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A simple method for removing chelated copper from wastewaters: $Ca(OH)_2$-based replacement-precipitation

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ABSTRACT

A simple $Ca(OH)_2$-based replacement-precipitation process was applied to the removal of EDTA-chelated copper from wastewaters. The effect of initial pH of the solution, molar ratio of Ca^{2+} to Cu(II), the presence of CO_2 on the removal efficiency was investigated. The experimental results showed that the $Ca(OH)_2$-based replacement-precipitation process could efficiently remove the chelated copper from wastewaters. When $12 \leqslant pH \leqslant 13$ and molar ratio of Ca^{2+} to Cu(II) $\geqslant 2$, the removal efficiency could reach 99% above, also being close to the theoretically simulated results. The presence of CO_2 in the air would exert negative effect on the removal efficiency, but the side effect could be effectively eliminated by the addition of flocculation agent polyacrylamide. Compared with Fe^{2+}-based replacement-precipitation technique applied in industrial practice, the method possesses the advantages of less sludge, lower cost, higher removal efficiency and higher controllability.

1. Introduction

The discharge of heavy-metal-laden wastewaters originating from industries, such as textile and paper manufacturing, photographic industry and metal industry, has invited growing concern due to their toxicity and nonbiodegradability (Dean et al., 1972; Dobson and Burgess, 2007). Many treatment strategies for metal-containing wastewaters have been developed, such as chemical precipitation (Guillard and Lewis, 2002; Giannopoulou and Panias, 2008), oxidation (Jiraroj et al., 2006; Korshin et al., 2007), membrane separation (Fatin-Rouge et al., 2006), ion exchange (Pan et al., 2007), adsorption (Barrera-Díaz et al., 2005) and bioadsorption (Yu et al., 1999; Yan and Viraraghavan, 2003). However, with the increasing application of strong chelating agents like EDTA, quadro, nitrilotriacetate and so on in these industries, heavy metals in wastewaters exist more and more in chelated forms. The removal of chelated heavy metals is much more technologically or economically challenging because of their higher degree of stability (Gyliene et al., 2002).

In response to this challenge and the increasingly stringent environmental regulations, many new treatment methods have been investigated and tentatively applied. Of these methods, the replacement-precipitation process has attracted much attention due to its favorable efficiency, relative simplicity, low cost (Nosier and Sallam, 2000). The so-called "replacement-precipitation" method namely involves two sequential processes: the chelated heavy metal ion is first replaced by a non-toxic metal ion and then removed by precipitation with a common alkali. For example, in Fe^{2+}-based replacement-precipitation process for the removal of copper from CuEDTA-containing wastewaters, the chelated copper is first replaced of CuEDTA by Fe^{2+} and then removed by precipitation with NaOH (Ku and Chen, 1992; Xue et al., 1995; Chang et al., 2007).

In our investigation, it was found that the chelated copper ions could be precipitated under certain conditions by the synergetic effect of Ca^{2+} replacement and OH^- precipitation. This finding encouraged us to develop a new $Ca(OH)_2$-based replacement-precipitation process for the treatment of wastewaters containing chelated heavy metals, in which $Ca(OH)_2$ was expected to act not only as a replacement agent but also as a precipitant.

In this particular research, CuEDTA was selected as a target pollutant in consideration of the extensive environmental impact of copper as well as the well-known affinity of EDTA for copper (Breault et al., 1996). The paper is mainly focused on the following four issues: (1) the feasibility of $Ca(OH)_2$-based replacement-precipitation process to remove chelated copper; (2) the effect of initial pH of the solution, molar ratio of Ca^{2+} to Cu(II), the presence of CO_2 and SO_4^{2-} in wastewater on the removal efficiency; (3) comparative investigation of $Ca(OH)_2$-based and Fe^{2+}-based replacement-precipitation processes; and (4) The theoretical simulation of experimental results.

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2. Materials and methods

2.1. Materials

HCl, PAM (Polyacrylamide), $Cu(NO_3)_2 \cdot 3H_2O$, NaOH, $CuSO_4 \cdot 5H_2O$, $Ca(OH)_2$, $Na_2EDTA \cdot 2H_2O$, $FeSO_4 \cdot 7H_2O$ were of analytical grade. All the chemicals above were purchased from Guangzhou Chemicals. Distilled water was used for the preparation and dilution of solutions. The wastewater samples were synthesized by mixing $Cu(NO_3)_2 \cdot 3H_2O$ or $CuSO_4 \cdot 5H_2O$ with $Na_2EDTA \cdot 2H_2O$ at a 1:1 molar ratio of Cu^{2+} to EDTA. The pH of solutions was adjusted to the desired values using either NaOH or HCl (7%).

2.2. Analytical methods

The concentrations of residual copper and calcium in solutions were determined by Z-5000 Polarized Zeeman Flame Atomic Absorption Spectrophotometry (FAAS). The pH measurements were performed using a pHS-3C pH meter. Precipitates were characterized by powder X-ray diffraction (XRD) using a D/MAX 2200 X-Ray Diffractometer with Cu Kα radiation ($\lambda = 0.1541$ nm, 2θ range: 5–85°).

2.3. Experimental procedures

2.3.1. Removal of copper using $Ca(OH)_2$-based replacement-precipitation process

Corresponding to the molar ratio of Ca^{2+} to Cu(II) adopted (0.5–9, respectively), a definite amount of $Ca(OH)_2$ was added to 100 ml CuEDTA solution containing 25 mg l^{-1} Cu(II). Adjusted to pH 12.5, the solution was then agitated at the speed of 100 rpm for 30 min. Samples were taken every 5 min and filtered through 0.45 μm filters. The concentrations of residual copper and calcium in these filtrates were measured by FAAS.

2.3.2. Removal of copper using Fe^{2+}-based replacement-precipitation process

For the sake of comparison, Fe^{2+}-based replacement-precipitation process was also experimentally investigated. Corresponding to the molar ratio of Fe^{2+} to Cu(II) (ranging from 8 to 20), a definite amount of $FeSO_4 \cdot 7H_2O$ was added to 100 ml CuEDTA solution containing 25 mg l^{-1} Cu(II) at pH 3. After 9 min agitation at the speed of 100 rpm, the mixture was adjusted to pH 10 and then stirred at the speed of 60 rpm. Samples were taken periodically up to 50 min, for the determination of residual copper concentrations.

3. Results and discussion

3.1. Replacement-precipitation reaction between $Ca(OH)_2$ and CuEDTA

It is well-known that CuEDTA is a rather stable complex and its chelated copper could not be precipitated by common alkali, such as NaOH. However, when $Ca(OH)_2$ was added into the CuEDTA solution at pH 12.5, some blue precipitates were formed immediately. The solution was decolorized, as shown in C of the inset of Fig. 1. The XRD image (Fig. 1) of the blue precipitates could all be well indexed in the orthorhombic $Cu(OH)_2$ structure with lattice constants $a = 2.949$ Å, $b = 0.59$ Å and $c = 256$ Å (JCPDS 35-0505).

Comparing with NaOH, $Ca(OH)_2$ is a relatively weak base and obviously impossible to precipitate the EDTA-chelated copper just in view of its OH^-. However, it was noticed that Ca^{2+} in $Ca(OH)_2$ could combine EDTA with a chelating constant of $10^{10.69}$ (Kónya and Nagy, 1998). Hence, we simply concluded that the formation of the blue precipitates involved a two-step reaction mechanism as follows:

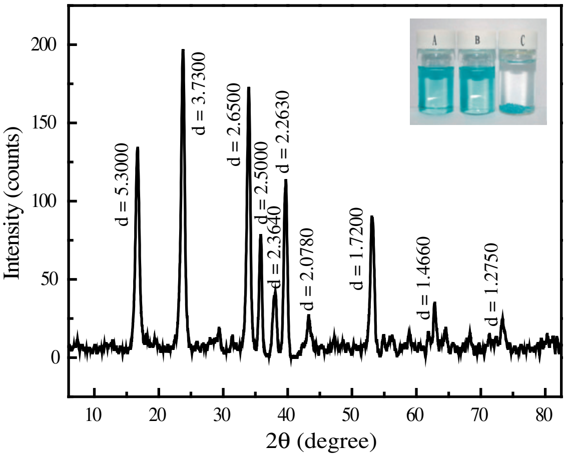

Fig. 1. XRD pattern of the blue precipitates (Inset: photos of virgin CuEDTA solution (A) and CuEDTA solution with the addition of NaOH (B), $Ca(OH)_2$ (C), respectively).

$$\mathrm{CuEDTA} + \mathrm{Ca}^{2+} \rightleftharpoons \mathrm{CaEDTA} + \mathrm{Cu}^{2+} \tag{1}$$

$$\mathrm{Cu}^{2+} + 2\mathrm{OH}^- \rightleftharpoons \mathrm{Cu(OH)}_2 \downarrow \text{(blue)} \tag{2}$$

$$\text{Overall reaction}: \ \mathrm{CuEDTA} + \mathrm{Ca(OH)}_2 \rightleftharpoons \mathrm{CaEDTA} + \mathrm{Cu(OH)}_2 \downarrow \text{(blue)} \tag{3}$$

That is, the chelated copper in CuEDTA was first replaced by Ca^{2+} and then precipitated in the form of $Cu(OH)_2$ by OH^-. Through this replacement-precipitation process followed by a simple solid–liquid separation, the chelated copper could be easily removed from solution. For example, at pH 12.5, 20.41 mg $Ca(OH)_2$ could reduce the copper concentration in solution (100 ml) from 25 to 0 mg l^{-1}. Therefore, it was expected that $Ca(OH)_2$-based replacement-precipitation could be developed as a simple and effective process for the removal of chelated copper from industrial wastewaters.

3.2. Dependence of removal efficiency on pH

It was found that the removal efficiency of copper was considerably dependent on the initial pH of the solution. As shown in

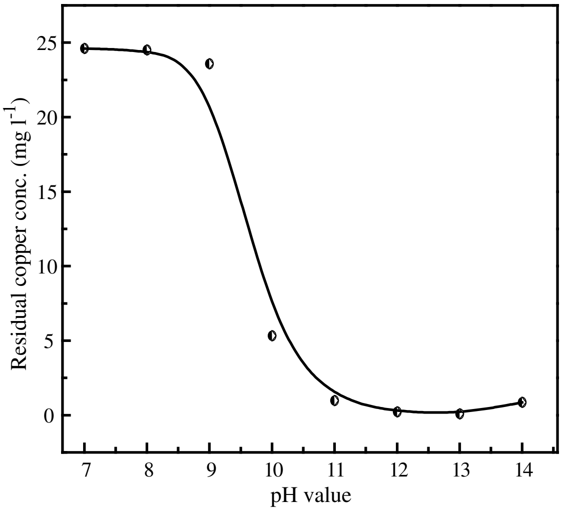

Fig. 2. Effect of initial pH value on residual copper concentrations in a nitrogen-purged reactor (molar ratio of Ca^{2+} to Cu(II) is 4, initial Cu(II) concentration is 25 mg l^{-1}).