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Decomplexation of Electroplating Wastewater in a Higee Electrochemical Reactor with Rotating Mesh-Disc Electrodes

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The metal complexes wastewater from electroplating industries is not as easy to be removed as metal ions. In this work, the destruction of Cu, Ni and Cr complexes from electroplating by electro-oxidation was investigated. A novel higee electrochemical reactor with rotating mesh-disc electrodes was developed to enhance the destruction ratio of metal complexes. The rotating electrodes consisted of four titanium mesh-discs as cathodes and three titanium-based lead dioxide mesh-discs as anodes were controlled by the variable speed motor. Some key operation parameters, such as rotation speed of electrodes, current density and initial pH of wastewater, were investigated during electrolysis. The experimental results showed that the rotation of electrodes enhanced the mass transfer of electrochemical process; current density influenced the destruction rate of metal complexes; acid or alkaline conditions were benefit for the destruction of metal complexes. Under the optimal operating conditions with initial pH of 11.0, current density of 10 mA/cm^2 and average high gravity factor of 1.07, the Cu, Cr and Ni complexes and colority of wastewater decreased to 0.87 mg/L, 0.47 mg/L, 0.64 mg/L and 5 times after 120 min electrolysis, respectively.

Keywords: electro-oxidation; electroplating wastewater; higee reactor; metal complexes

1. INTRODUCTION

Wastewater containing heavy metals from electroplating industries, metallurgical industries and mining operations, may cause serious health disorders and cancers even death due to heavy metals accumulating in living organisms [1]. Plenty of approaches have been developed to treat the heavy metals such as chemical precipitation [2], electrocoagulation [3], chemical oxidation [4], photocatalysis [5], chemical reduction [6], ion exchange [7], absorption [8], membrane separation [9, 10] and Fe-C micro-electrolysis [11]. Compared to metal ions easily removed from wastewater, complexed metals couldn't be precipitated directly. Complexed metals are the form of metals which are bound to strong complex agents, such as NH_3 or EDTA (ethylene diamine tetraacetic acid) and CN^-, keeping them in solution. It is necessary to destruct the complex bonding and transform into metal ions [12, 13].

Electro-oxidation process is an environmental friendly and greenchemistry technology to destruct metal complexes and mineralize organics [14-16]. Via application of this technology the metal complexes could be completely destroyed or converted into a form that does not interfere with conventional precipitation. Meanwhile, no extra chemicals reagents are used in anodic oxidation, and there is no secondary pollutants. However, there are still some challenges to improve the treatment efficiency in electro-oxidation technology, such as the development of high activity electrodes and intensification of mass transfer between electrode and solution during the treatment [17-19].

Higee, which is the most promising technology to intensify mass transfer, has been applied in chemical industry, energy and environmental pollution treatment [20-23]. In higee technique, gravity force is replaced by a centrifugal force to enhance mass transfer rate and mixing efficiency [24]. High mass transfer, uniform supersaturation and homogeneous nucleation could be achieved by higee [25]. W.J Albery designed rotating disc electrode for the first time. On the basis of calculation of fluid dynamics, the diffusion layer on the electrode is uniform. Higee rotating disc electrode reactor could change the diffusion rate of electrode react by the speed of rotating electrode. By the rotation of rotating electrodes generate a high gravity fields, the thin aqueous film on the electrode is continually refreshed; and the mass transfer is also enhanced [26]. Meanwhile, rotating disc electrodes could overcome the weakness of asymmetry of current diffusion layer in thin solution film on the electrodes surface. Jin Gao *et al* [27] had reported that using a higee electrochemical reactor to treat phenol wastewater, the COD removal efficiency reached to about 48% after 40 min electrolysis, which was about 2 times the value achieved in the normal gravity field. Dengjie Zhong *et al* [28] had studied de-colorization of reactive brilliant orange X-GN by a rotating electrochemical disc process. Half of disc electrodes, which consisted of granular activated carbon was filled between the anodes (graphite) and the cathodes (copper), was is exposed to the air to accelerate oxygen from air to liquid and speed up the organics on the electrode surface. 99.5% of color was removed after 60 min electrolysis.

In this study, a novel higee electro-oxidation reactor with rotating mesh-disc electrodes was developed to enhance mass transfer and destruct the metal complexes of electroplating wastewater. The rotation speed of electrodes, current density and initial pH of wastewater had been investigated. The operating parameters were optimized to shorten the treatment time, improve current efficiency, increase decomplexation load and reduce energy consumption.

2. EXPERIMENTAL

2.1 Metal plating wastewater

The electroplating wastewater samples were collected from one electroplating factory located in the region of Hangzhou, Zhejiang province, China. The physical and chemical characteristics of wastewater from electroplating industries were shown in Table 1.

Table 1. The physical and chemical characterization of wastewater from electroplating industries

Characteristics	Initial value	Unites
pH	12.56±0.2	-
Cu complex	195.32±3.0	mg/L
Cr complex	41.53±0.9	mg/L
Ni complex	22.49±0.4	mg/L
Color	blue	-
Chemical oxygen demand (COD$_{Cr}$)	1050±30	mg/L
Colority	128	times
Conductivity	11.68±0.3	mS/cm

2.2 Experimental apparatus

In this investigation, the novel higee electrochemical reactor consisted of rotating mesh-disc electrodes, electrolysis cell, rotating motor device and a constant current DC power supply. Titanium-based lead dioxide electrode (Ti/PbO$_2$) applied in previous research was used as the working electrode (anode), while titanium mesh-disc was used as the counter electrode (cathode), as shown in Fig. 1. Three anodes and four cathodes with an external radius of 35 mm and an internal radius of 7.5 mm were selected to compose the rotating disc electrodes, staggered with an interelectrode distance of 20 mm.

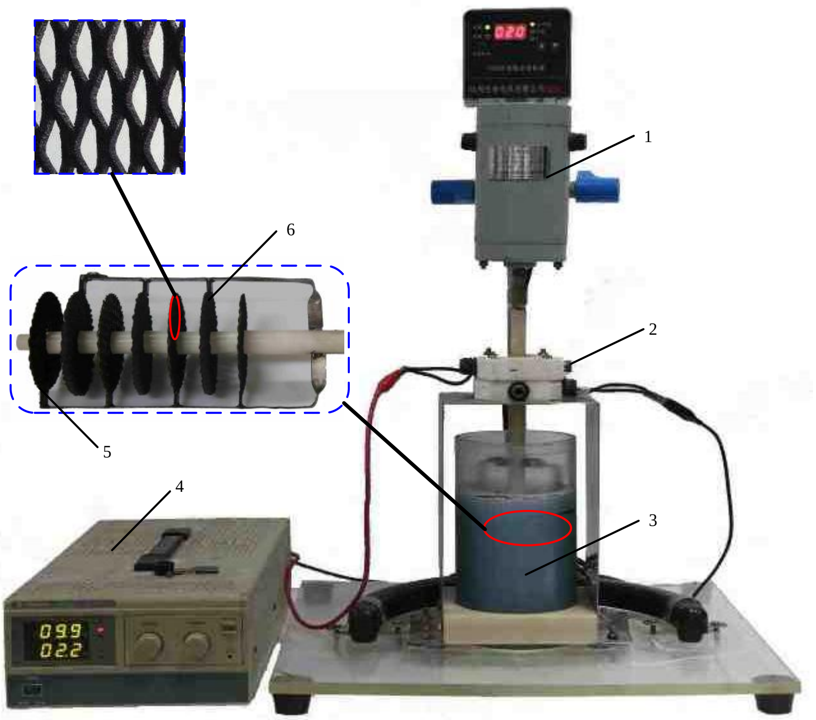

Figure 1. The schematic diagram of the electrode and apparatus 1. A variable velocity motor, 2. Connection of power supply, 3. Electrolysis cell, 4. DC power supply, 5. Cathode (mesh-structure titanium), 6. Anode (Ti/PbO$_2$)

The total effective surface area of electrodes was about 220 cm^2. The rotating mesh-disc electrodes were operated at a rotation speed of 0-400 rpm, which was controlled by the variable speed motor. The electrolysis cell made of plexiglass was designed as no cover cylinder-shaped with an inside diameter of 120 mm, 300 mm length and total volume of 3391 mL. The current applied in electrolysis was provided by a constant voltage/current-controlled DC power source (MPS 1001, TRADEX, China), in the range of 0-20 V and electrical current in the range of 0-50 A.

2.3 Experimental process

The destruction of metal complexes was carried out at room temperature (298-301 K) in novel higee electrochemical oxidation reactor filled with 1350 mL industrial wastewater (collected from an electroplating unit). The constant DC current was provided after the electrodes rotating 2 min at a setting rotation speed. Samples of 5 mL were periodically taken from the reactor then filtered to eliminate particles during electrolysis. The concentration of metal complexes was determined by an ELAN DRC-e mode inductively coupled plasma mass spectrometer (ICP-MS, PerkinElmer, US).

2.4 Analytical methods

The metal complexes could not be directly determined by the ELAN DRC-e mode ICP-MS. After electrochemical oxidation, the metal complexes were transformed to metal ions, which could be easily removed by precipitation. As we all know, if the concentration of metal ions was less than 10^{-5} mol/L, the metal ions converse to precipitation entirely from 0.1 mol/L metal solutions. On the condition of pH=12.0, we could obtain that the concentration of Cu^{2+}, Cr^{3+} and Ni^{2+} are much less than 10^{-11} mol/L. On this condition, Cu, Cr and Ni ions would react with OH^- and convert into precipitation completely. The residual concentration of Cu, Cr and Ni ions in pretreatment samples (pH=12) could be ignored comparing to metal complexes.

$$Cu^{2+}+2OH^- \xrightleftharpoons{k_1} Cu(OH)_2(s) \quad k_1 = 2.2\times10^{-20} \tag{1}$$

$$Cr^{3+}+3OH^- \xrightleftharpoons{k_2} Cr(OH)_3(s) \quad k_2 = 6.3\times10^{-31} \tag{2}$$

$$Ni^{2+}+2OH^- \xrightleftharpoons{k_3} Ni(OH)_2(s) \quad k_3 = 5.0\times10^{-16} \tag{3}$$

Therefore, the destruction efficiency (η) of metal complexes after electrochemical oxidation could be calculated by the formula (4).

$$\eta_t = \frac{C_0 - C_t}{C_0}\times 100\% \tag{4}$$

Where C_t and C_0 are the metal complexes of t (min) and 0 min, respectively.

The chemical oxygen demand (COD) was determined by potassium dichromate (GB11914-89) employing mercuric sulphate to remove chloride interference. The pH values of solution measured with a 25PHS-3E pH meter. Colority of wastewater was determined by the dilution method according to the standard method, water quality-determination of colority (GB 11903-89). The conductivity was measured with a METTLER TOLEDO Seven Easy S30K conductivity meter. Chlorine species were determined by ion chromatography (column, Dio-nex ICS-2000, with an Ion Pac AS19-HC Column, US). All the data were measured at least three times.

3. RESULTS AND DISCUSSION

3.1 Basic reaction processes in the electrochemical oxidation reactor

Electrochemical oxidation of pollutants occurs directly at anodes and indirectly by the activity substances (such as Peroxide, Fenton's reagent, Cl_2, hypochlorite, peroxodisulfate and O_3) [29]. These oxidants react with the organic substrates, eventually leading to their complete conversion to CO_2, H_2O and other inorganic components [30].

When a current is applied to the electrolysis cell, the metal complexes might be destructed in two ways as follows by electrochemical process.

$$MR \xrightarrow{k_4} M + \mathrm{CO_2} + \mathrm{H_2O} + R_1 \qquad (5)$$

$$\mathrm{2H_2O} \xrightarrow{k_5} \mathrm{O_2} + \mathrm{4H^+} + \mathrm{4e} \ \text{(acid medium)} \qquad (6)$$

$$\mathrm{2OH^-} \xrightarrow{k_6} \mathrm{H_2O_2} + \mathrm{2e} \qquad (7)$$

$$MR + \text{active radical} \xrightarrow{k_7} M + \mathrm{CO_2} + \mathrm{H_2O} + R_2 \qquad (8)$$

Where *MR* is metal complexes; and *M* is metal ions.

Metal complexes can be destroyed at the PbO_2/Ti electrodes (anodes). Meanwhile, liberated Cu^{2+}, Ni^{+} ions depositing and hydrogen evolution occur at the cathode, oxygen evolution occur at the anode, which are competing reactions and will reduce the current efficiency of decomplexation by electrolysis.

Therefore, the operating parameters such as pH, current density and reaction time play an important role in the destruction of metal complexes.

3.2 Effect of current density

The current density represented the electron amount through the unit area of working electrodes per unit time, meaning reacting energy which influenced the reaction rate and operating costs directly [31]. To explain the effect of current density on decomplexation, a series of experiments were carried out by running the electrochemical oxidation at different current densities of 5, 10, 15 and 20 mA/cm^2. The optimizing current density was obtained in terms of destruction efficiencies and electrical energy requirements. The other operating conditions were: natural temperature (298-301 K), rotation speed of electrodes of 0 rpm and the initial pH value of 12.6.

The increase of current density improved the destruction ratio of metal complexes. But, current density over the "limiting" current would reduce the current efficiency [3, 19]. Fig. 2 (a) showed the destruction ratio of metal complexes and the rate of energy of heating the wastewater (W_h) to electrical energy consumption (W_t) during electrolysis under different current density conditions. It was clear that the destruction rate of metal complexes increased with the current density increasing. But, the destruction rate of metal complexes did not increase as greatly as the current density changing from 5 to 10 mA/cm^2 during the current density over the 10 mA/cm^2. This meant that the current efficiency decreased greatly when the current density was over the 10 mA/cm^2.

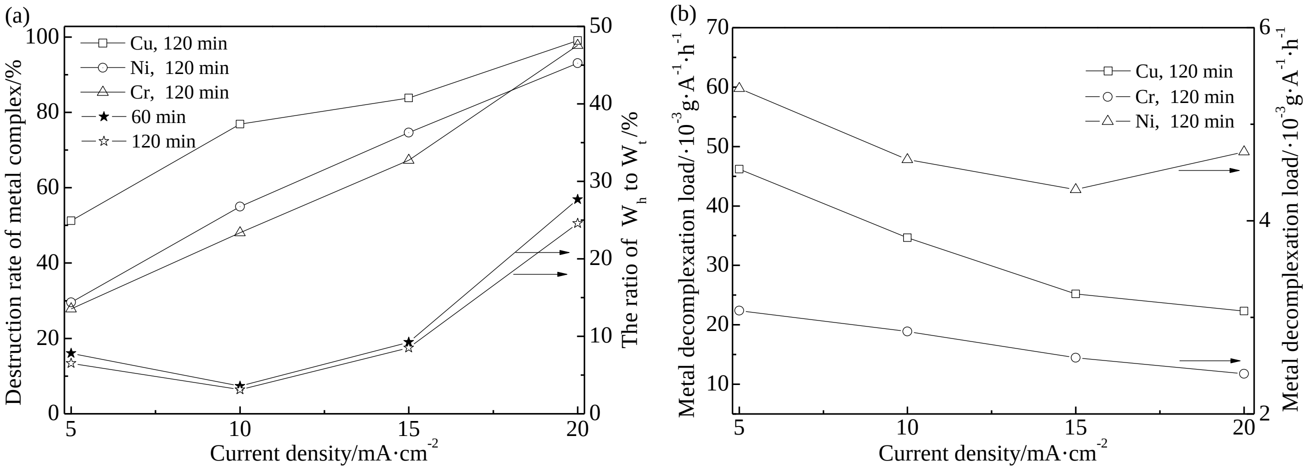

Figure 2. Effect of current density

At the current density of 20 mA/cm^2, the destruction ratio of Cu and Cr complexes after 120 min treatment was nearly 100%. In this condition, the temperature of wastewater increased about 15 K after 120 min electrolysis. However, it caused the lowest current efficiency and highest energy waste due to partial electrical energy heating the electrolyte (wastewater) and increased the running costs. In fact, at j=15 mA/cm^2, the value of W_h/W_t was 8.52%, only one-third that of j=20 mA/cm^2, which meant lower electro energy used to heat the wastewater. High current density caused more H_2 and O_2 evolution at electrodes and also reduced the current efficiency. Thus, an optimum point should be carefully determined to obtain a high destruction metal complexes rate and relatively low energy consumption.

The decomplexation load, which defined as the destruction amount of metal complexes per unit current within one hour, is a key parameter that reflects the current efficiency. High decomplexation load means more effective electron participating in metal complexes destruction. As shown in Fig. 2 (b), the decomplexation load for Cu and Cr complexes decreased with the current density from 5 mA/cm^2 to 15 mA/cm^2. However, the decomplexation load for Ni complex got the low point at j=15 mA/cm^2 after 120 min treatment. This might be explored that the mass transfer restricts the decomplexation load in electrochemical process. In our case, the current density of 10 mA/cm^2 was chosen according to low energy consumption, low residual metal rate and relatively high decomplexation load simultaneously.

3.3 Effect of the rotation speed

Mass transfer between solution and electrode interface is a key factor that affects the dynamics of electrochemical oxidation reaction. Rotating disc electrode enhances mass transport coefficient and reduces the thickness of aqueous film coated on the electrode surface, which could be calculated using the following equation [32].

$$\delta = 1.2\left(V_c\right)^{0.5}\left(10^{-4}\,\mathrm{m}\right) \quad (9)$$

$$V_c = R\omega \quad (10)$$

Where V_c is the vertical component of the peripheral velocity at the point where the disc emerges from the water; R is the distance between the disc center to the studied point; ω is the angular velocity.

The relationship of ω and the high gravity factor (β) could be expressed as follows:

$$\beta = \frac{\omega^2 r}{g} \quad (11)$$

In fact, the high gravity field has the characteristics of the cubic distribution, which is seen as a plane distribution when the packing is axially well-distributed. Therefore, the average high gravity factor (β') is described as the formula (12).

$$\beta' = \frac{\int_{r_2}^{r_1} 2\beta\pi dr}{\int_{r_2}^{r_1} 2\pi dr} = \frac{2\omega^2(r_1^2 + r_1 r_2 + r_2^2)}{3(r_1 + r_2)g} \quad (12)$$

Where r_1, r_2 are the inner radius and outer radius of the electrodes, respectively.

The β' of four different rotation speeds of electrodes used in this section was shown in Table 2.

Table 2. The average high gravity factor of rotating electrodes on different rotation speeds

Rotation speed	100 rpm	200 rpm	300 rpm	400 rpm
β'	0.27	1.06	2.39	4.24

In this section, the metal decomplexation experiment was carried out with the original pH of 12.6, current density of 10 mA/cm^2 and natural temperature. Fig. 3 (a) indicated the destruction ratio of metal complexes within electrolysis time of 90 min at different β'. It indicated that β' effected clearly the destruction ratio of metal complexes. The residual ratio of Cu, Cr and Ni complexes under β'=0.27 was almost 4 times, 1.5 times and 1.45 times that of β'=1.06, respectively. The thickness of thin film on the electrodes reduces with the β' increasing, so the destruction efficiency is enhanced [33, 34]. However, the destruction ratio of metal complexes did not always increase as β' from 1.06 to 4.24, which meant too high rotation speed was not necessary.

According to the Comninellis's model [35], mass transport coefficient (k_m, m/s) of pollutants during electrochemical oxidation could be expressed as the equation (13).

$$k_m = ln(C_0 / C_t)\frac{V}{A \cdot t} \quad (13)$$

Where t is the electrochemical oxidation process time (s); C_t and C_0 are the metal complexes of t (s) and 0 s; A is the area of electrodes (m^2); V is the volume of wastewater (m^3).

As shown in Fig. 3 (b), the k_m has a little decreased during the β' increasing from 1.06 to 4.24 after 90 min electrolysis. With vigorous stir of the solution, the gas generated in the electrochemical oxidation process led to a decrease in the diffusion layer which would decrease the k_m [36]. Too high rotation speed of electrodes would cause solution splashing out of the cell [37].

So, rotation of electrodes enhanced mass transfer and the optimized rotation speed of electrodes was 200 rpm (β'=1.06).

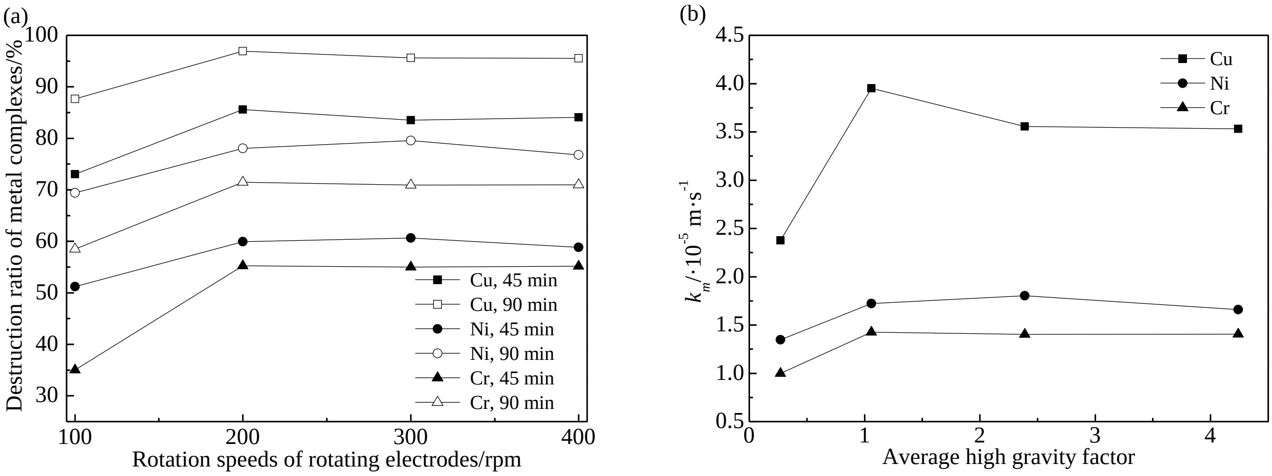

Figure 3 Effect of the rotation speed

3.4 Effect of initial pH

The concentration and form of metal ions in wastewater would change on the different pH, and that the pH value plays a key factor in the electrochemical oxidation process. The initial pH value of wastewater was adjusted to 3.0, 5.0, 7.0, 9.0, 11.0 and 12.6 by 1 mol/L H_2SO_4 and 1 mol/L NaOH solution, respectively. The other operating parameters were the current density of 10 mA/cm^2, the rotation speed of 200 rpm. The cell potentials and pH remained nearly constant during electrolysis.

Table 3. Predicated parameters of first-order removal of metal complexes of Cu at different pH with current density of 10 mA/cm^2 and rotation speed for electrodes of 200 rpm

pH	R^2	k (min^{-1})
3.0	0.9984	-0.0384
5.0	0.9956	-0.0324
7.0	0.9967	-0.0258
9.0	0.9961	-0.0337
11.0	0.9979	-0.0448
12.6	0.9982	-0.0420

As shown in Fig. 4 (a), (b) and (c), the metal complexes could be destructed in a large range of pH by electro-oxidation technology. The evolution trend of Cu, Cr and Ni complexes with different pH was similar, due to the same principle and mechanism of electrochemical oxidation. Within electrolysis time of 120 min and initial pH of 11.0, the residual concentration of Cu, Cr and Ni complexes declined from 187.74 mg/L, 21.81 mg/L and 39.26 mg/L to 0.87 mg/L, 0.47 mg/L and 0.64 mg/L, respectively.

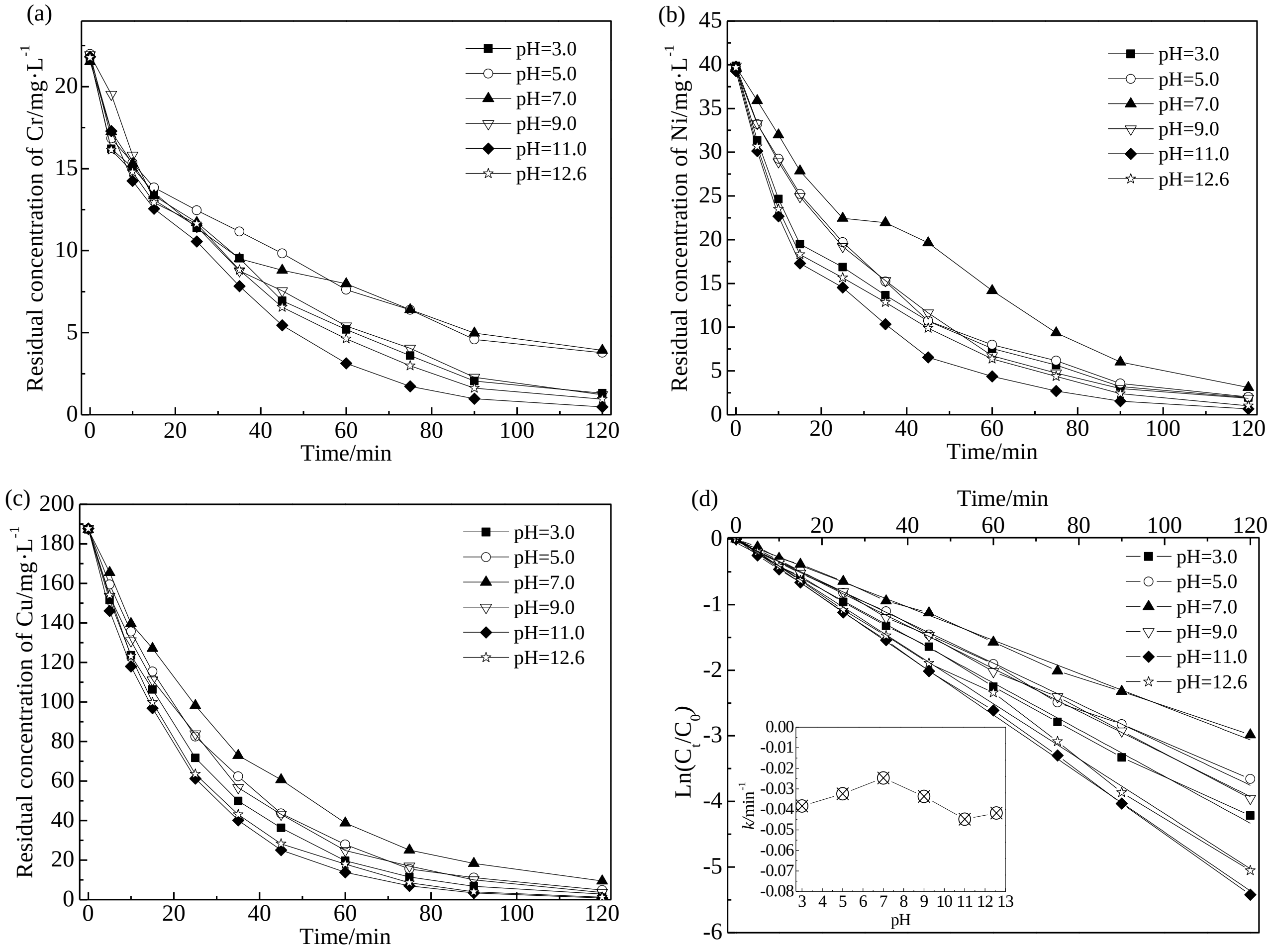

Figure 4. Effect of initial pH

According to the mass conservation, the destruction kinetics of Cu complex was considered for various pH of wastewater:

$$C(t)=C_0e^{-kt} \qquad (14)$$

Where k is the first-order rate constant, min^{-1}. The data of first-order rate constant (k) and squared-correlation coefficient (R^2) were given in Table 3. It indicated that the destruction of Cu complex in acid and alkaline solution was much more efficient than in neutral. In the acid solution, the destruction efficiency increases with the side reaction of oxygen evolution weaken, which is enhanced via direct oxidation. The evolution of H_2 gas is the main side reaction at the cathode which more or less reduces the current efficiency. However, the destruction efficiency incerased in a alkaline solution, attributing to the hydrogen peroxide generated by electrocheimcal [19, 38]. H_2O_2 could enhance the destruction efficiency of metal complex by indirect oxidation [39]. This is might the reason that the destruction efficiency of base solution is higher than that of acid solution. On the contrary, the O_2

evolution enhanced with the increasing pH [17]. And, the over base condition could impair the destruction efficiency. The destruction efficiency of metal complex increased from pH=7.0 to pH=11.0, but it decreases during the pH increasing from 11.0 to 12.6. The destruction of Cu complex at pH=11.0, was faster than the others pH, due to the hydrogen peroxide generated in a alkaline solution by the electrochemical oxidation. The k of pH=11 is -0.0448 min^{-1}, which meant the reaction rate is the fatest. Consequently, the pH of wastewater tremendously affected the reaction rate constant and the optimized pH of wastewater was pH=11.0.

4. CONCLUSIONS

The electrochemical oxidation was an effective process to remove metal complexes from electroplating wastewater. Rotation speed of electrodes has a large effect on destruction rate of metal complexes. Rotating of mesh-disc electrodes enhanced the mass transfer. Under the optimal operating parameters with initial pH of 11.0, current density of 10 mA/cm^2 and rotation speed of electrodes of 200 rpm, the destruction efficiency of Cu, Cr and Ni complexes were 99.54%, 97.85% and 98.37% within 120 min, respectively. The colority of wastewater declined from 128 times to 5 times.

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