A comparative study of nickel(II) removal from electroplating wastewater by pre-precipitation combined with Fenton-precipitation or Fenton-like-precipitation

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ABSTRACT

High nickel(II) electroplating wastewater is difficult to remove through traditional processes. A combined process, which was pre-precipitation, combined with Fenton-like-precipitation or Fenton-precipitation reaction, for treating high nickel complexing wastewater was investigated in this paper. The pre-precipitation pH, initial concentrations of Fe^{2+} or Fe^{3+} and H_2O_2, oxidation reaction pH, and precipitation pH were investigated, and the degradation processes of organic compounds in the treatment were analyzed. Results indicated that the combination of the two processes can effectively remove the high nickel ions. At the optimal experimental conditions, nickel(II) concentrations can be reduced from 2,240 to 0.25 mg/L or 0.31 mg/L by the pre-precipitation combined with Fenton-like-precipitation or Fenton-precipitation process. It demonstrated that the combination of the two processes is an economically and environmentally friendly process to remove the metal from the electroplating wastewater.

Keywords: Chelating heavy nickel; Fenton-like-precipitation reaction; Fenton-precipitation reaction; pre-precipitation; Degradation processes

1. Introduction

Electroplating wastewater often contains heavy metals such as nickel, copper, and so on. Heavy metals are controlled due to their toxicity in many countries. The removal of heavy metals from electroplating wastewaters could be divided into the chemical method, physical method, biological method and so on [1,2]. The biological method is difficult for the removal of nickel from high concentrations of electroplating wastewater, and the processing cycle is relatively long [3]. The traditional physical and chemical methods, such as ultrafiltration [4], reverse osmosis (RO) [5], adsorption processes [6], electrocoagulation [7], and ion exchange [8], usually have a higher cost of disposal, and produce easily secondary pollution [1]. Precipitation is widely used due to its high efficiency, cost-effectiveness and availability [9]. However, this technology is inhibited when the metal in complex states.
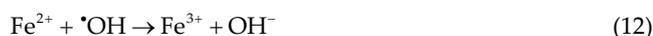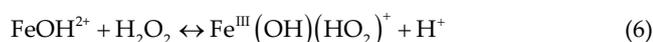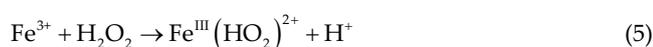
Advanced oxidation processes (AOPs), such as Fenton reaction has been developed for the degradation of chelating groups in electroplating wastewaters [10] and show a high efficiency for degrading macromolecule organic matter [11]. The degradation mechanism of organic pollutants by Fenton reaction is as follows [12,13].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \tag{1}$$

$${}^\bullet OH + RH \rightarrow R^\bullet + H_2O \tag{2}$$

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$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \tag{3}$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \tag{4}$$

But the main drawback of this technique is the high cost. For this reason, various investigations have been found that the Fenton-like reaction also shows high efficiency in the degradation of organic matter [14]. The mechanism of the Fenton-like reaction is different from the Fenton reaction. The Fe^{2+} ions and hydroperoxide/superoxide radicals ($H_2O^{\bullet}/O_2^{\bullet}$) are first produced by Fe(III)–hydrogen peroxide, and then hydroxyl radicals (${}^{\bullet}OH$) are produced by Fe^{2+} ions with hydrogen peroxide [15]. The degradation mechanism of organic pollutants by Fenton-like reaction is as follows [16,17].

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{III}\left(HO_2\right)^{2+} + H^+ \tag{5}$$

$$FeOH^{2+} + H_2O_2 \leftrightarrow Fe^{III}\left(OH\right)\left(HO_2\right)^+ + H^+ \tag{6}$$

$$Fe^{III}\left(HO_2\right)^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet} \tag{7}$$

$$Fe^{III}\left(OH\right)\left(HO_2\right)^+ \rightarrow Fe^{2+} + HO_2^{\bullet} + OH^- \tag{8}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \tag{9}$$

$${}^{\bullet}OH + RH \rightarrow R^{\bullet} + H_2O \tag{10}$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \tag{11}$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \tag{12}$$

Fenton or Fenton-like reaction is a common method in the treatment of electroplating wastewaters. However, there are few studies on the combination of precipitation and Fenton/Fenton-like reactions. Here we use this combination method, pre-precipitation by calcium hydroxide and then use Fenton or Fenton-like reaction to dispose of actual high nickel(II) complexing wastewater. The initial concentration of Fe^{2+}, Fe^{3+} and H_2O_2, reaction time, initial pH and pH value of chelating nickel precipitation were studied. Furthermore, the degradation processes of organic compounds in the treatment were investigated by GC-MS.

2. Materials and methods

2.1. Materials

The following analytical-grade reagents used in the experiment, $Ca(OH)_2$, H_2SO_4, NaOH, H_2O_2, $FeSO_4 \cdot 7H_2O$, $Fe_2(SO_4)_3$ were obtained from Sinopharm Chemical Reagent Factory. Distilled water was used throughout the experiment. High nickel(II) complexing wastewater was collected from the plating industries located in Shenzhen, China.

2.2. Experimental method

Pre-precipitation: 1 M of $Ca(OH)_2$ was added into 200 mL of the wastewater sample, and then the supernatant was collected after precipitation.

Fenton-precipitation and Fenton-like-precipitation: Firstly, the initial pH of the supernatant was adjusted to 6.0 using H_2SO_4 (1 M) or NaOH (1 M). Secondly, 98 mM of H_2O_2 and 15 mM of Fe^{2+} or 5 mM of Fe^{3+} were added into the supernatant and reacted 40 min. Thirdly, the pH value of the reacted solutions was adjusted by NaOH (1 M) and stirred at 200 rpm for 8 min. Finally, the turbid liquid was filtered by a filter membrane of 0.45 μm, and the total nickel(II) and Fe (Fe^{2+} and Fe^{3+}) concentrations in the solution were determined.

2.3. Analytical methods

Complexing nickel ions were determined by a UV-3000 PC spectrophotometer (MAPADA, China). The composition and relative content of organic functional groups were determined by Gas chromatography - mass spectrometry (GCMS-QP 2010 Plus). The total Ni (Ni^{2+} and Ni-complexing ions) and total Fe (Fe^{3+} and Fe^{2+}) concentrations were determined by Thermo M6 atomic absorption spectrophotometer (Thermo Fisher, America). The concentrations of chemical oxygen demand (COD) was determined by XJY-III Microwave digestion unit. The concentrations of total nitrogen (TN) were determined by TNM-1 TN measuring unit (Shimadzu, Japan). The concentrations of total organic carbon (TOC) were determined by TOC-VCPH TOC (Shimadzu, Japan).

3. Results and discussion

3.1. Pre-precipitation

The initial pH value of the electroplating wastewater was 5.85. With the addition of $Ca(OH)_2$, the pH of electroplating wastewater was changed to 8.44, and $Ni(OH)_2$ precipitation which is highly insoluble was formed. The characteristics of electroplating wastewater before and after pre-precipitation were shown in Table 1. The free nickel ions were almost removed after pre-precipitation. Meanwhile, the removal efficiency of COD, TN, and TOC were 42%, 32%, and 20%, respectively.

3.2. Degradation of organic matter during AOPs

As shown in Fig. 1a, there are two absorption peak occurs at 200–210 nm and 230–250 nm after pre-precipitation, which are attributed to the chelating functional groups of –Cl or –NO_2 [18] and conjugated double bonds or conjugated group of phenol (resembling humic compounds) [19],

Table 1
Characteristics of electroplating wastewater before and after pre-precipitation

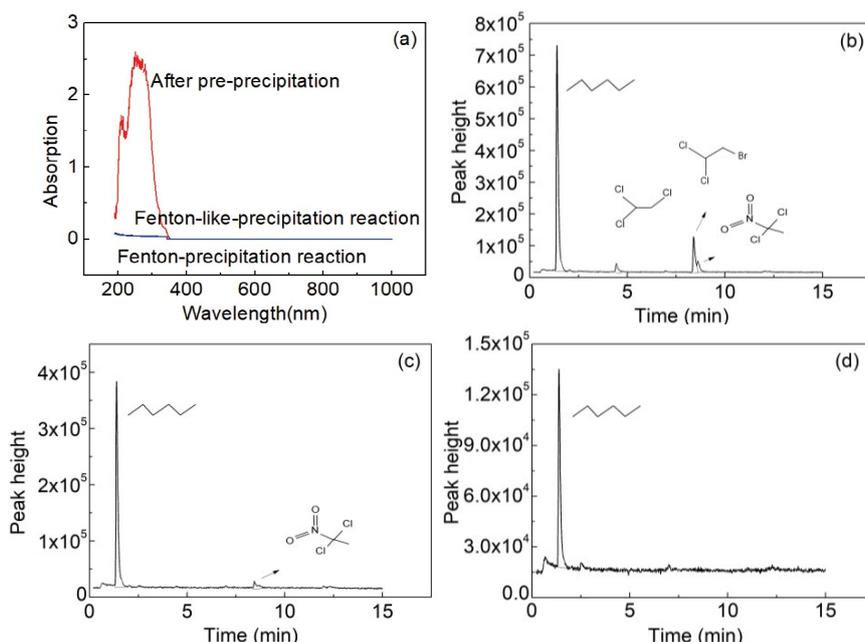| Parameter	Concentration (mg/L)	
	Before	After
Nickel	2,240 ± 20	14.42 ± 0.11
Ferrum	0.08 ± 0.02	0.02 ± 0.00
COD	5,700 ± 800	3,300 ± 300
TN	80 ± 20	55 ± 10
TOC	2,700 ± 300	2,147 ± 100

Fig. 1. (a) UV-vis spectra of electroplating wastewater after pre-precipitation, Fenton-like-precipitation and Fenton-precipitation, Gas chromatography - mass spectrometry (GC-MS) spectra of constituents of organic matter after (b) pre-precipitation, (c) Fenton-like-precipitation, and (d) Fenton-precipitation.

respectively. Nevertheless, the two strong absorption peaks disappeared completely after Fenton-like-precipitation and Fenton-precipitation. To further study the change of organic matter in this degradation process, we measured the GC-MS diagrams for each step. Fig. 1b shows the constituents of organic matters after pre-precipitation, which indicates that the compositions are complex. However, the organic matter contains the saturated alkane compounds and few conjugated compounds after Fenton-like-precipitation reaction (Fig. 1c), and the organic matter only contain single alkane compounds after Fenton-precipitation (Fig. 1d). Both the Fenton-like-precipitation and the Fenton-precipitation have great efficiency in the degradation of the chlorinated compounds. However, the higher chlorinated compounds removal with Fe(II) than Fe(III) in Figs. 1c and d, which indicates that Fe(II) was a more significant iron source than Fe(III) for the degradation of chlorinated compounds. The results of this experiment are in agreement with some studies [20,21]. In the Fenton system, Fe(II) shows high catalytic activity and excellent degradation efficiency at near-neutral pH [22,23]. In the Fenton-like system, Fe(III) performed highly efficiency in the degradation of nitro-compound. However, some nitro-compound cannot be degraded. This behavior may be explained by considering differences in the properties of the complexes or the poor pH conditions [24].

3.3. Removal of nickel during AOPs

As shown in Fig. 2a, the total nickel concentration decreased fast in the first 10 min and then maintained balance during AOPs. The Fenton-like-precipitation showed higher removal efficiency than Fenton-precipitation. Usually, the degradation rate of the Fenton reaction was much faster than that of the Fenton-like reaction

due to the $^{\bullet}OH$ produced immediately in the Fenton reagent [25]. The Fenton-like-precipitation process has better removal efficiency than the Fenton-precipitation process which can be explained by the mechanism of ligand exchange. This complex might have the following stability constants relation [26]:

$$\log\left(K\right)_{\text{Fe(III)-complex}} > \log\left(K\right)_{\text{Ni(II)-complex}} > \log\left(K\right)_{\text{Fe(II)-complex}} \quad (13)$$

Thus, the complex ligand exchange reaction happened and Ni^{2+} was released from Ni(II)-complex in the Fenton-precipitation system. The equation for the ligand exchange reaction is as follows:

$$Fe^{3+} + Ni\left(II\right) - complex \leftrightarrow Ni^{2+} + Fe\left(III\right) - complex \quad (14)$$
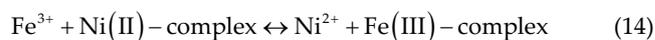
Thus, the Fenton-like-precipitation process displayed higher Ni(II) removal efficiency than the Fenton-precipitation process.

The nickel concentrations decreased to 0.25 mg/L with 5 mM of Fe^{3+} for Fenton-like-precipitation reaction (Fig. 2b), but decreased to 0.31 mg/L with 15 mM of Fe^{2+} for Fenton-precipitation reaction. For the Fenton-like-precipitation reaction, Fe(III) forms hydroxide colloids as the amount of Fe(III) increased, and then the hydroxide colloids gradually reduced the concentration of nickel at a nearly neutral pH [27]. Further increase of the amount of Fe(III), it can compete with nickel for OH^- to form hydroxide precipitates, increasing the nickel concentration. For the Fenton-precipitation reaction, with the increase of Fe(II), $^{\bullet}OH$ was rapidly formed, and the concentration of nickel gradually decreased. Further increase of the amount of Fe(II), a high

concentration of Fe^{2+} would be scavenging hydroxyl radicals as Eq. (12).

As shown in Fig. 2c, without the addition of H_2O_2, the total nickel concentration was very high due to the lack of hydroxyl radicals. Adding a sufficient amount of H_2O_2 can produce enough hydroxyl radical to scavenge the complexing groups, both Fenton and Fenton-like processes exhibited similar Ni(II) removal efficiency. Further increase in the amount of H_2O_2, it would also scavenge on the hydroxyl radical as equation (11).

Fig. 2d shows that when the initial pH increases from 3 to 6, the nickel concentration decreases quickly, increases when the pH is raised from 6 to 6.5. The results indicate that the Fenton reaction and Fenton-like reaction under weakly acidic conditions performing good removal efficiency. This may be

due to the solidification of iron species under neutral conditions. After the supernatant was treated by Fenton-like or Fenton reaction, the solution was converted to alkaline to remove the nickel concentration and Fe concentration. From Fig. 2e, with the pH values increasing from 8.5 to 10.0, the nickel concentration decreases gradually. Further increase of pH value, the total nickel concentrations keep balance. This may be due to the nickel ions competing with Fe ions in water to form hydroxide precipitates.

3.4. Removal of TN during AOPs

As seen in Fig. 3a, both Fenton-like and Fenton processes have a significant decrease in TN concentration.
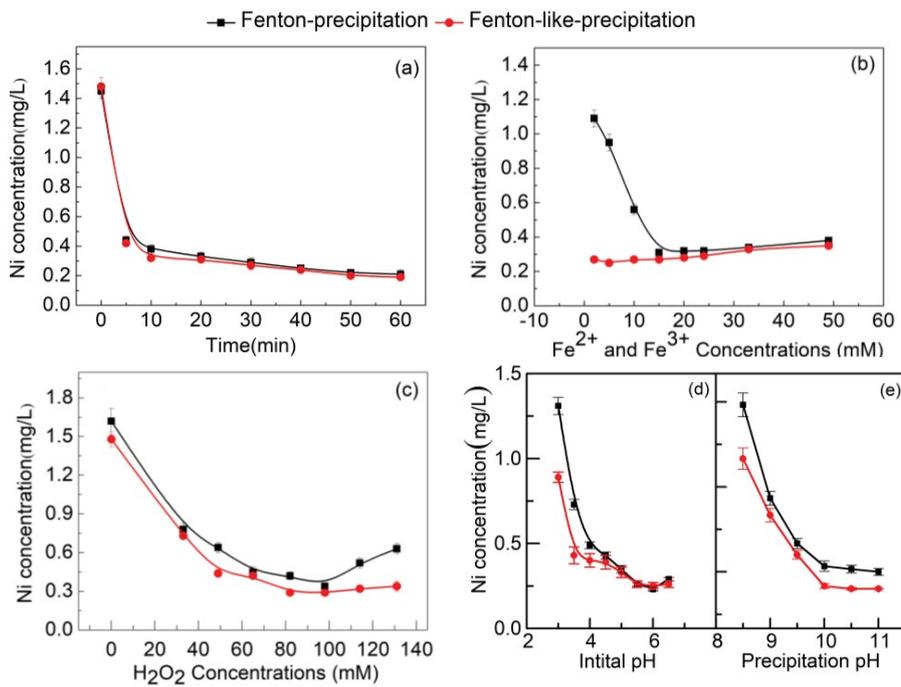

Fig. 2. (a) Effect of time on the nickel removal in Fenton-precipitation and Fenton-like-precipitation reactions. (b) Effect of Fe^{2+} or Fe^{3+} concentrations on the nickel removal in Fenton-precipitation or Fenton-like-precipitation reactions. (c) Effect of H_2O_2 concentrations on the nickel removal in Fenton-precipitation and Fenton-like-precipitation reactions. (d) Effect of initial pH and (e) precipitation pH on the nickel removal in Fenton-precipitation or Fenton-like-precipitation reactions.
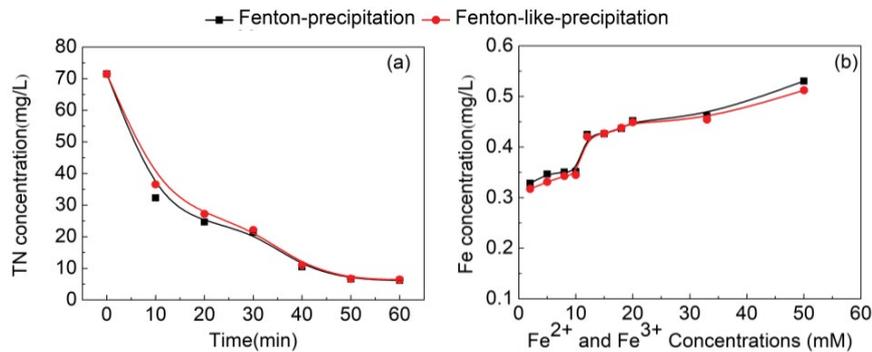

Fig. 3. (a) TN changes of complexing nickel wastewater. (b) Fe concentration changes of complexing nickel wastewater in Fenton-precipitation or Fenton-like–precipitation reactions.

The incomplete removal of TN content may be due to the incomplete removal of organic nitrogen or complex of the intermediate products [28].

In our research, 15 mM Fe^{2+} or 5 mM Fe^{3+} was added into the solution far higher than the European Union directives 2 mg/L requirements. Fig. 3b indicated that the residual concentrations were all below the detection limit 0.6 mg/L through form hydroxide precipitates [29].

4. Conclusions

In this study, the combination of pre-precipitation and Fenton-like-precipitation exhibits good performance in the treatment of high nickel complex wastewater. Experiments show that the pH of pre-precipitation, initial concentrations of Fe ions, oxidation time, concentrations of H_2O_2 and initial precipitation pH value have great influences on the removal efficiency. The optimum conditions are 98 mM of H_2O_2, 5 mM of Fe^{3+} or 15 mM of Fe^{2+}, initial pH of 6.0 and precipitation pH of 10.0. In these conditions, the residual nickel can be decreased to 0.25 or 0.31 mg/L. Hopefully, the pre-precipitation combined with Fenton-like-precipitation or Fenton-precipitation reaction will promote the development of the electroplating wastewater treatment technology.

Acknowledgment

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