, vomiting, and stomach cramps, high concentration of Ni bring cancer of lungs and kidney (Owalude et al, 2016). Since wastewater is the main source of diseases and the continuous growth for the human population, it needs to be treated to decrease the toxicity (Fu and Wang, 2011). The typical concentration
ceilings were reported by the United States Environmental Protection Agency (EPA). Therefore, the industries must be careful of the possibility of discharge these heavy metals to the environment after the wastewater management process. Typical heavy metals found in wastewater and their origins, in addition to the health problems brought on by excessive levels and the acceptable levels in drinking water in accordance with the World Health Organization's (WHO) recommendations as showed in table (1) (Qassem et al, 2022).

<table>
<thead>
<tr>
<th>The heavy metal</th>
<th>The systems and organs affected*</th>
<th>Permitted amounts (μg)**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper (Cu)</td>
<td>The gastrointestinal tract, the brain, the kidneys, the cornea, the lungs, the immune system, and the hematological system.</td>
<td>2000</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>The reproductive system, the immune system, the hematological system, the cardiovascular system, the bones, the liver, the kidneys, the brain, the lungs, and the spleen.</td>
<td>10</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>The endocrine, metabolic, cardiovascular, immune, and pulmonary systems, as well as the skin, lungs, brain, and kidney.</td>
<td>10</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>The digestive system, reproductive system, tastebuds, lungs, kidneys, liver, brain, pancreas, and skin.</td>
<td>50</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>Constipation, rashes on the skin, nausea, vomiting, anaemia, and convulsions.</td>
<td>3000</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>Organs such as the heart, lungs, liver, kidneys, lungs, testicles, brain, immune system, and bones.</td>
<td>3</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>Kidney, pulmonar fibrosis, gastrointestinal distress, lung, and skin.</td>
<td>70</td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>Organs such as the brain, lungs, kidneys, liver, immune system, cardiovascular system, endocrine system, and reproductive apparatus</td>
<td>6</td>
</tr>
</tbody>
</table>


** Demiral et al, 2021.

Table (1): Typical heavy metals in wastewater, their sources, and the health issues.

In this review, the various treatment options for removing heavy metals from industrial effluent are summarized. Industrial wastewater treatment aims to produce wastewater that will cause as little damage as possible when discharged into the surrounding environment, thus preventing pollution. The major goals are to give helpful details about the most important aspects of removal methods and to give an overview of various studies. We have divided the methods of wastewater decontamination into seven different techniques. They are membrane filtration, chemical precipitation, electrochemical treatment, adsorption, ion exchange, coagulation/floculation, and flotation. The benefits and drawbacks of various types of treatment are provided for the mentioned techniques. The important problems and negative health impacts of heavy metals are also included. In addition, we have incorporated latest research on heavy metal removal.

2. Wastewater and pollution:
Lee and Choi, 2002, applied a photocatalytic oxidation of arsenite in TiO$_2$ suspension. (Quero et al, 2015) reported the contamination of heavy metals, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in coastal area of Po River Prodelta (Northern Adriatic Sea). (Tee et al, 2016) applied the concept of accomplishing wastewater treatment and generate energy simultaneously has been a trend recently and can be done with hybrid wastewater treatment system.

One of the problems facing the world is the water scarcity. In addition, the increase in environmental pollution from industrial wastewater and sewage in wrong ways. Therefore, there is a tendency to reprocess this wastewater and reuse it again for various purposes, including: uses of cities and urban areas in irrigation of public parks, constructions and sports facilities, and cleaning streets, agricultural crops such as food crops and not intended for trade, pastures for animals, seeds, ornamental flowers, aquaculture, and viticulture. This represents 30% of the total uses. Industrial uses: such as recycling cooling towers, washing oil are representing 60% of the total uses. Recreational uses as golf courses and snow making, environmental uses as recharging groundwater in wetlands and planting forests, drinking uses and potable water are representing 10% (U.S. Environmental Protection Agency, 2009). The treated water is considered safe for use according to modern studies. It does not constitute a significant difference from groundwater. Industrial wastewater treatment can be challenging and necessitates specialized approaches to get rid of all sediments and dangerous substances and achieve the desired water quality. This treatment tack place in several stages.

It is noticed that the percent of heavy metal (especially Cd) in the river Nile in the latest year increased (Abotalib et al, 2023). According to local researches on the Nile Delta drains, the concentration of heavy metals and various contaminations in the sediments of the analyzed drains increased as a result of water recycling and the use of phosphate-rich sewage water for irrigation, which is frequently subject to partial or no treatment (Hegazy et al, 2020). The main sources of pollution in the river Nile include the discharge of sewage from open drains transporting industrial effluent, sewage, and agricultural return flows (Abd El-Hady, 2014).

Municipal wastewater production in Egypt is roughly 3.5 billion m$^3$/year, but the country's present treatment capacity is only about 1.6 billion m$^3$/year. By 2017, it was intended to increase treatment capacity by 1.7 billion m$^3$.

3. Common Methods for Wastewater Treatment:

For many years, researchers have used different methods for removing heavy metals from different wastewaters that can be classified as electrochemical treatments (electrocoagulation, electorfloatation, and electrodeposition), physicochemical processes (chemical precipitation, ion exchange), adsorption (activated carbon, carbon nanotubes, and wood sawdust adsorbents), or current methods (membrane filtration processes, photo catalysis processes, and nanotechnology). Treatment technologies are mainly based on physicochemical, electrochemical or advanced oxidation processes. Photo catalysis is one of the advanced removal of inorganics from water (Pincus et al, 2019). Beside all these, nanotechnology is practically used in wastewaters treatment.

3.1. Electrochemical treatment of wastewaters:

The electrochemical process is mostly used to treat wastewater. The method is based on the use of electrodes for discharging the ions in the wastewater. These charges will be neutralized and subsequently the corresponding ions start to coagulate (Tran et al, 2017) (Beauchesne et al, 2014).

Electrochemical technologies are in the unique position of not only being cost-competitive with other technologies, but they also are more efficient and important in some cases, the electrochemical technologies may be an essential step that cannot be neglected in treating wastewaters containing refractory pollutants (Khandegar and Saroha, 2013). In this method, three major electrochemical treatment technologies including electrocoagulation (EC) (El Karamany et al, 2020), electroflotation (EF) and electrodeposition (ED).

Electrochemical deposition is a simple and easy method. This treatment method is widely used for heavy metals removal from wastewaters. Beauchesne et al, 2014, applied two-stage process that combines electrochemical leaching and electrodeposition of copper (Cu) for the decontamination of sewage sludge was studied in a single cell. Electrochemical process was applied for purification of wastewater from either heavy metals or organic pollutants (Juttner and Galla, 2000).

3.2. Adsorption methods:

Adsorption technique for removing heavy metals from wastewaters has been successful in lowering the metal concentrations. Adsorption is based on solid-liquid transfer between the adsorbate and the adsorbent. Three key stages are involved: (i) the surface adsorption; (ii) adsorption on the adsorbent surface; and (iii) penetration in the adsorbent. These adsorbents provide large surface areas and high adsorption capacity. The good point is that the process can run in reversible mode and the adsorbents will be regenerated by desorption (Hayashi et al, 2022). Adsorbents can be derived from agricultural waste, industrial products, or natural materials. Some of the most used adsorbents in this process are discussed in this review.

Adsorption by activated carbon is commonly used for the removal of heavy metals and has been studied extensively on various carbon sources. Activated carbon is produced from biomass waste materials (Adinata et al, 2007; Hayashi et al, 2002), or newspaper (Okada et al, 2003). It was modified by heat treatment (Okada et al, 2003; Demiral et al, 2021). The process was based on washing the carbon source with deionized water and then heated at 450°C for 4 hrs. Activated charcoal usually has an internal surface area of 900-2000 m²/g, while non-activated charcoal may have a surface area of 400-800 m²/g (Cooney, 1995).

Carbon nanotubes (CNTs) are known with excellent properties for different applications. Heavy metals are sucked by CNTs according to a very complicated mechanism. Some researches (Kabbashi et al, 2008; Kandah et al, 2007) showed that CNTs have a great ability for removing heavy metals. CNTs by calcium alginate (CNT/AC) reduce the risks caused by discharging a lot of CNTs into the water environment (Okada et al, 2003). Worked on Cu(II) adsorption by CNTs and CNTs/AC. The results showed that optimum results at pH 5.074. (8%) removal efficiency by using CNTs and 83.3% by using CNTs/AC was achieved under the mentioned experimental conditions (amount of adsorbents: 0.05 g, concentration of Cu(II):20 mg/L) (Li et al, 2010).

Ku and Jung, 2001, studied the reduction of Cr(VI) to Cr(III) in aqueous solution by UV/TiO₂ reduction. The reduction rates of Cr(VI) adsorbed on TiO₂ by photocatalytic-induced elections were significantly higher for acidic solutions than those for alkaline solutions.

The use of polymeric material in heavy metal removal from wastewater is trending. Polyurethane (PU) was modified by activation with 0.1M HNO₃. Effects of different parameters such as, concentration of solution, contact time, flow rates and pH of adsorbent on the adsorption capacity were studied. Characterizations polyurethane (PU) were investigated using scanning electron microscope (SEM). Moreover, the adsorption capacities of some heavy metals such as, Zn(II), Fe(II), Ca(II), Ni(II), Cu(II) and Pb(II) onto PU-fom modified with dithiocarbamate derivative were studied (Murthy et al, 2011). The withdrawing of metal ions was remarkably affected by the pH of the solution, the valances of metal ions and its initial concentrations. Equilibrium isotherms and interrumpptible diffusivities were investigated through batch experiments in analyzing the of aqueous solutions of metal ions onto PU foam. The Freundlich constants k and 1/n and Longmuir constant q, had been calculated for each metal ion to represent both the ability and the affinity of that ions towards the withdrawing materials (PU). Meligy, 2008, used PU modified by grafting a mixture of two monomers acrylonitrile/acrylic acid (AN/Ac) by gamma irradiation method. He tested the adsoprtion capacities for different heavy metals like Zn(II), Fe(II), Ca(II), Ni(II), Cu(II) and Pb(II). Rojas et al, 2017, developed new biocomposites based on ionic liquids [BMIM][Cl], [BMIM][BF₄], [EOHMIM][Gly] supported on polyurethane foam, synthesized from castor oil as polyol and HDI as isocyanate. Zareh et ah, 2023, applied the use of PU without modification by any hazardous chemicals. They apply a two-stages model for the removal of lead from onndustrial wastewater with efficiency reeaching 85.6-98.6%. Removal of iron from water by Aspergillus niger was successfully applied based on adsorption mechanism by Zareh et al, 2022.

5.4. Ion-exchange methods:

In this method, a reversible exchange of ions between the two states (solid and liquid) occurs. A resin removes ions (either cation or anion) from an electrolytic solution and releases other ions of similar charge in a
chemically equivalent amount. The ion exchanger is usually synthetic matter containing an active ionic group, which is able to exchange with either cations or anions. The exchange process is not selective and highly sensitive to pH value (Barakat, 2011). Clinoptilolite, as one of natural Zeolites was shown to be selective for Pb(II), Cd(II), Zn(II), and Cu(II). The cation-exchange ability of clinoptilolite was based on the pre-treatment method and conditioning which improved its ion exchange ability and removal efficiency (Babel and Kurniawan, 2003; Bose et al., 2002).

5.5 Nanotechnology methods:

In the last two decades, nanotechnology is becoming a branch of science of nanomaterials. Recently, nanotechnology was used successfully for the removal of heavy metals from wastewater. The unique properties of nanomaterials are preferable for the metal removal. These properties include the high specific area, chemical reactivity, high magnetism behaviors, short intra particle diffusion distance and easier penetration (Kabbashi et al, 2009). Nanomaterials are great adsorbents due to their large surface area, also they are used widely in treating wastewaters containing heavy metals (Dutta et al, 2022) introduced a review about the use of the synthesized a bio-inspired carbon-based on nanomaterials for environmental application. That is be noticed the increasing in using nano adsorbents increase the risk of nano-pollutants in the environment.

Carbon nanotubes were applied for the treatment of wastewater (Saeran, and Zakwan, 2010). Carbon nanotube/calcium alginate composites were applied for removal of copper from aqueous solutions (Li et al, 2010).

Conclusions

Removal of heavy metals from wastewater is one of the greatest issues that have received great attention, because the fear of a lack of clean natural water sources. In addition, the population increase and the great industrial and technological progress that resulted in more water demands accompanied by water pollution. The most effective method for removing heavy ions from wastewater must be chosen based on a number of important considerations, such as the operation cost, initial concentration of the metal ions, environmental impact, pH levels, chemicals added, removal effectiveness, and economic viability. The treated wastewater and major methods of water treatment are reviewed. These are electrochemical, adsorption, ion exchange and nanotechnology treatments. Each method has its own removal efficiencies and the specific parameters that affect the removing.

REFERENCES


