

Removal of copper and cadmium from simulated wastewater using coupled internal electrolysis with flocculation: a comparison of effects and investigation of mechanisms

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ABSTRACT

A single factor experiment was conducted to analyze the impacts of initial pH (1.0–8.0), reaction time (10–120 min), aeration quantity (0–12 L/h), and flocculation pH (6.0–12.0) on the removal of Cu^{2+} and Cd^{2+} from simulated wastewater via coupled iron-carbon internal electrolysis with flocculation. The results showed that in the internal electrolysis reaction stage, the removal rate of Cu^{2+} remained steady at first and then slowly decreased with increasing initial pH, whereas the removal rate of Cd^{2+} continued to slowly increase. As the reaction time increased, the removal rate of Cu^{2+} increased steadily, and the removal rate of Cd^{2+} showed the same trend. With the growth of aeration intensity, the removal rate of Cu^{2+} increased rapidly and then decreased slowly, whereas the removal rate of Cd^{2+} continued to slowly increase. The removal rate of Cd^{2+} under different reaction conditions was lower than that of Cu^{2+} . In the flocculation reaction stage, as the flocculation pH increased, the removal rate of Cu^{2+} gradually increased at first and then stabilized, while the removal rate of Cd^{2+} rapidly increased at first and then stabilized. The Cd^{2+} removal rate could be increased to more than 90% by adjusting the pH to a suitable value. The internal electrolysis reaction followed the first-order kinetic model. Solution components after the reaction were determined by X-ray diffraction. It could be inferred that the underlying mechanism of coupled iron-carbon internal electrolysis with flocculation for the removal of Cu^{2+} was oxidation and reduction, while the mechanisms for the removal of Cd^{2+} were chemical precipitation and flocculation-adsorption.

Keywords: Iron-carbon internal electrolysis; Heavy metal wastewater; Flocculation; Reaction mechanism

1. Introduction

Metallurgy, electroplating, dyes, and other industries discharge a large amount of wastewater containing heavy metals every year. Heavy metals have no self-purification or biodegradability in water, allowing their concentration to increase and cause water pollution [1,2]. Copper and cadmium are two typical heavy metals, which directly harm human health through the food chain. Cadmium exposure

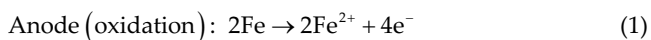
may cause kidney damage and copper exposure can cause severe damage to cell membranes [3]. Therefore, research on heavy metal wastewater treatment technology with high efficiency and cost-effectiveness is of great importance to environmental protection.

Currently, the main approaches explored for the treatment of heavy metal wastewater are chemical precipitation, ion exchange, adsorption, and membrane separation [4–7]. Chemical precipitation can easily cause secondary contamination if the sludge is not properly disposed [8].

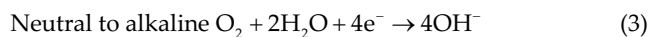
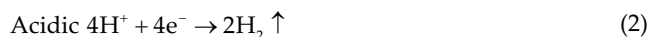
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The ion exchange method requires a heavy initial investment and high requirements for wastewater pre-treatment [9]. The adsorption process is not suitable for treating highly concentrated Cd^{2+} in wastewater because of its prohibitive cost of reprocessing [10]. Membrane separation is limited in large-scale applications due to its high investment and frequently blocked fenestra [11].

Internal electrolysis, also known as micro-electrolysis or the zero-valent iron method [12], is a wastewater treatment method developed in the past 40 years. Based on the principle of the primary battery, when a mixture of iron and activated carbon particles is in contact with wastewater, numerous microscopic galvanic cells are formed between the particles of iron and carbon [13]. The half-cell reactions can be represented as:



Cathode (reduction):



When the generated Fe^{2+} or Fe^{3+} is under neutral or alkaline conditions, it will continue to react to form $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ flocs, which have good flocculation ability and will precipitate a part of the pollutants [14,15]. It has currently been used in the pre-treatment of wastewater containing heavy metals or bio-refractory organic wastewater generated from the papermaking industry, dyeing and printing industry, pharmaceutical industry, and petrochemical industry, which includes coking plants [16–22].

Although internal electrolysis performs well in treating wastewater containing heavy metals, it still cannot be used on a large scale because most of the internal electrolysis fillers will become hardened and passive, and massive sludge will be produced after long use. To address this problem, the author has developed a new type of micro-electrolysis filler that has been patented [23]. These internal electrolysis fillers have a better performance in micro-electrolysis because they have high specific surface areas and can effectively prevent fillers from being passive and hardened.

Prior studies indicate that the treatment efficiency of internal electrolysis is influenced mainly by initial pH, reaction time, and aeration [24–26]. A single factor experiment was carried out to analyze the impacts of initial pH, reaction time, aeration quantity, and flocculation pH on the removal of Cu^{2+} and Cd^{2+} using homemade micro-electrolysis fillers coupled with flocculation. The results provide valuable information for practical applications of internal electrolysis, where potential usage is high owing to its low cost and operational simplicity for treating heavy metal wastewaters.

2. Materials and methods

2.1. Experimental water

Considering that the emphasis of the paper is the effects and mechanism of cadmium and copper removal, simulated

cadmium-containing wastewater, and simulated copper-containing wastewater are separately taken as the research object to eliminate the influence of other impurities and ions in actual wastewater. The threshold limit values of Cu^{2+} and Cd^{2+} prescribed in the Integrated Wastewater Discharge Standard (GB 8978–1996, China) are 0.5 and 0.1 mg/L, respectively [27]. The initial mass concentration of Cd^{2+} in the experimental water is 2.0 mg/L, which is 20 times the limit value. The initial mass concentration of Cu^{2+} in the experimental water is 5.0 mg/L, which is 10 times the limit value. The test water was prepared by diluting the stock solution (Cu^{2+} or Cd^{2+} initial concentration is 100 mg/L), which was prepared by dissolving copper sulfate pentahydrate or cadmium nitrate (from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) in ultrapure water. The main components of the experimental water are shown in Table 1. All chemicals employed in the experiment were analytically pure, and water was ultrapure water.

2.2. Experimental apparatus and procedures

The experimental apparatus is shown in Fig. 1. The catalytic internal electrolysis reactor was made of organic glass with an inner diameter of 0.15 m, height 0.5 m, and working volume 7.1 L. The bottom of the reactor was equipped with micro-aeration devices, and the reactor was filled with novel iron-carbon fillers as high as 0.35 m. Before the fillers were put into use, they were first activated by diluted (5%) hydrochloric acid for 0.5 h and finally cleaned by deionized water.

The experimental procedures are shown in Fig. 2. An appropriate amount of the effluent was fed into the reactor, and then the pH (adjusted by 5% hydrochloric acid) and aeration quantity were adjusted to set values. After a period of time, a small amount of supernatant was filtered through a 0.45 μm millipore filter, and then the heavy metal concentration was measured. This stage was called the internal electrolysis reaction process. Then, $\text{Ca}(\text{OH})_2$ and Polyacrylamide were added for flocculation and precipitation. Parameters of stirring were controlled with the following conditions: quick mixing for one min by stirring at a speed of 200 rad/min and then slow mixing for 15 mins by stirring at a speed of 60 rad/min. After precipitating for 30 mins, a small amount of supernatant was filtered through a 0.45 μm millipore filter, and then the heavy metal concentration was measured. This stage was called the flocculation precipitation process.

2.3. Analytical methods

The analytical methods used are shown in Table 2.

Table 1
Main components of the simulated wastewater

Main components	Mass concentration (mg/L)
$\text{Cd}(\text{NO}_3)_2$	4.21
CuSO_4	12.56
$\text{C}_6\text{H}_{12}\text{O}_6$	80
$(\text{NH}_4)_2\text{SO}_4$	5.0
KH_2PO_4	0.7

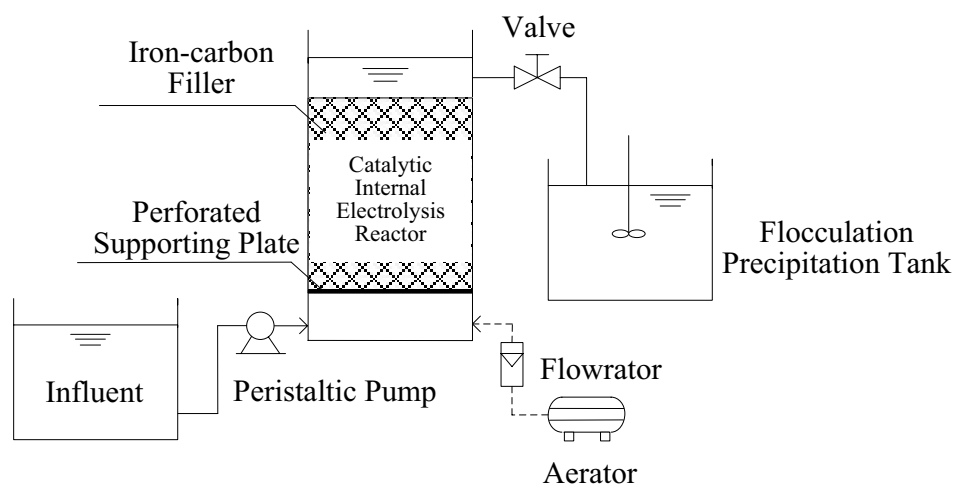


Fig. 1. Devices used for heavy metal-containing wastewater treatment by coupled catalytic internal electrolysis with flocculation.

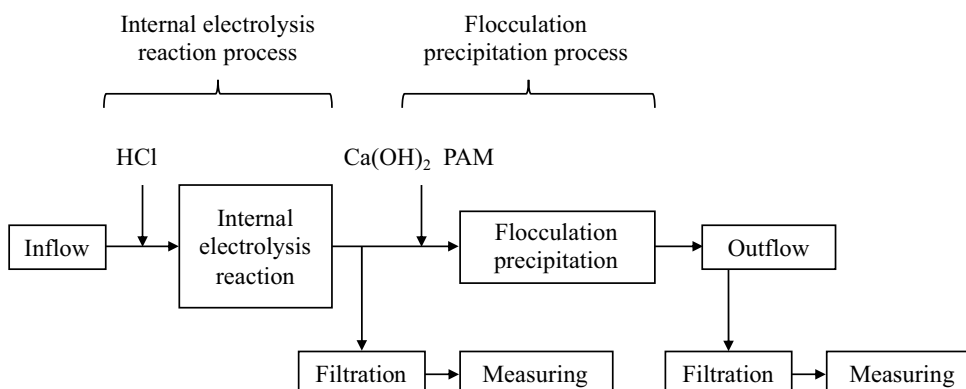


Fig. 2. Experimental procedures for heavy metal-containing wastewater treatment by coupled catalytic internal electrolysis with flocculation.

Table 2
Analytical methods

Parameters	Analytical methods
Cd ²⁺	Atomic absorption spectroscopy method (AAS; test range: 0.05–1 mg/L)
Cu ²⁺	AA-600 graphite atomic absorption spectrophotometer (Perkin-Elmer, US) [28]
XRD	D/max-rB rotating anode X-ray diffractometer (Rigaku, Japan)
pH	JENCO-6010M pH meter (Jenco, US)
DO	JPB-607A dissolved oxygen meter (REX, Shanghai)
Temperature	JPB-607A dissolved oxygen meter (REX, Shanghai)

3. Results and discussion

3.1. Effect of the initial pH value

The pH value determines the electrode potential difference of iron-carbon primary cell reactions and has a major influence on how much iron can be dissolved. Thus, pH affects the reaction rate to a certain degree [29]. The impacts of pH on heavy metal removal were studied when the reaction time was set at 60 min, the aeration quantity at 6 L/h

and the filler dosage at 0.2 kg/L according to the literature reviewed [30–32]. The results are presented in Fig. 3.

Fig. 3 shows that the removal rate of Cu²⁺ gradually decreases with increasing pH, while the removal rate of Cd²⁺ is the opposite and gradually increases with increasing pH. When the influent pH is between 1.0 and 7.0, the removal rate of Cu²⁺ is as high as 90% or more, and the difference between the pH of 1.2 and 7.1 is only 5%, indicating that the removal of Cu²⁺ by internal electrolysis is relatively stable

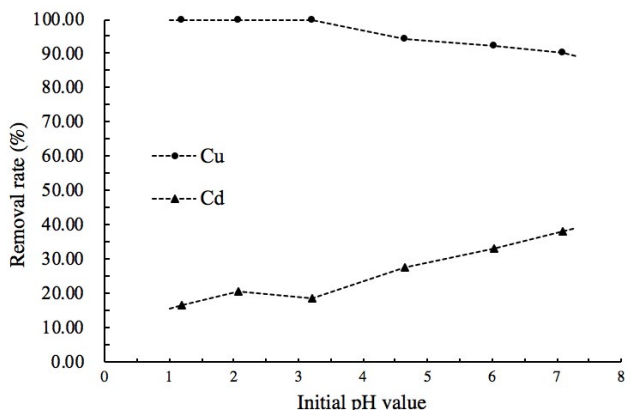


Fig. 3. Effect of initial pH value on Cu²⁺ and Cd²⁺ removal rate.

and basically does not change with the influent pH. When the pH is between 1.0 and 3.0, the Cd²⁺ removal rate is below 30%, and when the pH is over 5.0, the removal rate is above 30%. According to the activity series of metals, copper can be replaced by iron. The electrode potential difference between the two elements is very small ($\phi^{\ominus}\text{Fe}^{2+}/\text{Fe} = -0.44\text{ V}$, $\phi^{\ominus}\text{Cd}^{2+}/\text{Cd} = -0.4030\text{ V}$), indicating that the removal mechanism of cadmium is different from that of copper and that chemical precipitation is dominant.

3.2. Effect of reaction time

To what degree the reaction proceeds and whether it is complete, at a certain reaction rate, is subject to the length of reaction time [33]. Insufficient reaction time would lead to an incomplete reaction, while too long of reaction time would cause an excess of filler consumption and reactor volume. In the experiment, the initial pH was set at 5.0, the aeration quantity at 6 L/h and the filler dose at 0.2 kg/L to study the effects of reaction time on heavy metal removal. The results are shown in Fig. 4.

It can be seen from Fig. 4 that the removal rates of the two heavy metal ions increase with the extension of the reaction time and finally tend to be stable. The removal efficiency of Cu²⁺ is as high as 96% when the reaction time is 60 min, indicating that the internal electrolysis reaction is a relatively fast electrochemical reaction mechanism and that the copper removal effect is excellent. However, as time continues to increase, the removal rate increases slightly. Therefore, the optimal reaction time of copper ions is 60 min. The removal rate of cadmium is very low, and the highest removal rate is approximately 20%, indicating that the removal efficiency of cadmium by internal electrolysis is relatively low. The removal of cadmium is mainly due to the increase of the pH value of the solution after the reaction. A portion of the cadmium hydroxide is precipitated and removed, mainly by chemical precipitation.

3.3. Effect of aeration quantity

Aeration during the catalytic internal electrolysis process is to stir the fillers and wastewater and make them come into full contact with dissolved oxygen. Bubbles generated

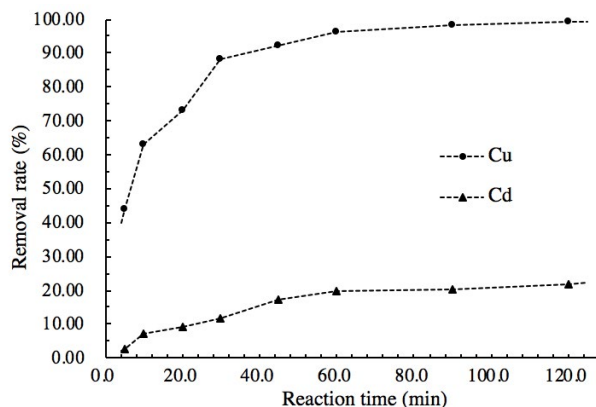


Fig. 4. Effect of reaction time on Cu²⁺ and Cd²⁺ removal rate.

from aeration can improve agitation and friction between fillers, which helps to remove the passive film on the filler surface and accelerate the mass transfer of the reaction system. In the experiment, the initial pH was set at 5.0, the reaction time at 60 min and the filler dosage at 0.2 kg/L to study the effects of aeration quantity on the heavy metal removal rate. The results are shown in Fig. 5.

Fig. 5 shows that with increasing aeration amount, the removal rate of Cu²⁺ first increases and then decreases and reaches a maximum of 99.6% when the aeration amount is 6 L/h. The removal rate of Cd²⁺ increases with increasing aeration. This is because when the system is aerated, some cadmium hydroxide precipitates will form. The larger the aeration, the higher the dissolved oxygen concentration, so the removal rate increases. Copper is largely removed by internal electrolysis, and the remaining heavy metal ions have difficulty precipitating with the OH⁻ in the solution according to the solubility equilibrium principle. In addition, when the system is not aerated, the removal rate of heavy metals is very low, with values of 42% for Cu²⁺ and 5% for Cd²⁺, which indicates that the aeration can fully mix the wastewater, increase the dissolved oxygen content, and thus increase the power of electrochemical corrosion of the primary battery. At the same time, a series of intermediate products, such as O², H₂O₂, and hydroxyl radicals ($\cdot\text{OH}$), have strong oxidizing properties, which are favorable for the oxidation reaction. The bubbles generated by the aeration can increase the agitation and friction of the iron filings, help to remove the passivation film deposited on the surface of the iron filings, increase the flocculation effect, accelerate the mass transfer rate of the reaction system, and thus accelerate the reaction rate. Moreover, aeration can also alleviate the problem of iron filings in practical applications and play a role in strengthening the internal electrolysis of iron.

3.4. Effect of flocculation pH value

Fe(OH)₂ and Fe(OH)₃ were generated after adding Ca(OH)₂ solution to the effluent. Intense hydrolysis and polymerization reactions occurred, and hydroxyl complexes were then produced. These hydroxyl complexes had a long linear structure, porous gel structure, and strong adsorption ability. They could adsorb and precipitate Cd(OH)₂ and thus

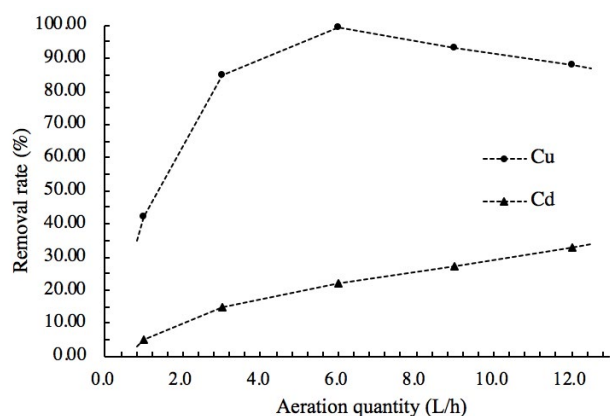


Fig. 5. Effect of aeration quantity on Cu²⁺ and Cd²⁺ removal rate.

enhance the removal ability of the system. In the experiment, the effluent pH after the reaction was adjusted to 7.0, 8.0, 9.0, 10.0, and 11.0. The effluent was first stirred quickly and then slowly for 1 and 15 min, respectively. After precipitation for 30 min, the supernatant of the effluent was collected and then filtered through a 0.45 μm millipore filter, and the heavy metal concentration was tested. The results are shown in Fig. 6.

Fig. 6 shows that the removal rates of Cu²⁺ and Cd²⁺ increase continuously as the flocculation pH increases. For Cu²⁺, when the pH is 7, the removal rate reaches 80.70%, and when the pH is 10, the removal rate is 99.60%. For Cd²⁺, the removal rate first increases rapidly and then drop slowly as the pH increases. When the pH is 10.0, the Cd²⁺ removal rate peaks at 98.1%. At this point, the generated flocs have excellent flocculation properties. When the pH is above 10.0, the removal rate decreases because Cd(OH)₂ is an amphoteric substance that may dissolve when the pH is too high [34].

4. Reaction dynamics and reaction mechanisms

4.1. First-order kinetic equation

The first-order kinetic model is currently used as the most suitable equation for describing the removal of contaminants in internal electrolysis because of its simple parameters and simple calculation process [35,36]. For the reaction of removing pollutants by iron (including internal electrolysis, zero-valent iron, and nano-iron, etc.), many scholars have fit the experimental data with the first-order kinetic equation and achieved good results.

The first-order kinetic equation expression is:

$$\frac{dc}{dt} = -k_{\text{obs}}c \quad (4)$$

Concentration integration on both sides of the equation:

$$c_t = c_0 e^{-k_{\text{obs}}t} \quad (5)$$

Logarithm of concentration on both sides:

$$\ln c_t = -k_{\text{obs}}t + \ln c_0 \quad (6)$$

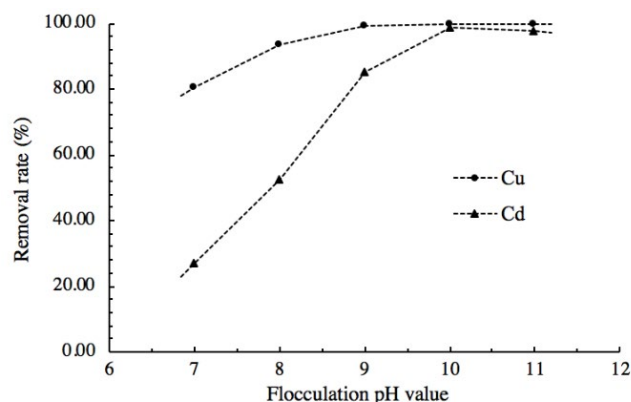


Fig. 6. Effect of flocculation pH value on Cu²⁺ and Cd²⁺ removal rate.

where c_t and c_0 represent the substrate concentration at time t and initial time, respectively, and k_{obs} represents the reaction rate constant. The electrochemical reaction is rapid, so experimental data collected during the first 30 min of the catalytic internal electrolysis reaction can fully demonstrate the underlying mechanism. In the experiment, data were collected during the first 30 min of the reaction under optimum reaction conditions with the influent Cu²⁺ concentration set at 5.0 mg/L and the influent Cd²⁺ concentration set at 2.0 mg/L. The fitting figures obtained from the experimental data are shown below in Fig. 7.

It can be seen from the first-order kinetic model that the removal of copper and cadmium by iron-carbon internal electrolysis basically conforms to the first-order kinetic equation model, which is supported by the research of Li et al. [37]. The apparent reaction rates of copper and cadmium were 0.0985 and 0.0051, respectively, indicating that the reaction rate of internal electrolysis for heavy metal ion removal is copper > cadmium. The correlation of copper ions is 0.9845, better than that of cadmium, which is 0.8848.

The apparent reaction rate of cadmium in the first-order kinetic model is much smaller than that of copper, which is consistent with the experimental results that the removal rate of cadmium in internal electrolysis is less than that of copper, indicating that the removal of copper is dominated by electrolysis and that the removal of cadmium is dominated by chemical precipitation.

4.2. Scanning electron microscopy analysis

To investigate the mechanism of Cu²⁺ and Cd²⁺ removal by internal electrolysis, the surface morphology and structure of the internal electrolysis filler were observed by scanning electron microscopy (SEM). The results are shown in Fig. 8.

It can be seen from the SEM observation that the surface of the filler before the reaction is rough and uneven with many pores. Many irregular particles, which are disorderly stacked, have a large specific surface area and can come into contact with heavy metal ions in the wastewater to undergo an electrochemical redox reaction. Studies have shown that iron-carbon surface reactions mainly occur in surface defects such as protrusions, cracks, and pits, which

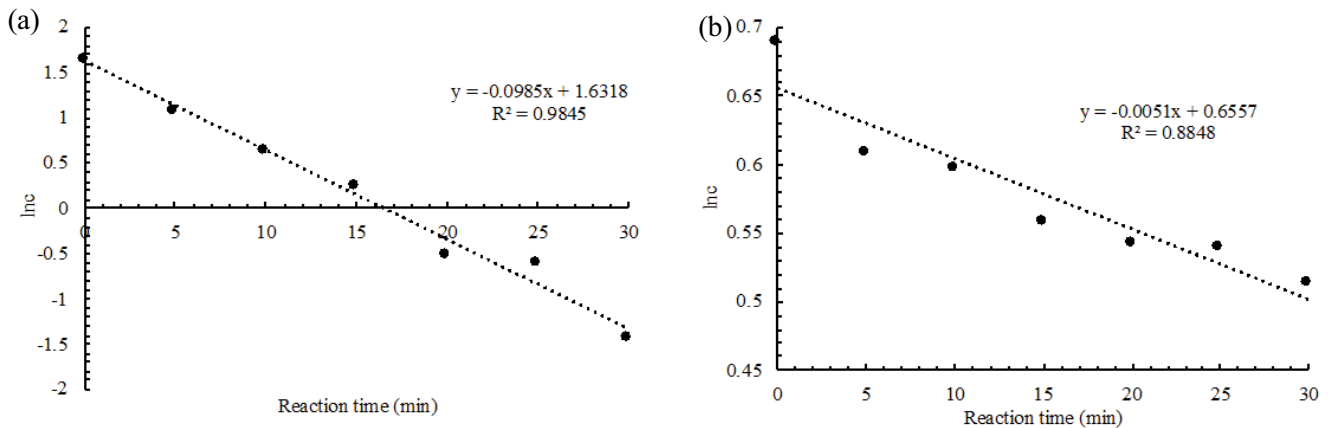


Fig. 7. First-order kinetic model of (a) Cu²⁺ and (b) Cd²⁺ removal via iron-carbon internal electrolysis.

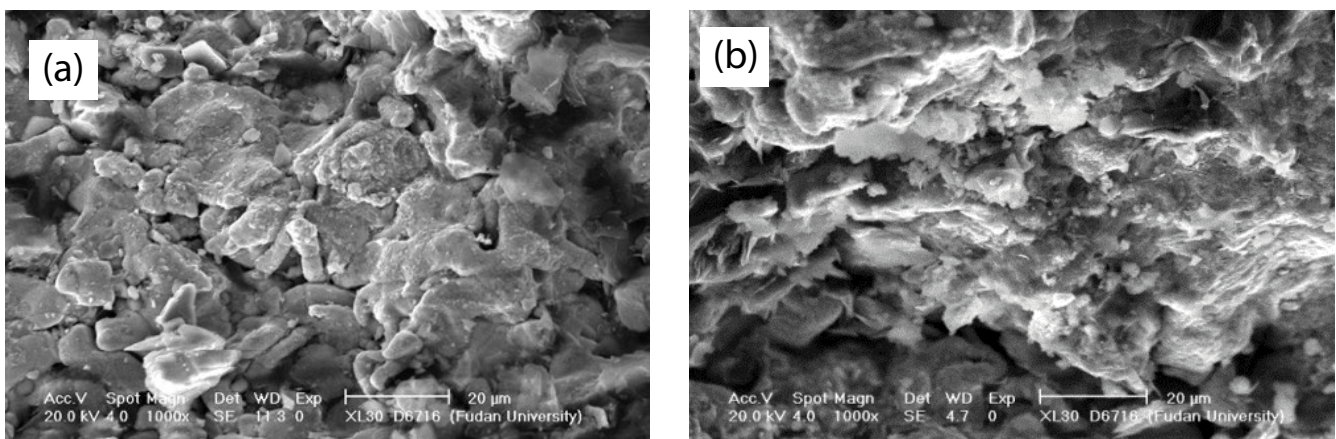


Fig. 8. SEM images of the iron-carbon filler (a) before and (b) after the reaction.

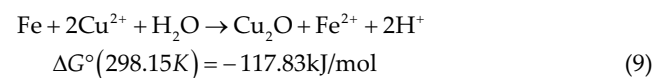
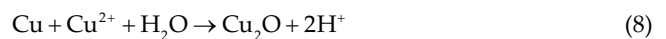
are reactive sites [38]. After the reaction, the surface of the filler is covered by large amounts of precipitate that adhere to the pores. After the internal electrolysis reaction, a small amount of iron oxides and products are formed on the surface of the filler, which is covered by an oxide film. The contact between the wastewater and the internal electrolytic filler is correspondingly reduced, and the surface area is reduced. As the reaction progresses, large amounts of precipitate that are formed during the internal electrolysis reaction hinder the mass transfer process between the wastewater and the filler, and the reaction rate decreases. The above observation also explains the phenomenon that the Cd²⁺ removal rate decreases in the late stage of the reaction.

4.3. XRD analysis

To further analyze the products and mechanism of Cu²⁺ or Cd²⁺ removal via iron-carbon internal electrolysis, the solution after reaction was vacuum dried, and the products were analyzed by X-ray diffraction (XRD). The results are presented in Fig. 9.

Fig. 9a shows that after the internal electrolysis reaction, the products are elemental Cu, Cu₂O, and FeCu₄, indicating

that the removal of Cu²⁺ is mainly achieved by oxidation and reduction. The reaction Eqs. (7), (8), and (9) are as follows:



In addition to the detection of elemental copper and cuprous oxide, FeCu₄ was also found in the experiment. This indicates that the formed elemental copper is solid-solved on the iron surface to form FeCu₄. The presence of FeCu₄ is beneficial to the galvanic cell reaction. Fan et al. [39] found that the effect of electrolytic filler in a bimetallic system is better than that of an iron-carbon internal electrolysis system. This is because in addition to iron in the bimetallic system, other metals, such as copper, act as catalysts and remain stable during the reaction. SEM and XRD analysis showed that the shape of the copper surface was basically unchanged after the reaction, and the chemical stability was good.

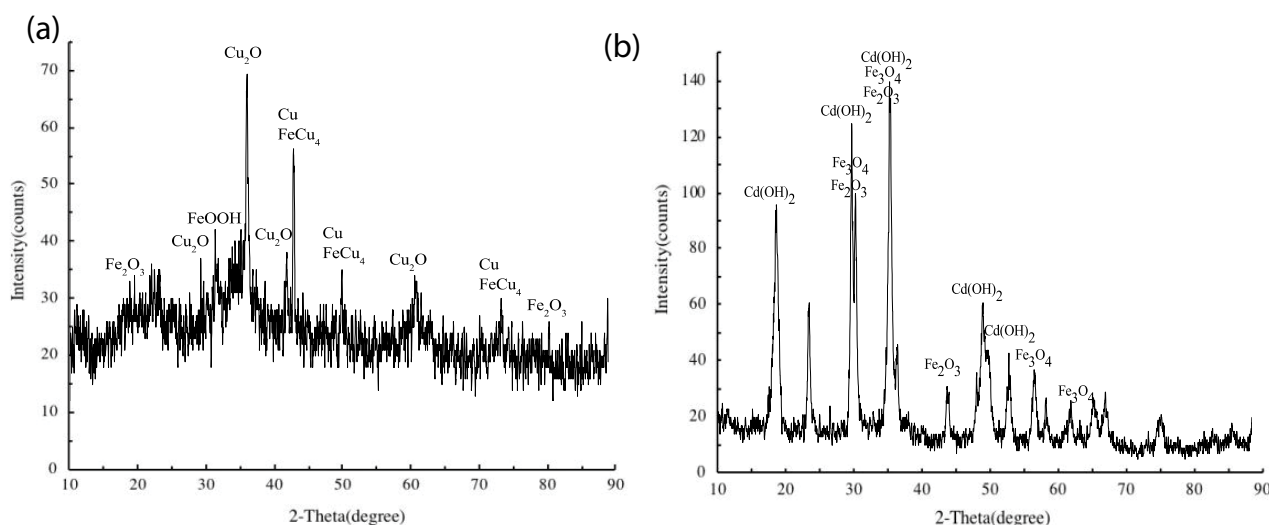


Fig. 9. (a and b) XRD pattern of the simulated wastewater effluent containing Cu^{2+} and Cd^{2+} .

FeOOH was found in the iron product, which is similar to that reported in the related literature [40]. XRD also detected the presence of Fe_2O_3 in the system.

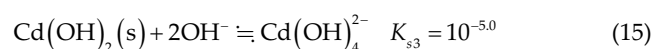
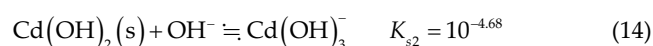
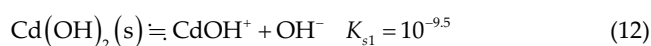
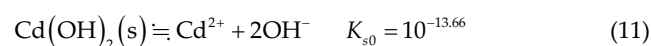
From Fig. 9b, it can be seen that the product containing cadmium generated after the catalytic internal electrolysis reaction was $\text{Cd}(\text{OH})_2$, showing that chemical precipitation, adsorption, and flocculation are the main mechanisms of cadmium removal. Cd^{2+} is transformed into hydroxide, which precipitates on the filler surface and in the sludge. The probable Eq. (10) for the reaction is:



However, no diffraction peaks for cadmium oxides or simple cadmium substances are observed during analysis. This is because the reduction effect of Cd^{2+} is relatively weak compared to other metal ions whose standard electrode potential is far greater than that of iron (such as Cu^{2+} , Ag^+ , and Hg^{2+}). The standard electrode potential of Cd ($\text{Cd}^{2+} + 2\text{e}^- \rightarrow \text{Cd}$, $\text{EA}/\text{V} = -0.403$) is close to that of Fe ($\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$, $\text{EA}/\text{V} = -0.44$), so Cd^{2+} is removed via being flocculated, adsorbed and precipitated under the action of the $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$ flocs. Thus, Cd^{2+} is mainly removed through formation of a complex with iron or formation of insoluble compounds with OH^- in solution.

4.4. Speciation analysis of the cadmium ion in the flocculation and precipitation stage

Cd^{2+} and OH^- can form polyhydroxyl compounds such as CdOH^+ , $\text{Cd}(\text{OH})_2$, $\text{Cd}(\text{OH})_3^-$, and $\text{Cd}(\text{OH})_4^{2-}$. Here are the following precipitation equilibrium relationships in the solution:



From Eqs. (11) and (16), we obtain:

$$\log[\text{Cd}^{2+}] = 14.34 - 2\text{pH} \quad (17)$$

From Eqs. (12) and (16), we obtain:

$$\log[\text{CdOH}^+] = 4.5 - \text{pH} \quad (18)$$

From Eq. (13), we obtain:

$$\log[\text{Cd}(\text{OH})_2(\text{L})] = -5.37 \quad (19)$$

From Eqs. (14) and (16), we obtain:

$$\log[\text{Cd}(\text{OH})_3^-] = -18.68 + \text{pH} \quad (20)$$

From Eqs. (15) and (16), we obtain:

$$\log[\text{Cd}(\text{OH})_4^{2-}] = -33 + 2\text{pH} \quad (21)$$

Fig. 10 of the dissolving equilibrium region of cadmium ions is obtained according to Eqs. (17)–(21). The pH value is taken as the abscissa and the logarithmic values of the cadmium ion complex concentration are taken as the ordinate.

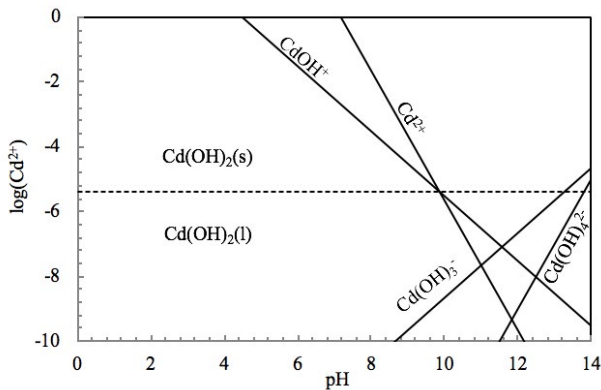


Fig. 10. The dissolving equilibrium region of cadmium ions.

As shown in Fig. 10, when the pH is between 11 and 12, the Cd^{2+} concentration is lower than 10^{-8} mol/L. To ensure that the Cd^{2+} concentration is lower than 1 ppm, that is, 10^{-6} mol/L, the solution pH should be kept in the range of 10.5–12.5. It can be seen from Fig. 10 that Cd^{2+} and CdOH^+ are generated when the pH is lower than 10.5; complex anions such as Cd(OH)_3^- and Cd(OH)_4^{2-} are generated when the pH is higher than 12.5. Both circumstances could lead to a decrease in the Cd^{2+} removal rate.

5. Conclusions

The characteristics of removing copper and cadmium from simulated wastewater using coupled iron-carbon internal electrolysis with flocculation were studied. The optimal reaction conditions were found by a single factor experiment. Moreover, the iron-carbon internal electrolysis reaction was found to follow the first-order kinetic model, and the underlying mechanism was studied through SEM and XRD analysis. The conclusions can be drawn as follows:

- Iron-carbon internal electrolysis has an excellent removal effect on Cu^{2+} . Under the optimum conditions of initial pH = 3.0, reaction time = 60 min, and aeration quantity = 6 L/h, the removal rate is as high as 99.9%.
- Iron-carbon internal electrolysis does not perform well in removing Cd^{2+} , while the removal rate can rise to 98% when coupled with flocculation. The optimum range of flocculation pH is 10.5–12.5.
- The iron-carbon internal electrolysis reaction was found to follow the first-order kinetic model. The removal of copper and cadmium can be expressed as follows: $y = -0.0985x + 1.6318R^2 = 0.9845$, $y = -0.0051x + 0.6557R^2 = 0.8848$.
- The underlying mechanism of coupled iron-carbon internal electrolysis with flocculation for the removal of Cu^{2+} is oxidation and reduction, while the mechanisms for the removal of Cd^{2+} is chemical precipitation and flocculation-adsorption.

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