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Synthesis of PZ-DTC and Its Application in the Removal of Mercury Ions from Wastewater

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ABSTRACT

In this study, a heavy metal chelating agent, PZ-DTC, containing two dithiocarbamate (DTC) groups, was synthesized using piperazine and carbon disulfide as raw materials for the removal of mercury ions from wastewater. The performance of PZ-DTC in removing Hg^{2+} was systematically investigated under various conditions, including pH, dosage, addition of flocculants (ferric chloride and polyaluminum chloride), and different filtration methods. The mercury removal efficiency of PZ-DTC was compared with that of the conventional chelating agent sodium dimethyldithiocarbamate (SDDC). The results indicate that PZ-DTC exhibits excellent Hg^{2+} removal performance under alkaline conditions (pH ≥ 11). At pH = 13 and a PZ-DTC: Hg^{2+} molar ratio of 3:1, the residual mercury ion concentration after filtration through a 0.22 μm membrane was 0.007 $mg \cdot L^{-1}$, corresponding to a removal efficiency of 99.86%, which meets the wastewater discharge standard established by the World Health Organization (0.01 $mg \cdot L^{-1}$). Compared with SDDC, which contains a single DTC group, PZ-DTC demonstrated higher removal efficiency and lower residual mercury concentrations under identical conditions. Particle size distribution analysis of the chelates revealed that the precipitates formed between PZ-DTC and Hg^{2+} were mainly distributed in the size range of 0.22–0.45 μm, and particle size increased with increasing dosage, facilitating solid–liquid separation. Upon the addition of polyaluminum chloride (PAC), the chelate particles significantly increased in size (>0.8 μm), the precipitation rate accelerated, and the mercury concentration in the supernatant was reduced to nearly zero. In summary, PZ-DTC exhibits superior Hg^{2+} removal performance under alkaline conditions, forming stable chelates with good precipitation characteristics, indicating its strong potential for engineering applications in mercury-containing wastewater treatment.

KEYWORDS

Heavy Metal Chelating Agent; Mercury Ions; Dithiocarbamate.

1. INTRODUCTION

Mercury ions are often present in high concentrations in wastewater discharged from industries such as electronics, batteries, non-ferrous metals, coal combustion, and waste incineration [1–3]. As one of the heavy metal ions posing the greatest threat to the environment and human health [4], mercury exhibits long-range atmospheric transport, persistence, and bioaccumulation in the food chain [5]. It has a strong affinity for proteins in living organisms [6,7]; when its concentration exceeds a threshold, it can cause damage to the immune system, cleft lip, impairment of the liver and kidneys, and cardiovascular diseases [8,9]. The World Health Organization (WHO) has set the maximum permissible limit for mercury in wastewater at 10 μg/L, and in drinking water at 1 μg/L [10,11]. Mercury exists in various forms, including inorganic species such as Hg^{2+} and elemental mercury (Hg^0), as well as methylmercury ($MeHg^+$), ethylmercury ($EtHg^+$), and other organic mercury compounds [12]. In aquatic environments, it typically exists as divalent cations; with increasing pH, mercury ions combine with hydroxide ions to form precipitates [13]. Common methods for mercury removal include chemical precipitation, ion exchange, coagulation-flocculation, electrochemical methods, and adsorption [14]. Chemical precipitation is one of the most widely used techniques; among its approaches, heavy metal chelation employs chelating agents that utilize coordination atoms such as N, S, and P to form stable chemical structures with heavy metal ions, thereby achieving removal [15]. Dithiocarbamate (DTC), owing to its strong coordination ability and the stability of the precipitates formed upon chelation with heavy metals, has been extensively studied as an effective heavy metal chelating agent [16,17].

In this study, piperazine and carbon disulfide were used as raw materials to fully utilize the two amino groups of piperazine, synthesizing a heavy metal chelating agent containing two dithiocarbamate (DTC) groups for the removal of mercury ions from water. The removal efficiency of the synthesized chelating agent, designated as PZ-DTC, under various conditions was investigated by controlling parameters such as pH, dosage, and the addition of flocculants including ferric chloride and polyaluminum chloride, as well as by employing different filtration methods. The performance of PZ-DTC was compared with that of the conventional agent sodium dimethyldithiocarbamate (SDDC) to validate its mercury removal capability, thereby providing a new environmentally friendly agent for the treatment of mercury-containing wastewater.

2. MATERIALS AND METHODS

2.1. Materials

The reagents used in the experiment included potassium hydroxide, anhydrous piperazine, carbon disulfide, and ferric chloride, all of analytical grade. Deionized water was used for synthesis. The sodium dimethyldithiocarbamate (SDD) reagent was purchased from Aladdin Group as a solution. The self-made heavy metal capture agent was designated as PZ-DTC.

Mercury-containing wastewater with a concentration of 5 mg/L was prepared by diluting a mercury standard solution obtained from Aladdin Group.

2.2. Synthesis Method and Capture Mechanism

A certain amount of piperazine was dissolved in water under continuous stirring. After complete dissolution, a potassium hydroxide solution was added, causing the solution to become turbid. Carbon disulfide was then added dropwise at low temperature. After the addition was complete, the mixture was allowed to react for 24 hours at room temperature. The resulting product was a yellow liquid, to which an appropriate amount of potassium hydroxide solution could be added as needed.

The sulfur atoms in sodium dimethyldithiocarbamate possess lone pair electrons, enabling strong coordination with mercury ions to form a stable four-membered ring chelate:

$$2(CH_3)_2NCS_2Na + Hg^{2+} \rightarrow [(CH_3)_2NCS_2]_2Hg\downarrow + 2Na^+ \quad (1)$$

Piperazine serves as a bifunctional backbone, connecting two efficient dithiocarbamate (DTC) capture groups within a single molecule, thereby enhancing the capture capacity and efficiency for heavy metal ions. The sulfur atoms in the DTC groups coordinate strongly with mercury ions, forming stable, insoluble chelate precipitates, thus facilitating the removal of mercury ions from water.

2.3. Experimental Methods

The prepared mercury-containing wastewater was placed in a beaker, and the pH was adjusted using sodium hydroxide. PZ-DTC and SDD solutions were added, followed by stirring at 250 r/min for 5 min and then at 150 r/min for 5 min, after which the mixture was allowed to stand for 30 min. The supernatant was collected to determine the residual mercury ion concentration. A ferric chloride solution was prepared. After adding the capture agent, the mixture was stirred at 300 r/min for 10 min. Following the addition of the ferric chloride solution, stirring continued at 100 r/min for 10 min. After standing for 1 h, the supernatant was collected for mercury ion concentration measurement. Heavy metal concentrations were determined using ICP-OES.

3. RESULTS AND DISCUSSION

3.1. Mercury Removal Efficiency of SDD

SDD (sodium dimethyldithiocarbamate) is a heavy metal chelating agent containing a single DTC group. Its mercury removal efficiency is shown in Figure 1. The results indicate that at the same dosage, the residual mercury ion concentration in solution decreased significantly with increasing pH. When the molar ratio of SDD to Hg^{2+} exceeded 1.5, the residual mercury ion concentration could be reduced to below 1.0 $mg \cdot L^{-1}$ under alkaline conditions (pH ≥ 9). This is primarily attributed to the enhanced formation of stable four-membered ring chelates between Hg^{2+} and the sulfur atoms in SDD under alkaline conditions, along with the increased hydrolysis tendency of Hg^{2+} at high pH, where some mercury exists as $Hg(OH)_2$, further promoting chelate precipitation. However, when the pH exceeded 7, further increasing the SDD dosage resulted in only marginal improvements in mercury removal efficiency. At pH = 12 and an SDD: Hg molar ratio of 3, the residual mercury ion concentration reached a minimum of 0.26 $mg \cdot L^{-1}$, still exceeding the wastewater discharge limit (0.01 $mg \cdot L^{-1}$) established by the World Health Organization (WHO). This suggests that SDD has limitations in removing trace amounts of mercury ions, possibly due to its single DTC structure, which limits its capture capacity, as well as the small particle size and incomplete precipitation of the chelates formed.

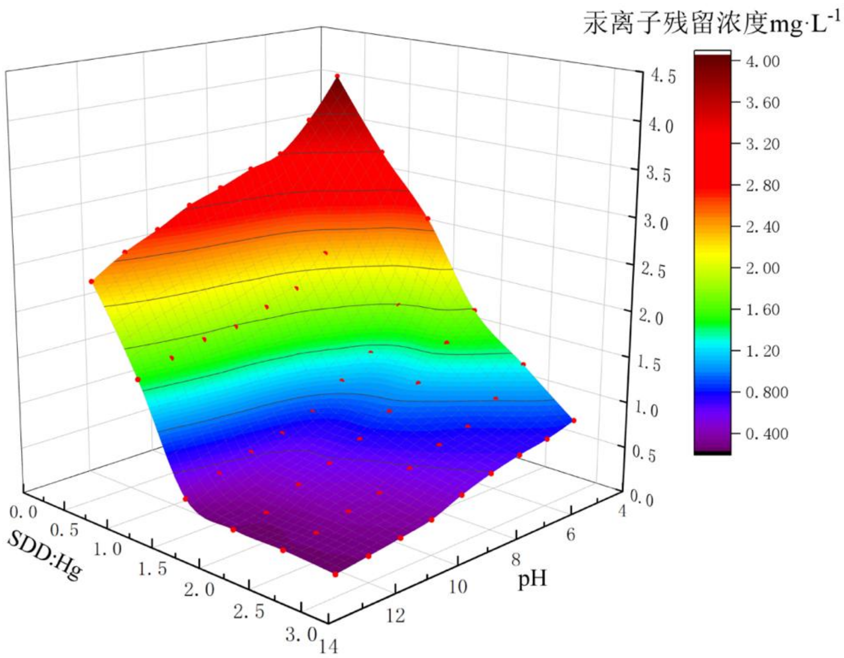

Fig 1 Effect of pH and SDD dosage on the removal of mercury ions

3.2. Mercury Removal Efficiency of PZ-DTC

3.2.1. Effect of pH and Dosage on Mercury Removal by PZ-DTC

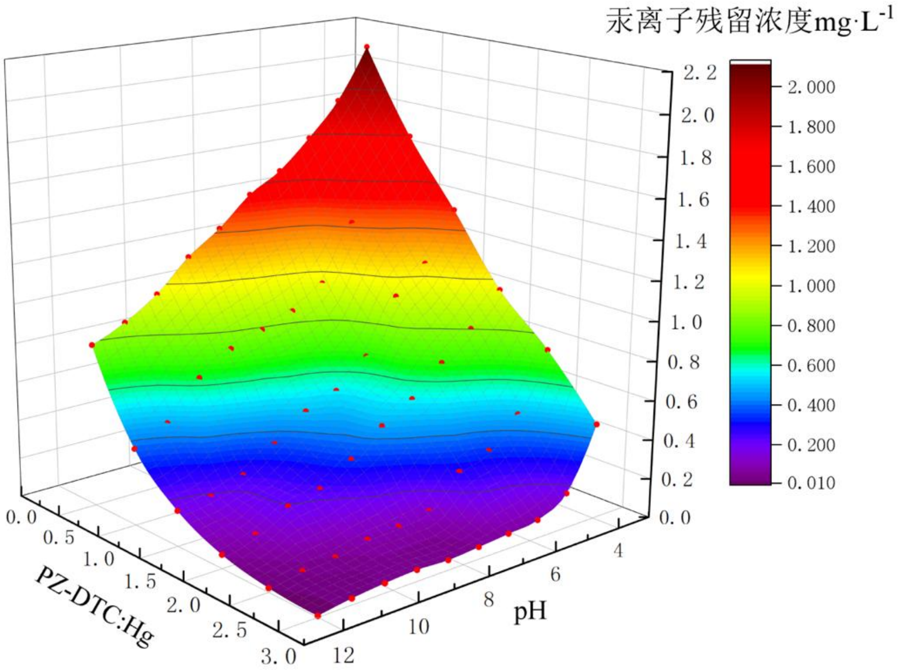

Fig 2 Effect of pH and PZ-DTC dosage on mercury removal

Compared with SDD, PZ-DTC exhibited superior mercury removal performance. As shown in Figure 2, under alkaline conditions, the removal efficiency of PZ-DTC for Hg^{2+} increased significantly, and the residual mercury ion concentration continued to decrease with increasing pH and dosage. At pH = 13 and a PZ-DTC: Hg molar ratio of 3, after filtration through a 0.22 μm membrane, the residual mercury ion concentration reached as low as 0.007 $mg \cdot L^{-1}$, fully complying with national pollutant discharge standards and WHO discharge limits. Mechanistically, the PZ-DTC molecule contains two DTC groups, enabling bidentate or multidentate coordination with Hg^{2+}, significantly enhancing the stability of the chelate. When pH > 7, the increased OH^- concentration facilitates deprotonation, increasing the electron density on the sulfur atoms of the DTC groups and thereby enhancing their nucleophilic attack capability toward Hg^{2+}. Furthermore, as the molar ratio increased from 1:1 to 2:1, the residual mercury ion concentration decreased most significantly, indicating that Hg^{2+} was nearly fully coordinated at this ratio. When the molar ratio was further increased to 3:1, the improvement in removal efficiency slowed, suggesting that the amount of Hg^{2+} available for capture in the system was extremely limited.

3.2.2. Effect of Filtration Pore Size on Residual Mercury Concentration

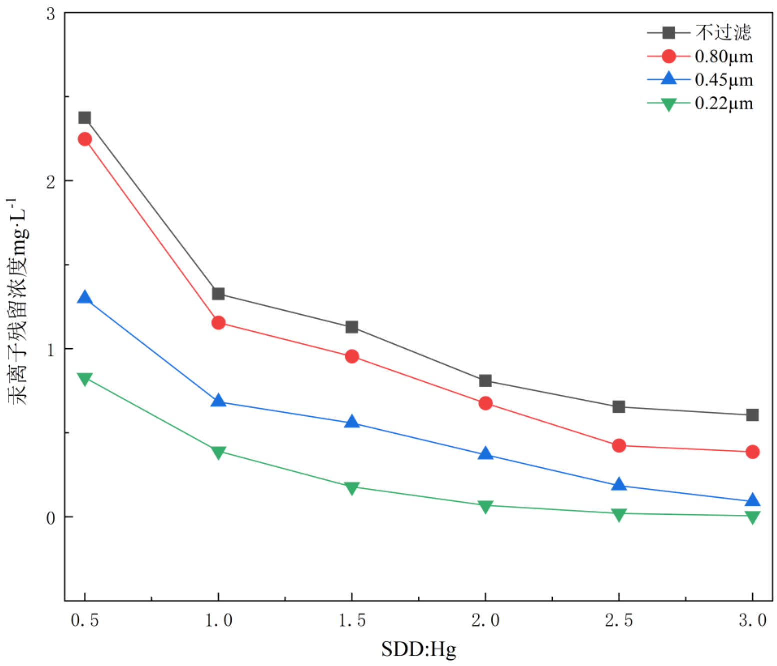

Fig 3 At pH = 13, residual mercury concentration after filtration with different pore sizes

To investigate the particle size distribution of the chelates formed between PZ-DTC and Hg^{2+}, experiments were conducted at pH = 13 using membrane filters with different pore sizes. The results are shown in Figure 3. The experiments revealed that the chelate particles were mainly concentrated in the particle size range of 0.22–0.45 μm. As the PZ-DTC dosage increased, the particle size of the chelates tended to increase, and the differences in residual mercury concentrations between different filtration treatments gradually narrowed. This phenomenon can be attributed to the fact that at high molar ratios, one Hg^{2+} ion may coordinate with multiple DTC groups, forming crosslinked structures or aggregates, thereby increasing particle size. At a PZ-DTC: Hg molar ratio of 3, after filtration through a 0.22 μm membrane, the residual mercury ion concentration was reduced to 0.007 $mg \cdot L^{-1}$, corresponding to a removal efficiency of 99.86%. In comparison, the residual concentration after filtration through a 0.45 μm membrane was 0.022 $mg \cdot L^{-1}$, still significantly better than the optimal treatment performance of SDD. This indicates that PZ-DTC not only exhibits higher capture efficiency but also forms chelates that are more readily removed through solid–liquid separation.

3.3. Effect of Coagulant on Mercury Removal by PZ-DTC

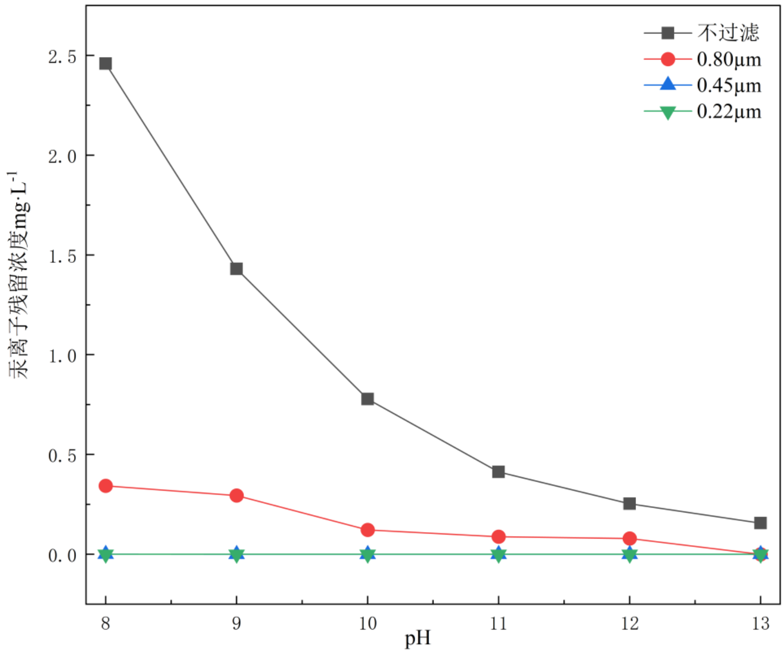

Fig 4 Effect of polyaluminum chloride (PAC) on mercury removal by PZ-DTC at different pH values with a PZ-DTC:Hg molar ratio of 3

The effect of polyaluminum chloride (PAC) as a coagulant on mercury removal efficiency was investigated at a PZ-DTC: Hg molar ratio of 3. The results are shown in Figure 4. After the addition of 3 mg of PAC, the residual mercury ion concentration decreased significantly. After standing for 1 h, the mercury ion concentration in the supernatant reached as low as 0.156 $mg \cdot L^{-1}$, and after filtration, it was reduced to nearly 0.00 $mg \cdot L^{-1}$, with a removal efficiency approaching 100%. Compared with the system without PAC, the precipitation rate was significantly accelerated, and the settling time was markedly reduced.

Further comparison of the filtration results using different membrane pore sizes revealed almost no difference in residual mercury ion concentrations after treatment with 0.45 μm and 0.22 μm membranes, and similar results were obtained with the 0.8 μm membrane, indicating that after PAC addition, the particle size of the chelates was generally larger than 0.8 μm. The polynuclear hydroxyl aluminum complexes generated during PAC hydrolysis exhibit strong bridging effects, promoting the aggregation and settling of small chelate particles, thereby enhancing solid–liquid separation efficiency. Additionally, the addition of PAC may enhance the collision efficiency and reaction rate between PZ-DTC and Hg^{2+} by modifying the ionic strength and surface charge distribution of the solution.

In summary, PAC not only significantly improves the mercury removal efficiency of PZ-DTC but also optimizes precipitation performance, providing a viable pathway for the rapid, efficient, and deep removal of mercury ions in practical wastewater treatment.

4. CONCLUSIONS

(1) In this study, a heavy metal chelating agent PZ-DTC containing two DTC groups was successfully synthesized, and its performance in removing Hg^{2+} from simulated wastewater was systematically investigated. The results indicate that solution pH and agent dosage are key factors influencing removal efficiency. Under alkaline conditions (pH ≥ 11), PZ-DTC exhibited excellent removal

capability for Hg^{2+}. At pH = 13 and a PZ-DTC: Hg molar ratio of 3, after filtration through a 0.22 μm membrane, the residual mercury ion concentration was as low as 0.007 $mg{\cdot}L^{-1}$, corresponding to a removal efficiency of 99.86%, meeting the wastewater discharge limit (0.01 $mg{\cdot}L^{-1}$) established by the World Health Organization (WHO).

(2) Compared with the conventional single-DTC chelating agent SDD, PZ-DTC demonstrated higher removal efficiency and lower residual mercury ion concentrations under the same conditions. When the PZ-DTC: Hg molar ratio reached 2:1, the removal efficiency stabilized, indicating that the dual-DTC structure effectively enhances the coordination capability with Hg^{2+}, forming a stable chelate structure and improving capture efficiency.

(3) The results of chelate particle size distribution and filtration experiments showed that the precipitates formed between PZ-DTC and Hg^{2+} were mainly distributed in the particle size range of 0.22–0.45 μm, and particle size increased with increasing dosage, facilitating solid–liquid separation. After the addition of polyaluminum chloride (PAC) as a coagulant, the chelate particles significantly increased in size (>0.8 μm), the precipitation rate accelerated, and the mercury ion concentration in the supernatant was reduced to nearly zero after standing for 1 h, further enhancing treatment efficiency and operational convenience.

(4) In summary, PZ-DTC exhibited significantly superior Hg^{2+} removal performance compared to the conventional agent SDD under alkaline conditions. The chelates formed are highly stable and exhibit good precipitation properties, indicating the potential of PZ-DTC as an efficient mercury ion capture agent for engineering applications. Future research may further investigate its applicability under complex water quality conditions, the interference mechanisms of coexisting ions, and the regeneration and reusability of the material, providing more reliable technical support for the treatment of actual mercury-containing wastewater.

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