Progress on Mercury-containing Wastewater Treatment

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Abstract. With the development of industry and economy in the world, a large amount of heavy metal industrial wastewater is difficult to decompose in nature and is discharged without treatment to form water pollution. It poses a major threat to the environment, ecology, and human health. Mercury is one of the highly toxic heavy metal elements in the environment. Mercury and mercury compounds are widely present in nature. This article introduces three methods for treating mercury wastewater including chemical precipitation, adsorption, and photocatalysis. Adsorbents such as activated carbon, iron oxide, and nanoparticles can remove mercury ions by adsorbing them. Precipitating agents such as sulfides and hydroxides can bind mercury ions to form precipitates, thereby achieving removal. Photocatalysis uses photocatalysts such as titanium dioxide to generate active oxygen species under light to oxidize and decompose inorganic mercury in wastewater, thereby achieving the purpose of mercury removal. Factors such as treatment efficiency, cost, sustainability, and environmental impact need to be comprehensively considered to select an appropriate method for treatment. Future research needs to further explore efficient and environmentally friendly methods for treating mercury in water.

Keywords: Mercury-containing wastewater, environmental protection, chemical precipitation, adsorption.

1. Introduction

Mercury is a toxic heavy metal often found in water bodies, especially industrial wastewater and wastewater discharged from mines. Mercury contamination of water bodies poses serious threats to human health and ecosystems. In the mid-20th century, mercury pollution posed a serious health threat to the Japanese city of Minamata. Minamata disease was one of the most serious and painful events in history to discover the dangers of mercury. Mercury and mercury compounds are highly toxic. Metallic mercury and inorganic mercury can damage the liver and kidneys, while organic mercury can damage the brain. Mercury can be converted into organic methylmercury $Hg\ (CH_3)_2$ by microorganisms in water bodies. Methylmercury has high bioaccumulation and is easily ingested by aquatic organisms accumulated in the body, and then enters the food chain and is harmful to aquatic organisms and fish. cause toxic effects. This will cause organisms in the food chain to accumulate mercury at higher and higher concentrations, causing damage to the ecosystem [1, 2]. For instance, in the process of Carbide, in the PVC production process, the synthesis of acetylene and hydrogen chloride to convert vinyl chloride requires the use of a mercury chloride catalyst. At high temperatures, mercury chloride is easily sublimated and lost, and enters the subsequent purification system with the synthesis gas, eventually producing a certain amount of mercury-containing waste. The mercury flows in the calcium carbide PVC production process are mainly waste mercury catalysts, mercury-containing waste activated carbon, mercury-containing waste hydrochloric acid, mercury-containing waste alkali, etc., accounting for 36%, 8%, 51% and 5% of the total use of mercury chloride respectively [1,3].

The main methods for treating mercury-containing wastewater include chemical precipitation, redox, activated carbon adsorption, ion exchange, electrolysis, microbial, and photocatalytic methods [4]. Mercury removal is achieved by adding chemical precipitants to convert inorganic mercury into insoluble precipitates. Studies have shown that some functionalized precipitants, such as sulfide, hydroxide, and other ion exchangers, have good mercury ion removal capabilities. The selection and design of these precipitants can be adjusted according to the characteristics of mercury ions in wastewater to improve removal efficiency and selectivity [5-7]. The chemical precipitation method is still the most widely used heavy metal treatment method due to its simple operation and economical advantages. Chen et al. introduced a combined method of treating mercury, combining chemical methods with physical methods-chemical precipitation methods, and redox methods. The results showed a removal rate of more than 99.95%. In the production of calcium carbide PVC, the water quality data of mercury wastewater after serious treatment can reach a pH of 7-8, the suspended solid mass concentration is smaller than 5mg/L, and the total mercury ion mass concentration is smaller than 0.0005mg/L. This combined method effectively achieves the treatment of mercury wastewater [1].

In this article, the commonly used treatment technologies, and methods for common mercury compounds in wastewater are reviewed, including chemical precipitation, adsorption, photocatalysis, and biological treatment. Finally, the advantages and disadvantages of various processing methods are compared and analyzed, and the direction and prospect of future research are proposed.

2. Treatment Methods for Mercury-Containing Wastewater

2.1. Adsorption Method

The adsorption method concentrates pollutants on the surface and pores of the porous adsorbent through physical and chemical effects on the adsorbent surface and then uses appropriate solvents, heating, or blowing to absorb heavy metal ions to achieve separation [8-10]. The adsorption method is a relatively common and effective method for treating mercury wastewater. It has the advantages of simple operation and relatively low cost. The mechanism of adsorption materials adsorbing mercury ions mainly involves the following aspects including van der Waals forces, ion exchange, surface oxides, and pore effects. Diverse adsorption materials can selectively remove mercury pollutants, so adsorption methods are widely used in mercury-containing wastewater treatment. Various adsorption materials include zeolites, activated carbon, chitosan, cellulose, aluminosilicates, sulfur compounds, etc. Among them, sulfide and sulfur-modified adsorption Adhesives have a strong binding force with mercury. Therefore, sulfide adsorbents are widely used [9, 10].

2.1.1. Biosorbent

Microbial adsorbents are a type of adsorbent that adsorb heavy metal ions through two processes: surface adsorption and intracellular accumulation of microorganisms. Biosorbents mainly include bacteria, fungi, algae, and some cell extracts. Research shows that when the mass concentration of metal pollutants in wastewater is 1 to 100 mg/L, low-cost and easily available microorganisms have a very good ability to enrich and separate heavy metals from the solution [10, 12]. Piedra et al. added lactic acid bacteria to aqueous solutions of Hg (II) and CH_3Hg or food samples and simulated gastrointestinal digestion of the mixture. Under simulated gastrointestinal digestive fluid conditions, Lactobacillus BL23 has a good adsorption effect on Hg^{2+} and methylmercury in water, with adsorption rates reaching 72% to 98% and 74% to 97% respectively [11]. The cell wall of lactic acid bacteria is mainly composed of peptidoglycan, teichoic acid, proteins, and polysaccharides. The proteins and polysaccharides contain some functional groups that can effectively remove heavy metals after surface coordination reactions with heavy metal cations [10]. Fig. 1 provides the mechanism of microbial adsorption of heavy metal.

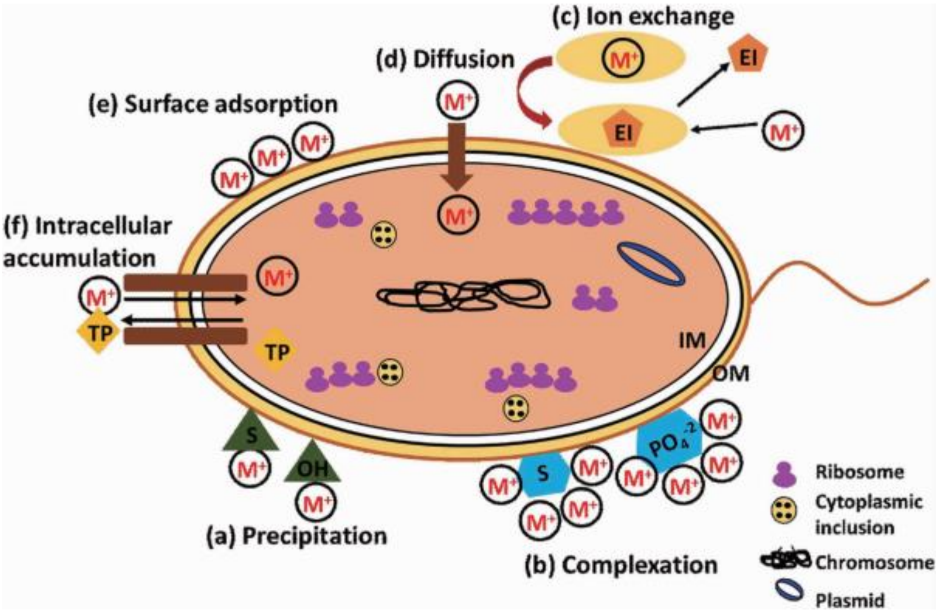

Figure 1. Mechanism of microbial adsorption of heavy metal [13].

2.1.2. Activated carbon adsorbent

Activated carbon is a porous material with a highly developed pore structure and a huge specific surface area, which gives it high adsorption capacity [14,15]. The activated carbon adsorption method mainly uses activated carbon's physical adsorption, chemical adsorption, and oxidation, A wastewater treatment method that uses its properties such as catalytic oxidation and reduction to remove harmful substances from the water. The adsorption performance of activated carbon is affected by many factors, including activated carbon type, solubility, temperature, pressure and pH. As well as the adsorption process parameters contact time, initial concentration, etc. The mercury wastewater is contacted with activated carbon so that mercury ions are adsorbed by the surface activated carbon. When the activated carbon is saturated and adsorbs mercury ions, the adsorbed mercury ions can be removed from the activated carbon through pyrolysis, steam regeneration, chemical elution, and other methods to restore the adsorption capacity of the activated carbon. It should be noted that after the adsorption is completed, the wastewater generated during the adsorption regeneration process must be treated to avoid secondary pollution. Studies have shown that polythiourea increases the adsorption of mercury on activated carbon. Because polythiourea has high mercury affinity. In addition, it can be used as a solid-phase adsorbent to separate mercury ions from wastewater [14].

Wang et al. induced three experiments, the coconut shell activated carbon was treated with hydrogen at high temperature and then further treated with nitric acid liquid phase oxidation to introduce oxygen-containing groups. The adsorption effects of two modified and unmodified activated carbons were compared. Mercury chloride solutions with different initial concentrations were selected for adsorption tests at room temperature. As shown in Fig. 2. As the concentration of mercury ions increases, the adsorption capacity of the three activated carbons continues to increase and then slowly slows down. It can be seen from the figure that at the same equilibrium concentration, the adsorption capacity of mercury ions of activated carbon (AC-H_2) treated with hydrogen is greater than that of untreated activated carbon, while the adsorption capacity of activated carbon treated with nitric acid is the least. Wang et al. used the Freundlich adsorption isotherm model and found that the n values of the three different activated carbons are all between 2 and 3. This shows that activated carbon itself has a strong adsorption capacity for mercury ions [16].

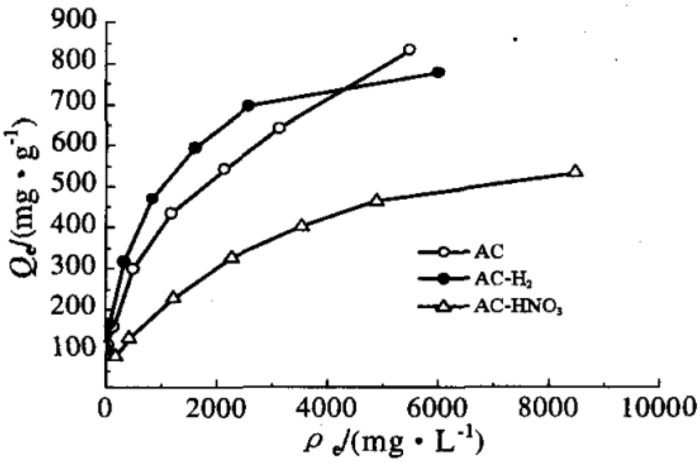

Figure 2. Adsorption isotherm of Hg^{2+} by three kinds of activated carbon [16].

2.2. Chemical Precipitation

The chemical precipitation method has become the most widely used heavy metal treatment method due to its simple operation and low cost. The principle is to add a specific chemical precipitant to wastewater containing heavy metal ions to form insoluble substances with the heavy metal ions in the wastewater, thereby achieving the purpose of removing heavy metal ions from the wastewater. Chemical precipitation methods can be further subdivided into coagulation precipitation method, vulcanization method, hydroxide precipitation method, ferrite method, and so on.

The coagulation and sedimentation method, also known as the flocculation method, is a commonly used ion exchange separation technology, and it is also the most widely used separation method. The coagulation precipitation method uses lime, iron salt, aluminum salt, etc. as coagulants to form coagulation precipitation, and then separates and purifies the mercury coagulation precipitation formed to better separate mercury from impurities. The coagulant is easily hydrolyzed in a weakly alkaline environment to form a hydroxide colloid. The hydroxide colloid is unstable and can easily form precipitates with other metal ions. Therefore, the coagulation and precipitation method are more suitable for treating a variety of heavy metal ions. However, the coagulation sedimentation method produces a large amount of sediment and has complex components that are difficult to separate, so it can easily cause secondary pollution [17]. The sewage treatment in the northern part of the Arthit gas field in the Gulf of Thailand adopts a cyclone-flocculation-flotation treatment process, which can remove most mercury-containing suspended matter and mercury-containing oil in the gas field water. The mercury content of water in the Arthit gas field ranges from 63 to 7219 μg/L. The mercury content in the discharged water after treatment by this process is less than 5 μg/L, and the arsenic content is less than 250 μg/L [18, 19].

The sulfide precipitation method is a method of removing heavy metal ions from polymerized water by precipitating them such as Na_2S. Since the solubility of mercury sulfide in water is extremely small and Hg^{2+} and S^{2-} have a strong tendency to combine, the mercury removal efficiency of the sulfide precipitation method is higher than that of the coagulation precipitation method. Since S^{2-} can also form insoluble precipitates with many heavy metal ions, the precipitates produced by the sulfide precipitation method also have shortcomings such as large amounts and complex composition, and the vulcanizing agent is toxic and easily produces H_2S highly toxic gas under strong acidic conditions. Safety hazards make it difficult for the sulfide precipitation method to be widely used. Compared with other precipitates, the precipitates generated by the combination of sulfides and heavy metals have smaller particle sizes and are prone to forming polymers that can clog the filter membrane [10,17,20]. Liu et al. performed a sulfide precipitation process to treat mercury. For wastewater with an initial mercury content exceeding 10 mg/L, the mercury removal rate can reach 99.9% after sulfide precipitation. Through other treatments, such as filtration, etc., the minimum mercury concentration in sewage can be as low as 10 to 100 μg/L [21].

2.3. Photocatalytic technology

Photocatalytic technology is currently a widely researched technology for treating organic and heavy metal ion pollutants. The main mechanism of photocatalytic reduction of metal ions can use electrons generated by light excitation to reduce highly toxic heavy metal ions to low-toxic or even non-toxic low-price metal ions on semiconductor materials [22,23]. The photocatalyst excites electrons by absorbing light energy to produce active oxidants or reducing agents, which then react with mercury ions. Commonly used photocatalysts include titanium dioxide (TiO_2), oxide (ZnO), semiconductor nanomaterials, and so on. These catalysts have good light absorption properties and separation capabilities of photogenerated electron-hole pairs and can produce strong oxidizing or reducing active species under light conditions.

In the process of photocatalytic treatment of mercury ions, mercury ions can be directly degraded or converted into more stable substances. For example, photocatalysts absorb light energy to generate active oxidants, such as hydroxyl radicals (•OH), which can oxidize with mercury ions and convert them into more stable mercury oxides. In addition, photocatalysts can also generate reducing agents, such as electrons (e-) and active hydrogen (H•), which can undergo a reduction reaction with mercury ions and convert them into more stable mercury metal. Factors affecting the photocatalytic reduction of TiO_2 include TiO_2 crystal form, TiO_2 surface structure, pH value of the solution, amount of photocatalyst, influence of mercury ion concentration, light source and light intensity, influence of anions, influence of dissolved oxygen, etc. For instance, the charge on the surface TiO_2 is affected by pH. The isoelectric point of TiO_2 in aqueous solution is about 6.25. When the pH of the solution is smaller than 6.25, the surface of TiO_2 is positively charged. When the pH is larger than 6.25, the surface of TiO_2 is negatively charged [22,24]. The process of photocatalytic removal of metal ions has the advantages of high efficiency and no need to add a large number of chemical reagents. There are certain development prospects in the future.

Metal-organic frameworks (MOFs)are a type of inorganic-organic hybrid porous materials formed by the self-assembly of metal ions or metal clusters with organic ligands. MOFs are widely used in fields such as catalysis, energy storage and separation [23]. Due to the porous structure of MOFs, they have obvious advantages as photocatalysts. Many studies have shown that MOF sensors have great potential in detecting heavy metals in aqueous solutions. The mechanism mainly involves host-guest electron transfer between heavy metals and sensors [25]. However, MOFs have problems with low response to visible light and large band gaps. Some metal ions may require longer reaction times or high-energy light irradiation to be effectively removed. Despite these challenges and shortcomings, photocatalysis remains a promising and sustainable approach to dealing with metal ion pollution.

3. Summary

Treating mercury in water is an important task to protect water resources and human health. In this article, chemical precipitation, adsorption, and photocatalytic technology were introduced. Chemical precipitation and adsorption are commonly used methods for treating mercury in water. The coagulation and sedimentation method solves the problem of hydroxide colloids easily forming precipitation with many metal ions based on the sulfide precipitation method. However, this technology uses a large number of chemical reagents, causing serious secondary pollution, and the chemical precipitant is selective. A single precipitant has great limitations in treating industrial wastewater containing a variety of heavy metal ions. Therefore, the chemical precipitation method lacks certain advantages in practical applications. Activated carbon adsorption is a common and effective method for removing mercury ions from wastewater. Activated carbon has a highly developed pore structure and abundant surface-active sites, which can adsorb and fix mercury ions. Biosorption methods are emerging methods for treating mercury in water and have potential and room for development. It shows advantages in terms of efficient removal and environmental friendliness. For biosorbents, lactic acid bacteria have greater effects on treating mercury wastewater. Because of the characteristics of the cell wall, some functional groups, such as -COOH, $-NH_2$, -SH, and -OH, etc.

Those ions react with metal cations on its surface. However, the microbial breeding cycle is long and is not suitable for the treatment of industrial wastewater. The application of MOFs-based photocatalysts in wastewater treatment currently faces some problems, and the understanding of the photocatalytic mechanism is not deep and specific enough. Photocatalysis of MOFs remains an attractive field with great development prospects and will play an increasingly important role in environmental remediation.

The selection of methods for treating mercury in water should comprehensively consider factors such as treatment efficiency, cost, sustainability, and environmental impact. Depending on the application scenarios and requirements, a single method or a combination of multiple methods can be used. Future research is needed to further explore efficient and environmentally friendly methods for treating mercury in water. This includes improving the processing efficiency of various methods, reducing costs, solving subsequent processing problems, and developing new technologies and materials. In summary, treating mercury in water is a challenging task, but through comprehensive utilization of existing treatment methods and continuous research, mercury pollution in water can be effectively reduced and water resources and human health can be protected.

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