Experimental Study on Chloride Ion Removal in High-Salt Wastewater System

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Abstract: Chlorine is usually present in the environment in an ionic state, is highly mobile and difficult to degrade. High-chlorine wastewater can corrode buildings and affect the growth of animals and plants. Therefore, how to solve the environmental problem of high concentration of chloride ions well and effectively has drawn the intensive attention of the society. In this paper, chloride ion is removed from wastewater with the method of coprous chloride precipitation, and investigation is made on the effects of pH, temperature, amount of precipitant, titration time and reaction time on the removal efficiency of chloride ions. The results show that: when \( n_{\text{CuSO}_4} : n_{\text{Na}_2\text{SO}_3} : n_{\text{NaCl}} : n_{(\text{ascorbic acid})} = 1.3:1.1:1:0.01 \), and reaction pH is 3, temperature is 80 °C, titration time of sodium sulfite is 20min, reaction time after titration is 30min, the chloride ion has the optimal removal efficiency. SEM method is used for the characterization of the precipitates formed by the reaction. The results show that the experimentally produced complex cuprous chloride is irregular polyhedron with uneven particle size.

1. Introduction

As a common element in the environment, chlorine is often present in a highly mobile and difficult-to-degrade anion state[1]. As a common anion, chloride ion has strong corrosiveness. In a high-chlorine environment, it will cause corrosion of metal pipes and structures, and the growth of animals, plants and crops will be affected. The massive deposition of chloride ions will lead to soil salinization; and Human direct or indirect intake of too much chlorine ions will cause serious harm to human health[2-5]. At present, the main techniques of chloride removal employed include ion exchange, precipitation, electrochemistry and membrane separation etc[6-10]. Precipitation is simple and effective; it mainly includes copper chloride complexation precipitation method and ultra-high lime aluminum method, etc[11]. By simulating the high chlorine wastewater as the experimental object in this paper, chloride ion is removed from wastewater with the method of coprous chloride precipitation, and investigation is made on the effects of pH, temperature, and amount of experimental reagent, titration time and reaction time on the removal efficiency of chloride ions.
2. Experiment

2.1 Experimental instruments and drugs
Main experimental instruments: ion chromatograph; magnetic stirrer.
Main experimental drugs: ascorbic acid, sodium chloride, concentrated sulfuric acid, sodium hydroxide, copper sulfate pentahydrate, anhydrous sodium sulfide.

2.2 Experimental method
Weigh a certain amount of sodium chloride to dissolve in water, add a certain proportion of cupric sulfate pentahydrate and ascorbic acid, adjust the pH and temperature of the solution, add a certain volume of sodium sulfite solution to high salt water and stir for a certain period of time.

2.3 Method of calculation
Calculation formula of chloride removal efficiency:
\[ \eta = \frac{m_1 - m_0}{m_0} \times 100\% \]  \hspace{1cm} (1)
\[ m_1 = c_1 \times v_1 \]  \hspace{1cm} (2)

In formula (1): \( m_1 \) is the mass of chloride ion in supernatant after reaction; g; \( m_0 \) is the mass of chloride ion in water sample before reaction, g.

In formula (2): \( c_1 \) is the concentration of chloride ion in the supernatant after reaction, mg\( \cdot \)L\(^{-1} \); \( v_1 \) is the volume of supernatant after reaction, L.

3 Experimental results and discussion

3.1 Effect of reducing agent dosage on chloride removal

Refer Figure 1 for the effect of reducing agent dosage on chloride removal. We can see that with the increase of sodium sulfite content, the removal efficiency of chloride first increases and then decreases. It as the optimal removal efficiency when \( n\text{Na}_2\text{SO}_3 : n\text{NaCl} = 1.1:1 \). When sodium sulfite is used as reducing agent and gradually added into the solution, copper ion is reduced to cuprous ion and reacts with chloride ion in solution to form complex cuprous chloride precipitation. As sodium sulphate continues to increase to a certain extent, pH of the solution increases gradually, and the complex cuprous chloride will hydrolyze to form cuprous oxide and chloride ion, and so the removal rate of chloride ion can be reduced.

![Figure 1. Effect of reducing agent dosage on chloride removal](image-url)
3.2 Effect of oxidant dosage on chloride removal

![Graph showing effect of oxidant dosage on chloride removal.](image1)

Refer Figure 2 for the effect of oxidant dosage on chloride removal. We can see that with the increase of copper sulfate in solution, the removal efficiency of chloride ion increases gradually at first and then almost remains unchanged. It has the optimal removal efficiency of 82.15\% when \( n_{\text{CuSO}_4} : n_{\text{NaCl}} = 1.3:1 \). In the experiment, oxidation-reduction reaction takes place, the standard electromotive force of the reaction \( E^\theta = \phi^{\theta}_{\text{Cu}^{2+} \rightarrow \text{CuCl}} - \phi^{\theta}_{2\text{SO}_4^{2-} \rightarrow 2\text{SO}_2} = 1.48V > 0 \). Based on the theory of thermodynamics, we can know that the reaction can be spontaneous and positive. According to the theory of thermodynamics and dynamics, with the increase of copper sulfate content, the more thorough and more effective of the forward process of redox reaction.

3.3 Effect of temperature on chloride removal

![Graph showing effect of temperature on chloride removal.](image2)

Refer Figure 3 for the effect of temperature on chloride removal. We can see that before the temperature rises to 80 °C, with the increase of temperature, the removal rate of chloride ion gradually increases; when the temperature continues to rise, the chloride ions have unapparent change in the removal rate. The redox reaction that occurred in the experiment belongs to the heat absorption reaction. Therefore, the temperature increase is conducive to the positive reaction, and the reaction rate can be speed up.
3.4 Effect of dropping time on chloride removal

Refer Figure 4 for the effect of dropping time of sodium sulfite on chloride removal. We can see that it has poor chloride removal effect when sodium sulfite is dripped within 10min. When the dropping time of sodium sulfite is increased, the effect of chlorine removal is significantly better. It has an optimal chlorine removal effect when the sodium sulfite is dripped within 20min. These results revealed that maybe the pH of the solution system changes too much in a short time due to that sodium sulfite is added too fast, and which led to side effects.

3.5 Effect of reaction time on chloride removal

Refer Figure 5 for the effect of reaction time on chloride removal obtained. We can see that the removal of chloride ions increases first and then decreases slightly. It has a maximum removal rate of chloride ion at 30min. The experiment indicates that it is not that the effect of chloride removal is better with time. In fact, the effect of chloride removal is slightly worse with time due to that the complex cuprous chloride with reaction has reverse dissolution.
3.6 Effect of pH on chloride removal
Refer Figure 6 for the change chart of solution pH with the addition of sodium sulfite. We can see that the following reactions occur when sodium sulfite is gradually added to the solution: 

\[
2\text{Cu}^{2+} + 2\text{Cl}^- + \text{SO}_3^{2-} + \text{H}_2\text{O} = 2\text{CuCl} \downarrow + \text{SO}_4^{2-} + 2\text{H}^+ 
\]

Due to the reaction, \(\text{H}^+\) is gradually generated, and pH of the solution decreases gradually. When sodium sulfite was added to a certain volume, \(\text{SO}_3^{2-}\) will neutralize with \(\text{H}^+\) in the solution, so the pH of the solution is gradually increased. Figure 7 is the effect of pH change on the removal efficiency of chloride ions. As shown in Figure 7, as the pH increases, the concentration of chloride after reaction first decreases and then increases. This is a result of that complex cuprous chloride will react to form cuprous oxide with the gradual increase of pH.

3.7 Characterization and analysis

Refer figure 8 for the precipitated products SEM. The experimental precipitation is irregular polyhedron with uneven particle size.

4. Conclusion
(1) Based on the above experiments, it can be concluded that the complex cuprous chloride method has a good effect on chloride removal. The experiments show that it has an optimal effect of chloride removal when \(n\text{CuSO}_4 : n\text{Na}_2\text{SO}_3 : n\text{NaCl} : n(\text{ascorbic acid}) = 1.3:1.1:1: 0.01\), reaction pH is 3, temperature is 80 °C and reaction time after titration is within 30min.
(2) From SEM analysis, it can be concluded that the experimental product is irregular polyhedron with uneven particle size.

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Reference
[1] Li Wenxiang, Liu Dongyun, Shen Dongsheng, Hu Lifang, Yao Jun and Long Yuyang 2020. Migration of inorganic chlorine during thermal treatment of mineralized waste. Waste Management, p 207-212.
[2] Pan Xudong and Wang Xiangming 2013. Chlorine Ion Control in Circulating Water and Discussion on Corrosion mechanism of Stainless Steel. Industrial water treatment, p 14-16.
[3] Li Minghui, Wang Jian and Wang Jianxiang 2012. Analysis on the Harm of Chloride Ion in Boiler Feed Water. Equipment manufacturing technology, p 240-241
[4] Xu Hui and Chen Jiankang 2020. Coupling effect of corrosion damage on chloride ions diffusion in cement based materials. Construction and Building Materials, 118225.
[5] Gopal K, Tripathy S S, Bersillon J L and Dubey S P 2007. Chlorination byproducts, their toxicodynamics and removal from drinking water. Journal of Hazardous Materials, p 1-6.
[6] Zhang Qiang, Xiao Shiwei, Sun Yonghua, Hou zhiming and Liu haixia 2015. Removal of Chloride From Wastewater by Precipitation. Chemical Engineer, p 20-22.
[7] Kameda T, Uchiyama N, Park K S, Grause G and Yoshiaki T 2008. Removal of hydrogen chloride from gaseous streams using magnesium-aluminum oxide. Chemosphere, p 844-847.
[8] Lv Liang, Sun Peide, Gu Zhengyu, Du Hangeng, Pang xiangjun, Tao Xiaohong and Xu Rufeng 2009. Removal of chloride ion from aqueous solution by ZnAl-NO3 layered double hydroxides as anion-exchanger. Journal of Hazardous Materials, p 1444-1449.
[9] Wu Xuelian, Liu Zhongqing and Liu Xu 2013. Chloride ion removal from Zinc sulfate aqueous solution by electrochemical method. Hydrometallurgy, p 62-65.
[10] Yu L B, Jiang L H, Chu H Q, Guo M Z, Zhu Z Y and Dong H 2019. Effect of electrochemical chloride removal and ground granulated blast furnace slag on the chloride binding of cement paste subjected to NaCl and Na2SO4 attack. Construction and Building Materials, p 538-546.
[11] Ahmed A W, Bill B and Jon S 2005. An equilibrium model for chloride removal from recycled cooling water using the ultra-high lime with aluminum process. Water Environment Research, p 3059-65.