



Effect of heavy metals on the stabilization of mercury(II) by DTCR in desulfurization solutions

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ABSTRACT

Several heavy metals, including Cu^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} , were investigated in simulated desulfurization solutions to evaluate their interferences with Hg^{2+} during the reaction with dithiocarbamate type chelating resin (DTCR). Appropriate DTCR dosage and the effect of pH were also explored with respect to restoration of high Hg^{2+} precipitation efficiency and reduction of mercury concentrations. The experimental results suggested that increasing heavy metal concentration inhibited Hg^{2+} precipitation efficiency to a considerable extent and the inhibition order of the four heavy metals was $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+}$. However, the coordination ability was closely related to the configuration and the orbital hybridization of each metal. In the cases of Cu^{2+} and Pb^{2+} , increased DTCR dosage was beneficial to Hg^{2+} precipitation, which could lay the foundation of practical applications of DTCR dosage for industrial wastewater treatment. The enhanced Hg^{2+} precipitation performance seen for increasing pH might have come from the deprotonation of sulfur atoms on the DTCR functional groups and the formation of metal hydroxides ($\text{M}(\text{OH})_2$, $\text{M} = \text{Cu}, \text{Pb}, \text{Hg}$).

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1. Introduction

The high toxicity of mercury to the human central nervous system and the strong bioaccumulation in human bodies through the food chain has triggered public concern over mercury contamination [1]. For instance, Minamata disease, caused by severe mercury poisoning, made thousands of victims suffer from a neurological syndrome in Japan. Mercury emission from anthropogenic activities is usually blamed for pollution and threats to human safety. Combustion utilities, such as coal-fired power plants and incinerators, constitute the major anthropogenic mercury sources [2,3].

In the flue gas emitted from coal combustion, mercury occurs in three forms: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}), and particle-bound mercury (Hg^p). Based on the unique physical and chemical properties of the three forms of mercury, research has been conducted to prevent mercury emission to the environment. Conventional mercury control technologies, such as electrostatic precipitators (ESPs), fabric filters (FFs) and flue gas desulfurization (FGD) systems, have been applied to remove Hg^{2+} , but none effectively remove elementary mercury. However, a novel technology, which involves the use of activated carbon injection upstream of a particulate control device (ACI), was reported to be able to remove both elemental and oxidized mercury [4]. Among the varieties of

mercury control devices, FGD could capture nearly 90% of Hg^{2+} and was also considered to be cost-effective [5,6].

In the FGD system, alkaline sorbents capture pollutants like Hg^{2+} and SO_2 and ions like Cl^- , NO_3^- , F^- , and Ca^{2+} [7]. SO_2 , however, which is absorbed by the alkaline sorbent and not entirely oxidized to SO_4^{2-} , has a high potential to reduce Hg^{2+} and to further generate Hg^0 [8]. Wo et al. reported that the pH, reaction temperature and ions in desulfurization solutions had a profound effect on Hg^{2+} reduction [8]. Other similar work has also discussed the reduction and reemission of mercury to the atmosphere. For example, Kirk et al. reported a rapid reduction and reemission of mercury deposited into snowpacks [9]. The residence time of the resulting Hg^0 in the atmosphere ranged from 0.5 to 2 years [10], so urgent steps need to be taken to develop novel technologies to inhibit Hg^{2+} reduction and Hg^0 reemission.

Dithiocarbamates (DTCs) are a versatile class of monoanionic 1,1-dithio ligands with a strong coordination and stabilization ability for transition metals [11]. Since the synthesis of dithiocarbamic acid was reported by Debus in 1850 [12], much attention has been focused on their applications and on structural identification of metal dithiocarbamates. Currently, a wealth of structural data for metal dithiocarbamates has demonstrated the strong affinity of dithiocarbamate ligands for metals. This strong affinity has boosted their use as pesticides in agriculture, industry and antidotes for metal poisoning, such as Pb poisoning [13–15].

Burgeoning interest in transition metal chemistry has also broadened their wide utilization in industrial applications. To meet increasingly stringent environmental regulations, DTCs were

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Table 1
Characteristics of the simulated FGD solution.

Element	Simulated FGD solution
Temperature (°C)	50
pH value	5.0
Cl ⁻ (mM)	100
SO ₄ ²⁻ (mM)	50
S(IV) (mM)	1
Ca ²⁺ (mM)	10
Mg ²⁺ (mM)	10
NO ₃ ⁻ (mM)	50
Hg ²⁺ (mg l ⁻¹)	0.1

employed as chelating agents to precipitate various heavy metals in industrial waste, including Hg²⁺, Cd²⁺, Cu²⁺, Pb²⁺, Mn²⁺, Ni²⁺, Zn²⁺, and Cr³⁺. Ito and co-workers demonstrated the stability of Hg(DTC)₂ by measuring the Hg–S bonds and electron distributions [16]. Furthermore, numerous studies have reported the utilization of DTC derivatives to precipitate aqueous Hg²⁺. Say et al. elaborated that mercury adsorption depended on the solution pH, mercury concentration and mercury speciation by DTC derivatives [17]. Tang et al. reported the precipitation efficiency of Hg²⁺ and the inhibition of Hg²⁺ reduction by one DTC derivative (DTCR) in desulfurization solutions [18]. Nevertheless, demonstrating that DTCR could be a promising precipitant to inhibit Hg⁰ release in FGD solutions is important. For this purpose, Lu et al. illustrated the high precipitation performance of DTCR for Hg²⁺ under varied conditions (e.g., initial pH value, SO₄²⁻ concentration, Cl⁻, NO₃⁻, and Ca²⁺ concentration) in FGD solutions [19].

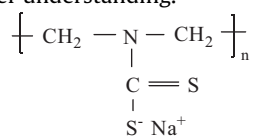
Trace heavy metals, such as Cu²⁺, Pb²⁺, Ni²⁺, and Zn²⁺, have been shown to be retained in FGD materials and fly ashes [7]. In spite of the outstanding Hg²⁺ precipitation efficiency and the inhibition potential of Hg²⁺ reduction, it was reported that coexisting heavy metal ions in FGD solutions had a negative influence on DTCR precipitation efficiency. The adverse effect of Cu²⁺ and Pb²⁺ on Hg²⁺ precipitation was studied by Tang et al., and the results showed that the Hg²⁺ removal rate decreased by 12.6% and 5.0%, respectively, in the presence of 1.0 mg l⁻¹ Cu²⁺ and Pb²⁺ [18]. The decrease of Hg²⁺ removal rate with increasing Hg²⁺ concentration in FGD solutions enhanced Hg²⁺ reduction and Hg⁰ reemission. Thus, it is very important to explore the effect of trace heavy metals on Hg²⁺ reduction inhibition under the presence of DTCR.

In this paper, the effect of four trace heavy metal ions, Cu²⁺, Pb²⁺, Ni²⁺, and Zn²⁺, on DTCR Hg²⁺ precipitation efficiency and Hg²⁺ reduction inhibition was studied. Furthermore, the optimal DTCR dosage and pH value were determined in simulated FGD solutions after adding Cu²⁺ and Pb²⁺. These studies will provide further insight into the proposed application of DTCR as a precipitant for stabilizing dissolved Hg²⁺ to prevent reemission of Hg⁰ in FGD solutions.

2. Experiments and methods

2.1. Simulated FGD solutions and heavy metal precipitants

The concentrations in the simulated FGD solutions were based on the concentration of elements in practical FGD solutions (Table 1). The DTCR (30%) solution was purchased from Prode Limited Co., Suzhou, China. The molecular structure of the precipitant is described for better understanding.



2.2. Effect of trace heavy metals on Hg²⁺ stabilization and reduction inhibition by DTCR

The batch experiments for stabilization and reduction inhibition of mercury in simulated FGD solutions were conducted in a 500 mL three-necked flask in a water bath at 50 °C. A specified amount Cl⁻, NO₃⁻, SO₄²⁻, Mg²⁺ or Ca²⁺ (Table 1) was added to the flask with 500 mL deionized water. A predetermined number of trace heavy metal ions were then added to the flask with continuous nitrogen flushing to prevent S(IV) oxidation. Next, S(IV) was added and the pH was adjusted to 5.0. Then, Hg²⁺ and the theoretical dosage of DTCR ($Q_{\text{th}} = 0.70 \text{ mL}$ of 0.01% DTCR) were added to the flask. The flush nitrogen then acted as a carrier to prohibit the accumulation of Hg⁰ in the solution. A 10% (v/v) H₂SO₄ and 4% (w/w) KMnO₄ solution in two impingers in series was employed to adsorb Hg⁰. After 2 h of reaction, the solutions in the flask and the two impingers were diluted and the mercury concentrations were determined.

2.3. Effect of DTCR dosage and pH on Hg stabilization and reduction inhibition

The batch experiments for DTCR dosage and pH value were carried out in 250 mL beakers containing 150 mL simulated FGD solutions with 0.1 mg l⁻¹ of Hg²⁺ and 100 mM of Cl⁻. After adding the heavy metal ions, the solution pH was adjusted and the temperature held at 50 °C. The solution was rapidly mixed using a quadruple magnetic stirrer for 15 min after the DTCR dose was added. Afterwards, 100 mg l⁻¹ of polyaluminum chloride (PAC) and 2 mg l⁻¹ of polyacrylamide (PAM) were added and the solution was slowly stirred. After standing for 30 min, the solution was centrifuged and 5 mL of the supernatant was diluted to 50 mL in a volumetric flask in which 5 mL of the stationary liquid (a solution with 0.5 g l⁻¹ K₂CrO₄ and 5% HNO₃, v/v) had already been added. The Hg²⁺ concentration in the sample was detected and the remaining Hg²⁺ in the beaker was calculated.

2.4. Analysis

Mercury concentrations were determined by a QM201 cold vapor Atomic Fluorescence Spectrometer coupled with a Mercury Analyzer (Qing'an Instrument Co., Suzhou, China). Mercury (Hg²⁺) in the samples was reduced with a 7% (w/w) SnCl₂ solution to generate elementary mercury vapor. Mercury vapor was then flushed out with argon as carrier gas and pumped into the mercury analyzer. A digital pH meter (Mettler-Toledo Co., Shanghai, China) was used to measure pH values in the FGD solutions.

The Hg²⁺ concentrations in the simulated FGD solutions were calculated directly from the data obtained from the mercury analyzer, while the concentrations of released Hg⁰ were extrapolated according to the adsorption equilibrium.

3. Results and discussion

3.1. Effect of trace heavy metal concentration

Trace heavy metals, such as Hg, Cu, Pb, Zn and Ni, were captured considerably by FGD chemistry and simulated in the water streams during re-circulation [7,20]. Because DTCR has the ability to strongly chelate many transition metals, Hg²⁺ might compete against other heavy metals in the reaction for DTCR, which could inhibit the stabilization of Hg²⁺ in the desulfurization solution. Thus, investigating the effect of the four heavy metals mentioned earlier on mercury stabilization and reduction inhibition is critical. The measured concentrations of the four investigated heavy metals in desulfurization solutions from four coal-fired power plants ranged from 0.46 to 0.72 mg l⁻¹ for Pb²⁺, 0.05 to 0.20 mg l⁻¹ for

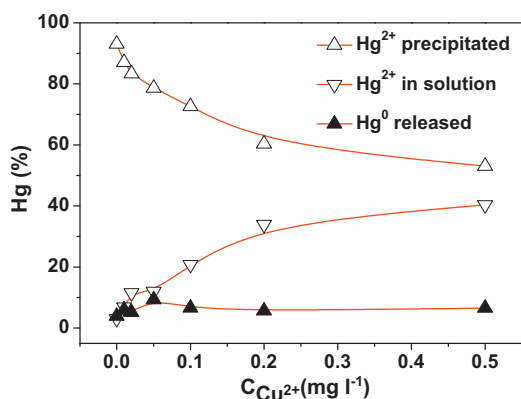


Fig. 1. Effect of Cu^{2+} concentration on mercury stabilization ($Hg^{2+} = 0.1\ mg\ l^{-1}$, $S(IV) = 1\ mM$, $Cl^{-} = 0.1\ M$, $NO_3^{-} = 50\ mM$, $SO_4^{2-} = 50\ mM$, $Mg^{2+} = 10\ mM$, $Ca^{2+} = 10\ mM$, $DTCR = 1.0Q_{th}$, $T = 50\ ^\circ C$, $pH = 5$).

Cu^{2+} , 0.0082 to $0.83\ mg\ l^{-1}$ for Zn^{2+} and 0.25 to $0.35\ mg\ l^{-1}$ for Ni^{2+} [21–24]. Therefore, the dosage of the four heavy metals in the subsequent experiments was based on these concentrations.

3.1.1. Effect of Cu^{2+} concentration

Fig. 1 illustrates the interference of Cu^{2+} with mercury stabilization and inhibition of Hg^0 release by DTCR. Compared to the controls without Cu^{2+} , mercury precipitation rate decreased sharply with increasing Cu^{2+} concentration. Meanwhile, the remaining fraction of Hg^{2+} in the simulated desulfurization solutions significantly increased. More specifically, when the Cu^{2+} concentration increased to $0.2\ mg\ l^{-1}$, the Hg^{2+} precipitation rate by DTCR decreased from 91.3% to 60.4%. At $0.5\ mg\ l^{-1}$ Cu^{2+} , the precipitation rate reached the lowest point at 53.0%. However, the remaining Hg^{2+} in the solutions increased from 2.1% to 40.4% as a result of the increased Cu^{2+} concentration. In contrast, the rate of Hg^0 release remained stable at 6.0%. In the case where Hg^{2+} concentrations remained higher in the solutions, the reduction of Hg^{2+} to Hg^0 was favored. Thus, it was important to remove Cu^{2+} from the simulated desulfurization solutions prior to Hg^{2+} stabilization.

This phenomenon of evident interference of Cu^{2+} might be attributed to its atomic structure and its coordination ability with DTCR. Throughout Cu^{2+} chemistry, vast numbers of Cu^{2+} complexes are known and Jahn–Teller distortions are generally observed (d^9 configuration) [25]. Thus, a coordination number of 4 predominates in complexes containing S^{-} donor ligands, as shown in Eq. (1). In the $Cu(DTCR)_2$ complex, a lone pair in the p-orbital of Cu^{2+} and the alternating single and double bonds in the DTCR molecule could generate a conjugated system, which might reduce the overall energy and increase the stability of the complex. Furthermore, according to the theories of conjugation and verified by a large number of crystallographic studies, the coordination geometry is a square planar configuration [26]. Another contributing factor might lie in the DTCR polymer structure. Numerous-CSS-ligands in the DTCR molecule could generate insoluble polymer matrices with a cross-linked network structure [27], strengthening the stability of the $Cu(DTCR)_2$ complex and in turn inhibiting mercury stabilization by DTCR.

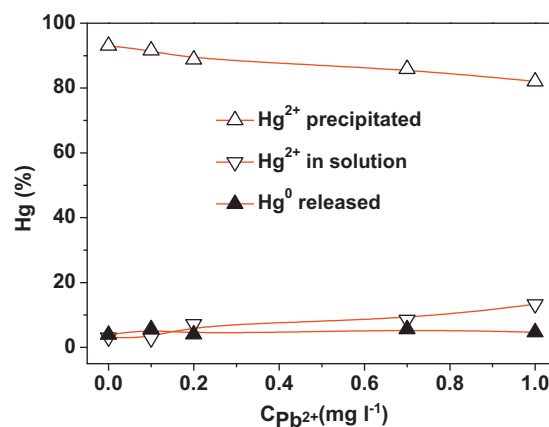
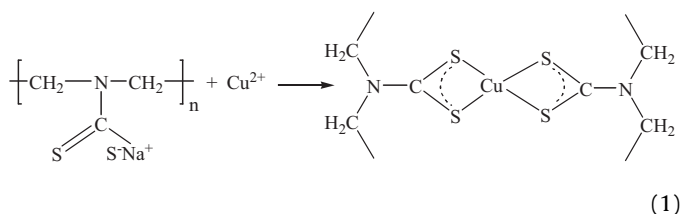


Fig. 2. Effect of Pb^{2+} concentration on mercury stabilization ($Hg^{2+} = 0.1\ mg\ l^{-1}$, $S(IV) = 1\ mM$, $Cl^{-} = 0.1\ M$, $NO_3^{-} = 50\ mM$, $SO_4^{2-} = 50\ mM$, $Mg^{2+} = 10\ mM$, $Ca^{2+} = 10\ mM$, $DTCR = 1.0Q_{th}$, $T = 50\ ^\circ C$, $pH = 5$).

3.1.2. Effect of Pb^{2+} concentration

Fig. 2 depicts the effect of Pb^{2+} on the stabilization of mercury by DTCR. When the Pb^{2+} concentration increased, the precipitation efficiency of mercury decreased from 92.0% to 82.0%, while the remaining Hg^{2+} in the solutions increased to 13.3%. However, the amount of released Hg^0 remained stable (approximately 4.0%). Thus, mercury precipitation by DTCR was inhibited by Pb^{2+} , but to a lesser extent than by Cu^{2+} .

The Pb^{2+} ion is formed by losing two p electrons, and the electron configuration is $[Xe] 6s^2 5d^{10}$. Thus, there is no unoccupied d-orbital for orbital hybridization, so sp^3 hybridization is obtained. This arrangement forms a tetrahedral geometry for $Pb(DTCR)_2$. However, the binding capacity is inhibited by the relatively large ionic radius of $1.19\ \text{\AA}$ and the complicated orbitals, decreasing the stability of $Pb(DTCR)_2$. Therefore, as compared with Cu^{2+} , the addition of Pb^{2+} interferes less with mercury stabilization.

3.1.3. Effect of Ni^{2+} concentration

As shown in Fig. 3, the precipitation efficiency of Hg^{2+} decreased when the Ni^{2+} concentration increased to $0.1\ mg\ l^{-1}$. When the Ni^{2+} concentration ranged from 0.1 to $0.4\ mg\ l^{-1}$, the Hg^{2+} precipitation efficiency remained constant at 83%. In addition, the amount of Hg^{2+} remaining in the solution increased slightly and reached a plateau of 10%. Finally, the Hg^{2+} reduction rate maintained stable at approximately 6.0%.

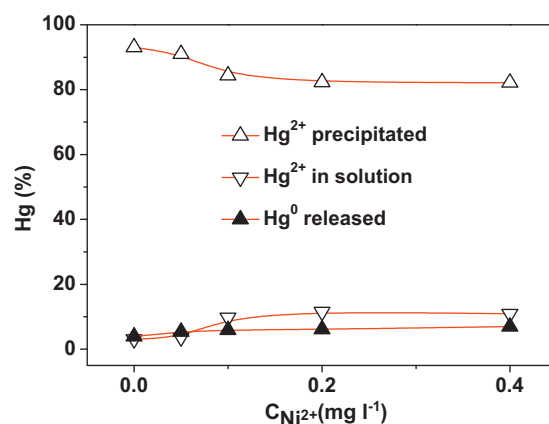


Fig. 3. Effect of Ni^{2+} concentration on mercury stabilization ($Hg^{2+} = 0.1\ mg\ l^{-1}$, $S(IV) = 1\ mM$, $Cl^{-} = 0.1\ M$, $NO_3^{-} = 50\ mM$, $SO_4^{2-} = 50\ mM$, $Mg^{2+} = 10\ mM$, $Ca^{2+} = 10\ mM$, $DTCR = 1.0Q_{th}$, $T = 50\ ^\circ C$, $pH = 5$).

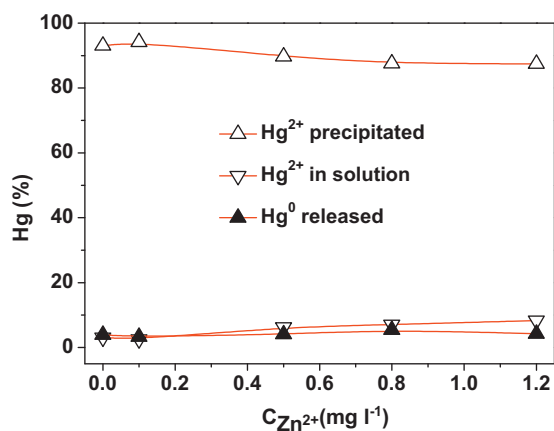


Fig. 4. Effect of Zn^{2+} concentration on mercury stabilization ($Hg^{2+} = 0.1 \text{ mg l}^{-1}$, $S(IV) = 1 \text{ mM}$, $Cl^- = 0.1 \text{ M}$, $NO_3^- = 50 \text{ mM}$, $SO_4^{2-} = 50 \text{ mM}$, $Mg^{2+} = 10 \text{ mM}$, $Ca^{2+} = 10 \text{ mM}$, $DTCR = 1.0Q_{th}$, $T = 50^\circ \text{C}$, $pH = 5$).

The electronic configuration of Ni^{2+} is $[Ar] 4s^2 3d^8$, which contributes to orbital hybridization with s-orbitals and d-orbitals. Thus, the configuration of the Ni^{2+} complex varies from octahedral to tetrahedral and square planar geometries. However, due to intraligand $\pi-\pi^*$ transitions mainly associated with $N-C=S$ and $S-C=S$, the coordination around the metal ions is assumed to be square planar [28]. Furthermore, Hogarth reported that Ni^{2+} complexes showed square-planar coordination environments with bite angles at nickel ranging from 78 to 80° [29]. Thus, the effect on mercury stabilization might be explained by the high stability of $Ni(DTCR)_2$ complexes.

3.1.4. Effect of Zn^{2+} concentration

According to Fig. 4, the addition of Zn^{2+} had little effect on mercury stabilization by DTCR. Specifically, the precipitation efficiency of Hg^{2+} decreased only slightly from 93.0% to 87.5% with increasing Zn^{2+} concentration. The same phenomenon occurred for the remaining Hg^{2+} in the solutions (approximately 8.3%). The Hg^{2+} reduction rate remained the same at 4.0%.

Coordination numbers of 4–6 are the most common for Zn^{2+} complexes. However, the $Zn(II)$ -dithiocarbamate complexes contained a $Zn(S_4)$ coordination environment [30]. Hogarth found that the simplest zinc complexes formed centro-symmetric dimers with one terminal and one bridging dithiocarbamate ligand per zinc center [31]. The low effect of Zn^{2+} on mercury stabilization might be attributed to its electronic configuration of $[Ar] 3d^{10}$. Ions of d^{10} configuration have apparent distortion and polarization capabilities and the tendency to chelate with C, S and N donors. Therefore, the distortion ability of Zn^{2+} was affected by its smaller ionic radius (0.74 Å). Thus, as compared with Hg^{2+} , another ion of d^{10} configuration, Zn^{2+} , had relatively weak coordination with DTCR.

3.2. Mechanism of interference with Hg^{2+} precipitation efficiency by four heavy metals

3.2.1. Electronic structure and chelating ability of heavy metal ions

The Hg^{2+} precipitation rates for the four metal ions Cu^{2+} , Ni^{2+} , Pb^{2+} , and Zn^{2+} at 0.2 mg l^{-1} are shown together in Fig. 5. As shown, Cu^{2+} had the greatest impact on the precipitation efficiency of Hg^{2+} . The decrease in precipitation efficiency could be placed in the following order: $Cu^{2+} > Ni^{2+} > Pb^{2+} > Zn^{2+}$. In contrast, the percentage of Hg^{2+} in the solutions increased and released Hg^0 remained stable. The trend could also be seen by fixing metal concentrations to achieve 88.0% precipitation efficiency (Table 2). In Table 2,

Table 2

Concentrations of four heavy metals at an Hg^{2+} precipitation efficiency of 88.0%.

Heavy metal	mg l ⁻¹	mM
Cu^{2+}	0.0077	0.12
Ni^{2+}	0.0724	1.23
Pb^{2+}	0.3387	1.63
Zn^{2+}	0.7305	11.24

the data are presented in mM units to better demonstrate the interference between the metal ions and the stability of the DTCR complexes. Based on these results, the stability of the four heavy metals was in the following order: $Cu^{2+} > Ni^{2+} > Pb^{2+} > Zn^{2+}$, which was in accordance with the findings reported by Sachinidis and Grant [32].

It should be noted that the configuration of metal ions might have an effect on the chelating capacity of ions and the stability of the chelate. The four heavy metals under investigation have different d-orbitals, and thus, the chelating abilities to DTCR may also differ. According to the ligand field stabilization energy (LFSE) theory, the lattice energy, which is considered to be the “thermochemical LFSE” values, for first row d-block metals is in the order $d^1 < d^2 < d^3 > d^4 > d^5 < d^6 < d^7 < d^8 < d^9 > d^{10}$ [33]. Therefore, as Ni^{2+} , Cu^{2+} and Zn^{2+} are d^8 , d^9 and d^{10} ions in the first d-block row, the stability order for the complexes are $Ni^{2+} < Cu^{2+} > Zn^{2+}$. Thus, the stability order obtained from this theory was consistent with the results obtained in this experiment, where Cu^{2+} dominated in the reaction with DTCR. Despite the fact that both Zn^{2+} and Hg^{2+} belong to group 12 in the periodic table, Hg^{2+} had the stronger chelating capacity because Hg^{2+} has a soft metal center and coordination to S-donors is favored according to Pearson’s rule [34].

Hackett et al. determined the coordination ability order $Ag^+ > Hg^{2+} > Cu^{2+} > Sb^{3+} > Pb^{2+} > Cd^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+}$ [35]. Those different results might be obtained under unique experimental conditions. In this experiment, spectator ions might have made a difference in the chelating ability between Ni^{2+} and Pb^{2+} . Ions, such as Cl^- , SO_4^{2-} , NO_3^- and Ca^{2+} , were sufficient to impact the practical concentration of heavy metals in the simulated desulfurization solutions. Due to the insolubility of $PbSO_4$ and the formation of $PbCl_x^{2-x}$ complexes in the simulated solutions, concentrations of aqueous Pb^{2+} decreased and in turn the reaction rate with DTCR was inhibited. As a result, Ni^{2+} had a stronger chelating capacity than Pb^{2+} in the simulated FGD solutions.

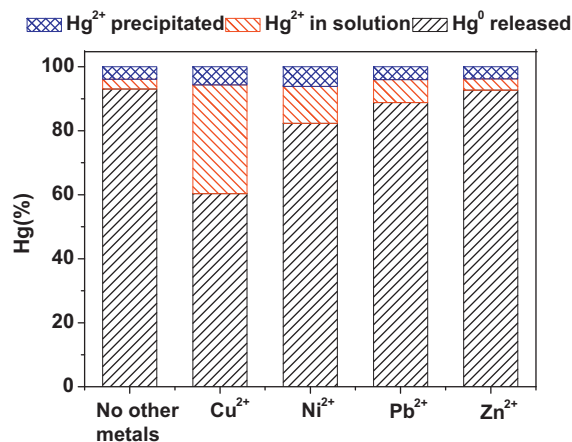


Fig. 5. Effect of four heavy metals on mercury stabilization at a DTCR dose of 0.2 mg l^{-1} .

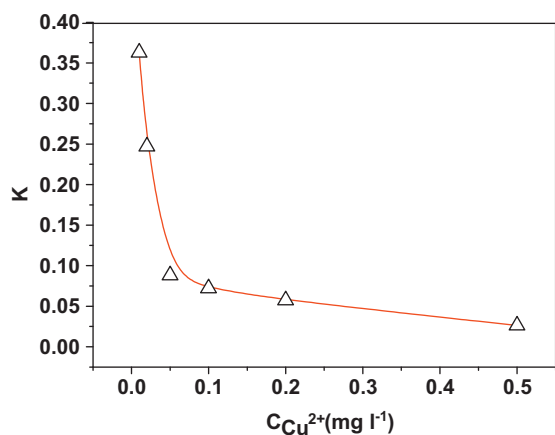


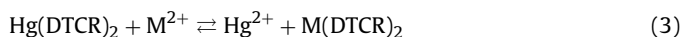
Fig. 6. Equilibrium constants of Cu^{2+} and Hg^{2+} in the reaction with DTCR ($Hg^{2+} = 0.1\ mg\ l^{-1}$, $S(IV) = 1\ mM$, $Cl^{-} = 0.1\ M$, $NO_3^{-} = 50\ mM$, $SO_4^{2-} = 50\ mM$, $Mg^{2+} = 10\ mM$, $Ca^{2+} = 10\ mM$, $DTCR = 1.0Q_{th}$, $T = 50\ ^\circ C$, $pH = 5$).

3.2.2. Equilibrium constants of reaction

The reaction between DTCR and heavy metals is described in Eq. (2).



The subtraction of Eq. (1) from Eq. (2) resulted in Eq. (3), which describes the competition between the four heavy metals and Hg^{2+} in the reaction with DTCR.



where $M^{2+} = Cu^{2+}$, Ni^{2+} , Pb^{2+} , and Zn^{2+}

Thus, the equilibrium constant of Eq. (3) in Fig. 1 can be expressed as:

$$K = \frac{C_{Hg^{2+}}}{C_{Cu^{2+}}} \quad (4)$$

From Eq. (4), the calculated equilibrium constants at different Cu^{2+} doses are shown in Fig. 6. The small equilibrium constants (<1) indicated that the reaction generated large quantities of $Hg(DTCR)_2$. Thus, Hg^{2+} has a stronger affinity for DTCR than Cu^{2+} .

Interestingly, the equilibrium constant decreased from 0.363 to 0.0264 when the Cu^{2+} concentration increased. Despite the fact that the equilibrium constant theoretically remains the same when the temperature is constant at $50\ ^\circ C$, the inconsistency between experimental data and theory might be attributed to the experimental error. In this experiment, the amount of Cu^{2+} chelated by DTCR only occupied a small portion of the total Cu^{2+} in solution. When the Cu^{2+} concentration increased, the reaction moved to the right to reduce the Cu^{2+} concentration and keep the equilibrium constant unchanged. However, the small decrease in Cu^{2+} in solution could be neglected due to the large initial concentration of Cu^{2+} . Thus, the theoretical Cu^{2+} concentration was increased and the equilibrium constant decreased in response.

3.3. Effect of DTCR dose and pH

From the figures for the interferences of the four heavy metals with Hg^{2+} stabilization, the released Hg^0 remained nearly the same as a minor portion of the total mercury. Thus, released Hg^0 was neglected in the following experiments. Furthermore, it is hard to detect released Hg^0 in practical industrial treatments, but it is easier to measure the removal rate of Hg^{2+} by precipitants. Thus, by measuring the mercury removal in the solutions, we obtained the fundamental experimental results for industrial applications.

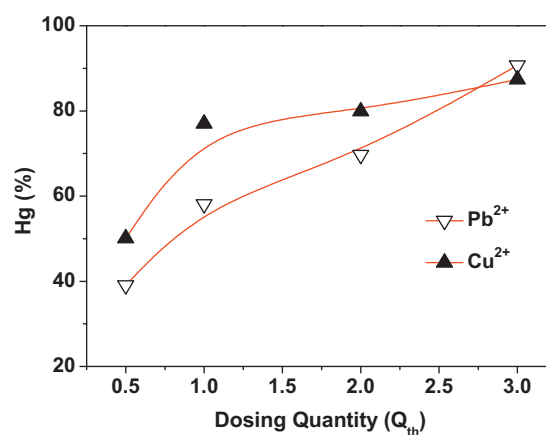


Fig. 7. Effect of DTCR dose on Hg^{2+} removal with the addition of heavy metals ($pH = 5$, $T = 50\ ^\circ C$, $Pb^{2+} = 0.5\ mg\ l^{-1}$, $Cl^{-} = 100\ mM$, $Cu^{2+} = 0.1\ mg\ l^{-1}$, $Hg^{2+} = 0.1\ mg\ l^{-1}$).

Among the four heavy metals, Cu^{2+} dominated the reaction with DTCR. However, the Pb^{2+} concentration was the highest in the practical desulfurization solutions [21]. Thus, Pb^{2+} and Cu^{2+} were the main interferences with the precipitation rate of Hg^{2+} . In the subsequent experiments, Pb^{2+} and Cu^{2+} were chosen to determine the optimal DTCR dosage and the influence of pH.

3.3.1. Effect of DTCR dosage

In the presence of Cu^{2+} or Pb^{2+} , the mercury precipitation efficiency was inhibited. This decreased precipitation might cause the Hg^{2+} in wastewater discharge to exceed allowable limits. Thus, more DTCR has to be utilized to control the Hg^{2+} concentration in practical desulfurization solutions.

Fig. 7 illustrates the effect of DTCR dose on Hg^{2+} removal efficiency. When the concentration of Cu^{2+} was $0.1\ mg\ l^{-1}$, the Hg^{2+} removal rate significantly increased from 39.1% to 90.7% with increasing DTCR dosage from $0.5Q_{th}$ to $3.0Q_{th}$. When the DTCR dosage was $3.0Q_{th}$, the equilibrium constant K (calculated from Eq. (4)) was 0.089, which corresponded to the results presented in Fig. 6. For $0.5\ mg\ l^{-1}$ Pb^{2+} , the Hg^{2+} removal rate rose sharply to 77.0% at a DTCR dose of $1.0Q_{th}$ and then increased slightly to 87.4% removal. The results verified the dominance of Cu^{2+} over Pb^{2+} for competition with Hg^{2+} . Furthermore, the results provided a practical DTCR dose when dealing with industrial wastewater treatment.

3.3.2. Effect of pH

In the practical desulfurization solutions, pH values varied from 4.0 to 6.5 and affected the Hg^{2+} removal performance. Hence, a pH variation experiment was carried out. Due to the low removal of Hg^{2+} at a DTCR dose of $1.0Q_{th}$, a DTCR dose of $2.0Q_{th}$ was added to guarantee a relatively high removal rate.

As shown in Fig. 8, the Hg^{2+} removal rate increased rapidly from 63.9% to 79.9% at a pH of 5.0 in the desulfurization solution containing $0.1\ mg\ l^{-1}$ Cu^{2+} . When the pH increased from 5.0 to 9.0, the Hg^{2+} removal rate increased slightly to 88.9%. However, Hg^{2+} removal with the addition of Pb^{2+} was more sensitive to pH variation. When the pH increased from 3.0 to 6.5, the Hg^{2+} removal rate increased significantly, peaking at 93.6%. The removal efficiencies reached a plateau when the pH was higher than 6.5.

Several major factors might be responsible for the observed behavior under different pH values, with the most influential being the formation of $Cu(OH)_2$ and $Pb(OH)_2$ as pH increased. At a low pH, copper and lead remain in solution and competitive with Hg^{2+} . When the pH value rises, the OH^{-} concentration increases and forms insoluble $Cu(OH)_2$ and $Pb(OH)_2$. Thus, the concentration of

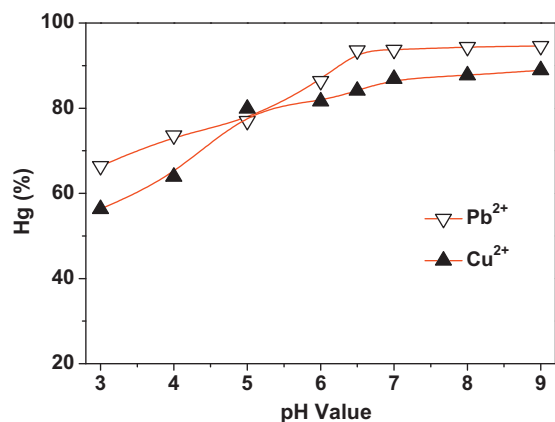


Fig. 8. Effect of pH value on Hg^{2+} removal with addition of heavy metals ($T = 50^\circ\text{C}$, $\text{Cu}^{2+} = 0.1 \text{ mg l}^{-1}$, $\text{Cl}^- = 100 \text{ mM}$, $\text{Pb}^{2+} = 0.5 \text{ mg l}^{-1}$, $\text{DTCR} = 2.0Q_{\text{th}}$, $\text{Hg}^{2+} = 0.1 \text{ mg l}^{-1}$).

aqueous ions decreased and the interference with Hg^{2+} stabilization diminished.

Another factor contributing to Hg^{2+} removal with pH was the protonation of sulfur and nitrogen atoms in DTCR at low pH values. Positively charged functional groups generate a Coulombic repulsion against Hg^{2+} , which reduced the chances of collision between DTCR and Hg^{2+} and inhibited the coordination of Hg^{2+} [18,36]. In contrast, deprotonation occurred along with increasing pH, promoting coordination and high removal rates for Hg^{2+} .

It is well established from speciation studies that mercury exists as Hg^{2+} in solutions of $\text{pH} < 3.0$ and as HgCl_2 , HgCl^+ , HgClOH and $\text{Hg}(\text{OH})_2$ in solutions of $\text{pH} 3.0\text{--}7.0$ [37]. The increasing pH contributed to the generation of HgClOH and $\text{Hg}(\text{OH})_2$, which reduced the working Hg^{2+} concentrations in aqueous solutions. The $\text{Hg}(\text{OH})_2$ in the solutions was then removed by precipitation, which increased the overall removal efficiency.

4. Conclusion

An evaluation of the influence of four heavy metals on Hg^{2+} precipitation and stabilization was successfully performed, and the results revealed that the metals interfered with Hg^{2+} precipitation by DTCR. In contrast, the amount of Hg^{2+} remaining in the simulated desulfurization solutions increased significantly, while the released Hg^0 was stable in spite of the addition of heavy metals. The inhibitory effect on Hg^{2+} precipitation was found to be $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+}$. In addition, increasing the pH of the desulfurization solutions impacted Hg^{2+} removal, which might have been caused by decreases in the Cu^{2+} and Pb^{2+} concentrations, the deprotonation of sulfur atoms in the DTCR complex or the formation of $\text{Hg}(\text{OH})_2$. In the presence of $0.1 \text{ mg l}^{-1} \text{ Cu}^{2+}$ or $0.5 \text{ mg l}^{-1} \text{ Pb}^{2+}$, $3.0Q_{\text{th}}$ of the DTCR dose resulted in a considerable removal rate for Hg^{2+} , which emphasizes the importance of removing Cu^{2+} and Pb^{2+} from desulfurization solutions. Therefore, the pretreatment of the desulfurization solutions, such as adjusting the pH or reducing the concentration of other heavy metals, is essential for high precipitation of Hg^{2+} by DTCR. This paper provides a theoretic foundation for optimal DTCR dose and pH in industrial wastewater treatment to achieve cost maximization.

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