Research and development on industrial heavy metal wastewater treatment technology

Bo Chen¹, Yuchao Chen¹, Lufeng Xu¹, Yiming Zhang¹, Haixiang Li¹,2*

¹College of Environmental Science and Engineering, Guilin University of Technology, Guilin, 541006, China;
²Guangxi Key Laboratory of Environmental Control Theory and Technology, Guilin, 541006, China
*Corresponding author’s e-mail: lihaixiang0627@163.com

Abstract. With the development of industrial technology and the improvement of industrialization, the discharge of heavy metal wastewater gradually increases. Heavy metals are the main sources of water pollution, and heavy metal wastewater mainly comes from mines, smelting, electrolysis, electroplating, pesticide, medicine, paint, pigment and other enterprises. In this paper, the common heavy metal wastewater treatment technology is summarized, and the characteristics and treatment methods of industrial wastewater are mainly introduced.

1. Introduction
In China, overall water resources are relatively abundant, ranking sixth in the world, but the per capita water volume is relatively low, only 1/4 of the global per capita water volume level. In recent years, with the rapid development of industrialization, the discharge of industrial wastewater has seriously damaged the ecological environment. Among the many industrial waste waters, heavy metal industrial wastewater is the most harmful. The inadequate management of heavy metal pollution has gradually caused serious consequences. Major pollution incidents involving heavy metals have occurred frequently in some river basins and regions, and the ecological environment has been severely damaged.

The pollution of heavy metal ions in the water ecosystem where industrial wastewater is mainly discharged has become a serious problem, and the harm to humans and other organisms is becoming more and more serious. Once heavy metals enter the human body, they will accumulate in the human body and cause damage to the human body. Plumbum, mercury, cadmium, chromium, zinc, and copper ions are considered to be pollutants that must be removed from wastewater. In particular, plumbum can heat the hematopoietic system, leading to anemia, encephalopathy, hepatitis, etc. Since wastewater is the main source of diseases and hinders the sustainable growth of human beings, it needs to be treated to degrade pollutants into less toxic forms. The standard concentration limits of heavy metals specified by the U.S. Environmental Protection Agency (EPA) are shown in Table 1.

Heavy metals have high solubility in the aquatic environment and are easily absorbed by fish and vegetables. Therefore, they may accumulate in the human body through the food chain and food web. A variety of wastewater treatment methods have been developed and used to reduce heavy metal concentrations, such as technical chemical treatment, physical chemical treatment and biological treatment[1]. This article will describe several industrial wastewater treatment methods for heavy metals.
Table 1. Standard concentration limits set by the U.S. Environmental Protection Agency (EPA).

| Heavy metal name | MCLG (mg/L) | MCL or TT (mg/L) | harm |
|------------------|-------------|------------------|------|
| Cd               | 0.005       | 0.005            | Kidney damage |
| Cr (total)       | 0.1         | 0.1              | Allergic dermatitis |
| Cu               | 1.3         | 1.3              | Short-term exposure: gastrointestinal discomfort; Long-term exposure: liver or kidney damage |
| As               | 0.01        | 0.01             | Skin damage or circulatory system problems may increase the risk of cancer |
| Pb               | 0           | 0.015            | Infants and children: physical or mental development is hindered; Adults: kidney problems; |
| Ni               | 0.20        | 0.20             | Dermatitis, nausea, chronic asthma, cough, human carcinogen |
| Zn               | 0.80        | 0.80             | Depression, lethargy, neurological symptoms, and thirst |
| Hg               | 0.002       | 0.002            | Kidney damage |
| Be               | 0.004       | 0.004            | Intestinal disease |
| Ti               | 0.0005      | 0.0005           | Hair loss; blood changes; kidney problems |

2. Heavy metal treatment methods and cases

2.1 Heavy metal treatment methods

2.1.1 Chemical treatment method

The chemical method can be divided into chemical precipitation method, electrolysis method and redox method.

1) Chemical precipitation method

In actual treatment work, people use instruments and reagents to fuse metal ion solutions with industrial wastewater by preparing heavy metal ion solutions, industrial wastewater, and adsorbents. Calcium hydroxide and other solutions are put into the industrial wastewater solution and directly chemically react with the heavy metal ions in it. Through a series of processes such as decomposition reaction, precipitation, and heavy metal ion concentration detection, a precipitate that is insoluble in water is finally formed, which is adsorbed by the biofilm adsorbent, so that industrial wastewater can be well purified. This method is suitable for the purification treatment of heavy metal ions such as mercury, zinc, lead and chromium. However, chemical precipitation requires many chemicals to reduce metal ions to acceptable emission limits, but sometimes this is not achieved, and these chemicals will be a major source of further pollution.

When Ruiping Wu et al.[2] used chemical precipitation to remove heavy metals, they found that related influencing factors such as pH value, adsorption time, adsorbent dosage, initial concentration of metal ions, and temperature have an impact on the removal effect. The removal rate of heavy metal ions varies with the pH value. When there is no metal precipitation, the removal effect is best when the pH value is 5. Dursun et al.[3] use the most effective condition for removing mercury in wastewater by chemical precipitation is that the pH value is between 7 and 8, and the ambient temperature is 1 hour. The amount of Na₂S (precipitate) added has an effective effect on the treatment process. Its characteristics are low cost and simple operation. The results show that the mercury removal efficiency of this method can reach 99%.

2) Electrolysis method

Electrolysis technology mainly used the mixed filler of iron filings, activated carbon particles and cast iron filings produced during industrial processing to process printing and dyeing, pharmaceuticals, electroplating, and coking the refractory wastewater in other fields is an "environmentally friendly"
technology. This method is mainly suitable for the purification treatment of heavy metal ion wastewater such as cadmium and chromium.

Mohammed and Najwa used electrocoagulation to remove metal cadmium in wastewater[4]. The study found that the pH value increased from 5-7, and the removal rate of cadmium increased, but when the pH value was greater than 7, the removal rate decreased. When pH is 7, the initial concentration is 50 mg/L, and the applied voltage is 20 V, the removal effect is the best, reaching 90%.

3) Redox method

When the toxic heavy metals in the wastewater are reducing substances, a specific oxidizing agent is added to oxidize the toxic heavy metals into non-toxic or less toxic heavy metal ions or precipitate through the interaction between the ions. This method is called chemical oxidation method. The most commonly used chemical agent in the treatment of heavy metal wastewater is oxychloride, that is, adding oxychloride-containing agents such as liquid chlorine, bleaching powder, etc. The principle is that the hypochlorite generated by the chemical agent has a strong oxidizing effect.

Lixin Xie[5] used a 5052 aluminum alloy ring filled in an ion exchange tower as a reducing agent to remove copper ions from seawater. The results showed that the removal rate of copper ions can reach 88%. The decrease of flow rate and the increase of temperature increase the removal rate of copper ions; the increase of copper ion concentration reduces the removal rate of copper ions.

2.1.2 Physical and chemical treatment method

The physical and chemical treatment methods can be divided into: physical/chemical adsorption method, ion exchange method, and membrane separation method.

1) Physical/chemical adsorption method

The basic principle of the adsorption method is mainly physical adsorption and chemical adsorption. There are many kinds of physical adsorbents, all of which express the characteristics of developed pores and huge specific surface area. Activated carbon is the most common physical adsorbent. Chemical adsorbents that usually used are humic acid substances, which are suitable for treating mine wastewater with large water volume and various heavy metal ions but low concentration.

For the adsorption of pollutants on the adsorbent, three key stages are involved:

a) Pollutants penetrate from the bulk solution to the surface of the adsorbent;

b) The adsorption of pollutants on the surface of the adsorbent;

c) The penetration of pollutants in the adsorbent structure.

Camilla et al[6]. used the adsorption method to remove metal cadmium. In the research experiment, the intermittent test method was used to study the concentration of zinc and cadmium between 10 ~ 200mg/L, and the effect of different adsorbent dosages (10 ~ 60g/L) on clininite zeolite adsorption performance. Starting from the clininite concentration of 10g/L, when the metal concentration in the solution is low, both zinc ions and cadmium ions can be completely adsorbed. Then as the amount of metal continues to increase, until 200mg/L, the adsorption capacity decreases.

2) Ion exchange method

Ion exchange treatment is based on the reversible exchange of ions between the solid phase and the liquid phase. The whole process starts from the ion exchange reaction, where heavy metal ions are physically adsorbed, forming complexes between counter ions and functional groups, and finally, hydration occurs on the surface of the solution or the pores of the adsorbent[7].

In ion exchange, a reversible exchange of ions occurs between two phases (solid and liquid). In this method, the resin removes ions from the electrolytic solution and releases other ions with similar charges in a chemical equivalent[8]. During this process, any structural changes in the resin will occur. The recovery of valuable heavy metals from inorganic wastewater can also be carried out by ion exchange[9].

In this process, the insoluble resin is used to remove heavy metal ions in the wastewater and release other ions with similar charges, while the resin itself has no structural changes. Ion exchange resin is a good choice for treating wastewater to eliminate or separate heavy metal ions[10]. Among all available types, synthetic polymer resins are preferred, such as styrene-divinylbenzene[11]. Another option is gel-
like, which is sometimes more efficient and less costly. Macroporous resin has a sponge-like structure, which provides better physical stability and leads to more stress relief[10].

At this time, the adsorption capacity of Co$^{2+}$, Mn$^{2+}$, and Ag$^+$ reached the maximum. It is 63.5, 71.6, 61.7 mg/g. And when the temperature is between 20-40°C, the adsorption capacity of Dowex 50W-x8 resin for metal ions increases as the temperature increases.

Nomngongo et al[12]. used Dowex 50W-x8 resin to remove Co$^{2+}$, Mn$^{2+}$, and Ag$^+$ from ethanol at 40°C. At this time, the adsorption capacity of Co$^{2+}$, Mn$^{2+}$, and Ag$^+$ reached the maximum, It is 63.5, 71.6, 61.7 mg/g. And when the temperature is between 20-40°C, the adsorption capacity of Dowex 50W-x8 resin for metal ions increases as the temperature increases.

3) Membrane separation method

Membrane separation technology is a method of separating or concentrating solvents and solutes based on the difference in the selective osmosis of the different components of the mixture under the action of external pressure without changing the chemical form of the solution. The current membrane separation technologies mainly include microfiltration, ultrafiltration, electrodialysis, reverse osmosis, and nanofiltration.

Naghddali et al[13]. used the biomimetic membrane (protein membrane) of aquaporin (AQP) based on the forward osmosis process (FO) and optimized the rejection of Cr by response surface method (RSM) to remove chromium. The use of CCD-RSM is the key to the FO process. The parameter predicted water flux, Cr inhibition rate and reverse solute flux (RSF) were 9.8 L/m²h, 96.3% and 7.16 g/m²h, respectively; the experimental results under the best conditions were 10.66, 97.67% and 8.33, respectively. However, the particle size of heavy metal ions is relatively small. Under normal circumstances, microfiltration and ultrafiltration membrane technology cannot remove them. It needs to be combined with other processes to have a better treatment effect on heavy metal ions.

2.1.3 Biological treatment method

As a new type of treatment method, biological method has the advantages of high efficiency, low cost, no secondary pollution, and environmental protection. It mainly includes biological adsorption method, biological flocculation method, biological surfactant repair and other methods.

1) Biosorption method

The biological treatment technology in wastewater treatment, also known as biological adsorption method, is to make full use of the biological body's own chemical structure and composition characteristics to make it adsorb heavy metal ions in the wastewater, and then remove the wastewater by separating solid and liquid in heavy metal ions.

Elahi et al[14]. used microorganisms such as bacteria, yeast and algae to bioremediate Cr$^{6+}$. In soil and sediment, Cr$^{3+}$ spontaneously oxidizes to Cr$^{4+}$ with the help of molecular oxygen and manganese oxide (MnO$_2$) (1); However, Cr$^{6+}$ is reduced to Cr$^{3+}$ is carried out by a variety of reducing carbon compounds (2), such as hydroquinone in the soil. Studies have found that chromate reducing bacteria have the ability to detoxify chromium through the conversion of Cr$^{6+}$ to Cr$^{3+}$, and can be used in situ and on-site bioremediation.

$$Cr^{3+} + 1: 5MnO_2 + H_2O \rightarrow HCrO_4^- + 1: 5Mn^{2+} + H^+$$  
$$C_6H_4O_2 + CrO_4^{2-} + 2H_2O \rightarrow 0.5Cr_2O_3 + 1: 5C_6H_4O_2 + 2.5H_2O + 2OH^-$$  

2) Biological flocculation method

Biological flocculant is a natural organic polymer flocculant made of microbial metabolites or chemically modified. A new type of flocculant is developed by cultivating microorganisms. Its main chemical components are glycoprotein, polysaccharide, protein, nucleic acid and cellulose.

Hou Rong et al[15]. used the specific charge density (SCD) index to comprehensively consider the influence of the molecular weight and charge density of the flocculant, and evaluated the performance of the ionic polymer flocculant PDADMAC. The results show that PDADMAC with high SCD value is an effective factor affecting pollutant removal.

3) Biosurfactant repair
Biosurfactant is an amphoteric compound with a certain surface and interface activity secreted by microorganisms in the metabolic process, and contains both hydrophilic and hydrophobic groups. Biosurfactants help to improve the contact behavior of the pollutant-water-microbial cell interface, and can speed up the utilization and degradation of pollutants by microorganisms by enhancing the hydrophilicity of hydrophobic organic substances and the hydrophobicity of cell membranes.

Zhou Jian et al. [16] used additives to enhance the electric remediation effect of heavy metal contaminated sludge, and added biosurfactants separately. The highest removal rates of Zn, Cu, Ni and Cd in the anode zone were sophorolipid (53.85%), rhamnolipid (44.26%), rhamnolipid (56.33%), sophorolipid (34.43%); after compound with citric acid, the removal rate of anode heavy metals can generally be increased by 0.90% compared with the addition of biosurfactant alone ~16.08%, citric acid can significantly improve the accumulation of heavy metals in the middle.

3. Significance of reuse after treatment of heavy metal industrial wastewater
The scientific and effective treatment of heavy metal industrial waste water to discharge it after reaching the national standard has the following significance:

1) Reduce environmental pollution and protect the living environment;
2) The recycling of rare heavy metals can effectively save related resources;
3) Protect the ecological chain and ecological network and protect human health;
4) Recycling of water resources.

4. Summary and Outlook
Toxic substances widely distributed in industrial wastewater such as heavy metals, phenolic compounds and other non-biodegradable pollutants are considered harmful to humans and the environment. This article reviews several commonly used heavy metal wastewater treatment methods, including chemical treatment, physicochemical treatment and biological treatment. The heavy metal ions in industrial wastewater are removed by single or combined waste water treatment method, which reduce the discharge of pollutants, protect the environment and reuse heavy metals, and achieve the secondary utilization of resources. But there are still the following shortcomings:

1) The traditional wastewater treatment process of industrial heavy metal wastewater has the disadvantages of high cost, slow response, easy to cause secondary pollution, and difficult to treat low-concentration wastewater. Therefore, we should devote ourselves to the transformation of traditional crafts and the development of new crafts;

2) As a new type of treatment method, biological method has the advantages of high efficiency, low cost, no secondary pollution, and environmental protection. However, it is necessary to find a suitable microbial flora, so we should devote ourselves to micro-level exploration;

3) The composition of industrial heavy metal wastewater is complex, and it contains many types of heavy metals and different concentrations. Therefore, it is necessary to consider the combined process of multiple water treatment methods to achieve the best heavy metal removal effect.

References
[1] Azimi A, Azari A, Rezakazemi M, et al. (2017) Removal of Heavy Metals From Industrial Wastewaters: a Review[J]. Chembioeng Reviews, 4(1): 37-59.
[2] Ruiping W. (2019) Removal of Heavy Metal Ions from Industrial Wastewater Based on Chemical Precipitation Method. [J]. Ekoloji Dergisi, 107(107): 2443-2452.
[3] Dursun Sukru 1, Navruz Hamza. (2017) removal of heavy metal from the metal finishing industry wastewater by chemical precipitation. [J]. International Journal of Ecosystems & Ecology Sciences, 7(1): 9-12.
[4] Salem mohammed alameen, Majeed Najwa. (2020) Removal of Cadmium from Industrial Wastewater using Electrocoagulation Process[J]. Engineering Journal, 26(No.1): 24-34.
[5] Lixin X, Zhiguo T. (2012) Removing copper ion from seawater with redox method[J]. Chemical Industry and Engineering Progress, 31(9): 1899-1902, 1925.
[6] Galletti C, Dosa M, Russo N, et al. Zn$^{2+}$ and Cd$^{2+}$ Removal From Wastewater Using Clinoptilolite as Adsorbent[EB/OL]. [S.l.]: Springer Science and Business Media Llc, 2020(2020-3-16) [2020-6-30]. https://dx.doi.org/10.1007/s11356-020-08483-z. 10.1007/s11356-020-08483-z.

[7] Ferreira SL, De brito CF, Dantas AF, et al. (1999) Nickel Determination in Saline Matrices By Icp-aes After Sorption on Amberlite Xad-2 Loaded with Pan[J]. Talanta, 48(5): 1173-1177.

[8] Rengaraj S, Yeon K, Moon S. (2001) Removal of Chromium From Water and Wastewater By Ion Exchange Resins[J]. Journal of Hazardous Materials, 87(1): 273-287.

[9] Dąbrowski A, Hubicki Z, Podkościelny P, et al. (2004) Selective Removal of the Heavy Metal Ions From Waters and Industrial Wastewaters By Ion-exchange Method[J]. Chemosphere, 56(2): 91-106.

[10] Gode Fethiye, Pehlivan Erol. (2006) Removal of chromium (III) from aqueous solutions using Lewatit S 100_ the effect of pH, time, metal concentration and temperature. [J]. Journal of hazardous materials, 136(2): 330-337.

[11] Alyüz B, Veli S. (2009) Kinetics and Equilibrium Studies for the Removal of Nickel and Zinc From Aqueous Solutions By Ion Exchange Resins[J]. Journal of Hazardous Materials, 167(1): 482-488.

[12] Nomngongo, Ngila, Msagati, et al. (2014) Kinetics and Equilibrium Studies for the Removal of Cobalt, Manganese, and Silver in Ethanol Using Dowex 50w-x8 Cation Exchange Resin[J]. Separation Science and Technology, 49(12): 1848-1859.

[13] Naghdali Z, Sahebi S, Mousazadeh M, et al. (2020) Optimization of the Forward Osmosis Process Using Aquaporin Membranes in Chromium Removal[J]. Chemical Engineering & Technology, 43(2): 298-306.

[14] Elahi A, Arooj I, Bukhari DA, et al. (2020) Successive Use of Microorganisms to Remove Chromium From Wastewater[J]. Applied Microbiology and Biotechnology, 104(9): 3729-3743.

[15] Ling L, Yadan G, Wenchao Y, et al. Application Progress of Bioflocculant on Treatment of Heavy Metal Wastewater[C]/Proceedings of 2016 5th International Conference on Environment, Materials, Chemistry and Power Electronics(emcpe 2016), [S.l.]: [s.n.], 2016: 20-24.

[16] Jian z Lichuang W, Fanglei Z, Yanli T. (2019) Electrokinetic Repair of Heavy Metals in Sludge by Biosurfactant and Its Combination with Citric Acid[J]. Journal of Hunan University (Natural Sciences), 46(6): 109-119.