Application of a Novel Nano-composite Reagent to the Treatment of Wastewaters Containing Chelated Copper

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Abstract. A novel nano-composite reagent (NCR) was prepared for the treatment of wastewaters containing copper chelates, such as CuEDTA, CuNTA, CuCA and CuDTPA etc. The experimental results showed that NCR could effectively remove chelated copper from wastewaters under conditions of pH ≥ 10 and NCR dosage ≥ 200 mg L-1, where the removal efficiency could reach as high as 98.94%. The turbidity of wastewater could be decreased to 1 NTU below after settling for 50 min, which indicated a good settling performance of the yielded precipitates.

Introduction

Of the current methods for removing heavy metals from wastewaters, chemical precipitation is widely applied due to its convenient operation, capability to treat large volume of wastewater, low cost and so on. However, conventional chemical precipitation process possesses poor efficiency and is unable to meet the increasingly stringent environmental regulations when it comes to the treatment of wastewaters contaminated by chelated metals. In response to this challenge, many new treatment technologies have been developed over the past few decades. For example, activated carbon adsorption, ion exchange, micellar-enhanced ultrafiltration (MEUF), heavy metal chelating agents, reverse osmosis, iron chipping microelectrolysis, biochemical method, photocatalytic oxidation, etc. However, inherent shortcomings such as high cost, low removal efficiency and troublesome operation hampered their wide use for the removal of chelated metals from wastewaters.

In our recent research, we found that the chelated copper ions could first be replaced by Ca2+ or Fe3+ and then removed by precipitation under certain conditions. Basing on this finding, we proposed a replacement-precipitation coupling process for the treatment of wastewaters containing chelated heavy metals. The coupling process of replacement and precipitation exhibits a great potential in removing chelated heavy metals from wastewaters since it could both overcome the limitations and maintain the merits of routine chemical precipitation process.

Further research revealed that the removal efficiency of chelated heavy metals from wastewaters using replacement-precipitation process could be effectively promoted by the addition of a nano reagent. This encouraged us to develop a novel nano-composite reagent (NCR) for which a patent product was pending.

Since copper is a common contaminant and citric acid, EDTA, NTA, DTPA are strong chelating agents, CuCA, CuEDTA, CuNTA and CuDTPA are chosen as
target pollutants of industrial wastewaters in this particular research. The paper is mainly focused on the following three issues: (1) affecting factors of copper removal efficiency including initial pH of the solution and NCR dosage; (2) settling performance of the yielded precipitates; (3) removal efficiency of chelated copper from wastewaters using NCR.

Materials and Methods

Materials
Reagents including C₆H₈O₇, Na₂EDTA, Na₃NTA, Na₅DTPA, Cu(NO₃)₂.3H₂O, HCl, NaOH, KHC₈H₄O₄, Na₂CO₃ and NaHCO₃ were analytical-grade and obtained from Guangzhou Chemicals. Nano reagent was supplied by Huijingya Nanometer and New Material Co., Ltd (Shanghai, China). NCR was self-prepared in laboratory [12,13]. Distilled water was used for preparation and dilution of solutions. Wastewater samples were synthesized by mixing Cu(NO₃)₂.3H₂O with citric acid.

Analytical Methods
Residual copper concentrations of solutions were determined by Z-5000 Polarized Zeeman Flame Atomic Absorption Spectrophotometry (FAAS). The pH measurements were performed using a pHS-3C pH meter. Turbidity of the solution was tested by a Hach model 2100N Laboratory Turbidimeter. Total organic carbon (TOC) was measured by a Shimadzu 5000A TOC analyzer.

Experimental Procedures
A definite dose of NCR (50-300 mg L⁻¹) was added to 500 ml cupric citrate solution containing 50 mg L⁻¹ Cu(II). Adjusted to pH 0-14, the solution was agitated at the speed of 200 rpm for 2 min and then at the speed of 70 rpm for 10min. Supernatant samples were taken periodically for examination of turbidity. The resulting solutions were filtrated for determination of residual copper concentration.

Results and Discussion

Effect of pH on Removal Efficiency

![Graph showing the effect of pH on removal efficiency](image)

Figure 1. Residual concentrations of copper and TOC at different pH (NCR dose: 200 mg L⁻¹, initial Cu(II) concentration: 50 mg L⁻¹) (Inset: photos of virgin cupric citrate solution(A) and cupric citrate solution with the addition of NCR(B), respectively).
The effect of initial pH on copper removal efficiency was investigated in CuCA-containing wastewater treatment. As depicted in Fig. 1, the addition of NCR could hardly remove the chelated copper as pH < 6.5. When pH was above 7.5, blue precipitates appeared (as shown in inset B of Fig. 1) and residual copper concentration decreased quickly. For example, the residual copper concentration was decreased to 20.86 mg L\(^{-1}\) at pH 7.99 and to 0.22 mg L\(^{-1}\) at pH 11.91, denoting 58.28\% and 99.56\% copper removal efficiency, respectively. Meanwhile, TOC in resulting solution was decreased 1.55\% at pH 7.99 and 5.57\% at pH 11.91. Considering the absorbent ability of the surface of precipitates, we concluded that NCR was unable to remove the organics in solution. Therefore, the reaction between NCR and cupric citrate solution could be described as the following replacement-precipitation process:

\[
\text{Cu}_3(C_6H_5O_7)_2 + 3\text{Ca}^{2+} \rightleftharpoons \text{Ca}_3(C_6H_5O_7)_2 + 3\text{Cu}^{2+}. \tag{1}
\]

\[
\text{Cu}^{2+} + 2\text{OH}^- \rightleftharpoons \text{Cu(OH)}_2 \downarrow \text{(blue).} \tag{2}
\]

Overall reaction:

\[
\text{Cu}_3(C_6H_5O_7)_2 + 3\text{Ca(OH)}_2 \rightleftharpoons \text{Ca}_3(C_6H_5O_7)_2 + 3\text{Cu(OH)}_2 \downarrow \text{(blue).} \tag{3}
\]

As pH ≥ 10, residual copper concentration could be decreased to 0.5 mg L\(^{-1}\) below (the emission standard of copper in China EPA’s regulation). Therefore, it was suggested that the applicable pH value for wastewater treatment by NCR should be above 10.

**Effect of NCR Dosage on Removal Efficiency**

The effect of NCR dosage on copper removal efficiency in treating CuCA-containing wastewater was researched. Copper removal efficiency was proved to be considerably dependant on NCR dosage. As shown in Fig. 2, the residual copper concentration decreased with the increase of NCR dosage. Moreover, this changing tendency was much more obvious when NCR dosage was below 150 mg L\(^{-1}\). For example, the residual copper concentrations at 50, 100, 150 and 250 mg dosage of NCR were 19.24 mg L\(^{-1}\), 3.93 mg L\(^{-1}\), 1.09 mg L\(^{-1}\) and 0.0 mg L\(^{-1}\) respectively, denoting 61.52\%, 92.14\%, 97.82\% and 100\% copper removal efficiency, respectively. The residual copper...
Concentration maintained stable basically and be decreased to 0.5 mg L\(^{-1}\) below (the emission standard of copper in China EPA’s regulation) when NCR dosage was 200 mg L\(^{-1}\) or above. For example, the residual copper concentration was 0.47 mg L\(^{-1}\), denoting 99.06% copper removal efficiency at 200 mg L\(^{-1}\) dosage of NCR. Therefore, it’s suggested that NCR dosage should be above 200 mg L\(^{-1}\).

**Settling Performance of the Yielded Precipitates**

![Settling Time vs. Turbidity](image)

Figure 3. Influence of settling time on turbidity (initial copper concentration: 50 mg L\(^{-1}\), initial pH: 8.0, NCR dosage: 200 mg L\(^{-1}\)).

In practical wastewater treatment, solid-liquid separation is usually carried out by sedimentation. Therefore, settling performance of the precipitates yielded from wastewater treatment by NCR was also investigated. As a direct reflection of the amount of suspended particles, solution turbidity was measured to assess the settling performance. Lower turbidity implied less suspended particles in solution and more complete settlement of precipitates\(^{[16]}\). Experimental results indicated that suspended particles yielded in wastewater treatment by NCR were compact and could aggregate into bigger precipitates quickly. As depicted in Fig. 3, turbidity of the solution was decreased to 18.06 NTU after settling for 10 S and to 1 NTU below after settling for 45 min (the quality standard for drinking water in China’s MOH regulation). Therefore, precipitates yielded from wastewater treatment by NCR possessed good settling performance.

**Treatment Efficiency of Wastewaters Containing Chelated Copper by NCR**

CuEDTA, CuNTA, CuCA and CuDTPA are the common copper chelates in industrial wastewaters. As indicated in Fig.4, NCR possessed good treatment efficiency for common industrial wastewaters containing chelated copper. When the initial pH was 9.13, the residual copper concentrations of wastewaters containing CuEDTA, CuNTA and CuDTPA were decreased from 50 mg L\(^{-1}\) to 2.06 mg L\(^{-1}\), 9.86 mg L\(^{-1}\) and 3.08 mg L\(^{-1}\), where the copper removal efficiencies reached 95.88%, 80.28% and 93.84%, respectively. While the initial pH was 11.5, the residual copper concentrations of wastewaters containing CuEDTA, CuNTA and CuDTPA were 0.22 mg L\(^{-1}\), 0.49 mg L\(^{-1}\) and 0.27 mg L\(^{-1}\) respectively, which were all below 0.5 mg L\(^{-1}\) (the emission standard of copper in China EPA’s regulation).
Conclusions

(1) NCR possessed good treatment efficiency for common industrial wastewaters containing chelated copper such as CuCA, CuEDTA, CuNTA, CuDTPA etc.
(2) The optimized conditions of NCR treating wastewaters containing chelated copper were pH $\geq$ 10 and NCR dosage $\geq$ 200 mg L$^{-1}$.
(3) Precipitates yielded from wastewater treatment process possessed good settling performance.

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