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Electrocoagulation of chromium in tannery wastewater by a composite anode modified with titanium: parametric and kinetic study

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ABSTRACT

To overcome the color index problem of the iron electrode and guarantee the high treatment efficiency of chromium (Cr), this study used a titanium electrode to remove Cr from the synthetic and real tannery wastewater. The effects of electrode material, reaction voltage, pH value and reaction time on the removal efficiency of Cr ions were investigated by electrocoagulation (EC). The results demonstrate that (Al + Ti)–C composite electrode had a high Cr removal efficiency (98.88%) and did not increase the color index of effluent. The optimal EC conditions were the pH value of 6 and a voltage of 5 V that contributed to the around 100% current efficiency. Regarding the morphologies of Cr, a majority of removed Cr was accumulated in the residual sludge, and the Cr^{3+} in wastewater was mainly formed by the combination of Cr and hydroxide, e.g. $[Cr(OH)_2^+]$ and $[Cr(OH)^{2+}]$. Finally, the kinetics of removing Cr and chemical oxygen demand by EC was in accordance with the pseudo-first-order kinetic model and pseudo-second-order kinetic, respectively. Overall, the composite anode modified by titanium to remove Cr can increase the treating effect without the increase of the color index.

Keywords: Electrocoagulation; Cr; Composite anode; Tannery wastewater

1. Introduction

At present, tannery wastewater in China is one of the most polluted industrial wastewaters. In 2015, the annual output of tannery wastewater reached 262.28 million tons [1]. The tanning process uses animal skin treated by alkaline chromium sulfate solution, which makes the tanning wastewater contain a large amount of organic matter and heavy metal chromium (Cr) ions arriving at 2–4 g/L. The heavy metal Cr ion has been identified as a strong carcinogen by the International Anti-Cancer Research Center and had a baneful impact on the environment. According to the national water pollutant discharge standards (GB 30486-2013) [2], the discharge concentration of total Cr (both Cr^{3+} and Cr^{6+}) and chemical oxygen demand (COD) should be limited under 0.5 and 60 mg/L, respectively [2].

The Cr ions in the tannery wastewater exist in two states of Cr^{3+} and Cr^{6+} (individual or mixed existence), and the wastewater from a tannery is usually treated by chemical precipitation to precipitate the dissolved Cr^{3+} mainly in the form of chromium hydroxide under alkaline conditions [3]. In general, the chemical precipitation method can reduce Cr^{3+} wastewater concentration from 2,000~4,000 mg/L to 2~10 mg/L, removal efficiency up to 99%. The production of chromium sludge can be reused for chrome tanning agents [4]. However, the use of traditional chemical methods has been unable to meet the latest discharge limits. Because Cr in the tannery wastewater combines with organic substances to form a stable complex [5], the increase of Cr solubility in wastewater weakens the treatment effect. Also, the toxicity

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of tannery wastewater makes traditional biological methods incapable to achieve the desired treating effect. So it is imperative to explore advanced treatment methods to treat tannery wastewater.

In recent years, several studies have shown that electrocoagulation (EC) is an effective alternative method to traditional chemical coagulation. Soluble ionic substances in wastewater, especially heavy metals, can be successfully removed by using EC processes [6]. EC removes heavy metal ions including Zn^{2+}, Mn^{2+}, Cr^{6+}, Cu^{2+} and Ni^{2+} [7–10], etc. The researchers used electrochemical methods to remove contaminants from tannery wastewater, proving that EC is one of the effective methods for removing chromium. The EC reaction is based on the action of the current, and the sacrificial anode metal is used to produce flocculants. Currently, the widely used anode metal plate materials are aluminum and iron, and metal hydroxide is formed in a suitable pH range to form the destabilized and aggregated suspended particles. Thus, a large number of dissolved pollutants are precipitated and adsorbed. Due to the action of hydrolysis and flotation, the metal Cr can be co-precipitated with metal hydroxides to be removed. At the same time, hydroxyl radicals are generated during the electrolysis process, and their strong oxidation can oxidize complex organic substances into CO_2 and reduce COD in the effluent.

The iron electrode can remove heavy metal ions [11], and aluminum is also used as the anode material [12]. Many studies have compared these two electrodes, indicating that the iron electrode has a better treatment effect [13,14]. However, the iron electrode after electrolysis makes the color of effluent yellowish-brown. The longer the electrolysis time, the greater the color index due to the higher concentration of Fe^{2+} dissolved in water. The subsequent treatment is required to remove iron ions. However, aluminum electrode reduced color index, because the Al electrode generates Al^{3+} ions through EC and forms $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al_2(OH)_2^{4+}$, $Al(OH)_4^-$ that is finally converted to $Al(OH)_3$. These aluminum polyhydroxy complexes can be a gelatinous solid in wastewater, helping to decrease color index [15,16]. Thus, the aluminum electrode was used in place of the iron electrode. However, the treating efficiency of the aluminum electrode was still lower than that of the iron electrode. Recently, it has been reported that titanium can remove various contaminants [17,18], and a composite anode modified by titanium bears the potential to remove chromium. At present, there are few studies on the experiments of double anodes in worldwide. Furthermore, the Ti electrode is reported to do not passivate during the reaction and share part of the current of the Al or Fe electrode. Thus, the double anodes might weaken the drawbacks of Al and Fe electrodes with the addition of Ti.

The aim is to promote the treatment effect of composite electrodes without increasing the color index of effluent. The composite anodes are prepared by combining Ti and Al or Ti and Fe. The optimal conditions and conversion kinetics of composite electrode to treat Cr^{3+} and Cr^{6+} wastewater were comprehensively investigated. Specifically, the effects of EC and chromium removal by different anode combinations were compared. Moreover, the effects of current parameters, reaction voltage, pH value and reaction time on the total Cr removal efficiency were studied. The morphologies of removed Cr after EC were comprehensively investigated. Finally, the removal kinetics of Cr and COD were studied by numerical modeling.

2. Materials and methods

2.1. Wastewater components

The synthetic wastewater containing 50 mg/L Cr^{3+} and 50 mg/L Cr^{6+} was prepared by dissolving the chromium chloride and potassium dichromate (AR, Guangfu Fine Chemical Research Institute, Tianjin, China) in distilled water. The real tannery wastewater was the effluent from the secondary sedimentation tank that was pretreated by physicochemical precipitation and biological treatments. The quality indicators of real tannery wastewater and discharge standard of treated water [2] are shown in Table 1.

2.2. EC reactor

Fig. 1 shows the EC reaction device made of polymethyl methacrylate (L × W × H: 30 cm × 30 cm × 20 cm). The anode and cathode were set at two opposite sides of the device (L × W × H: 0.3 cm × 28 cm × 18 cm). The electrode was connected with the DC regulated power supplies. Different combinations of aluminum, iron, titanium, and graphite were used to prepare four kinds of electrodes in the form of anode-cathode: Al–C, Fe–C, (Al + Ti)–C and (Fe + Ti)–C.

Table 1
Quality indicators of real tannery wastewater and discharge standard of treated water

	Real tannery wastewater	Discharge standard
Total Cr, mg/L	10	0.5
Cr^{6+}, mg/L	0.055	0.050
pH	6.00	6.00~9.00
COD, mg/L	1,000	60

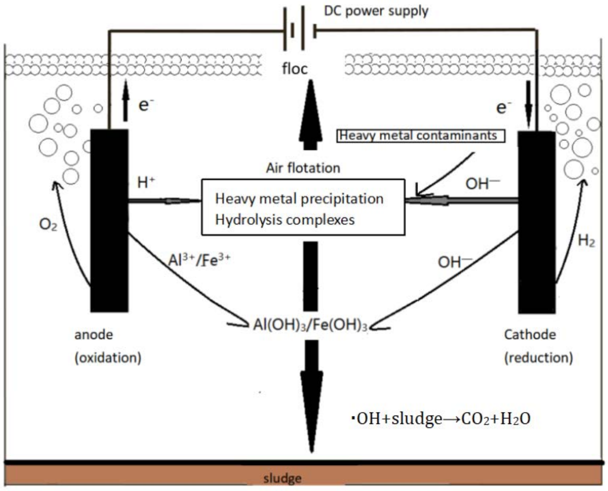

Fig. 1. Schematic diagram of experimental reaction process.

The electrode materials were pretreated by polishing and cleaning with a sulfuric acid-nitric acid solution with a pH value of 1 and were completely soaked in tannery wastewater to eliminate the effect of adsorption. The EC reaction was carried out at room temperature. The supernatants and the precipitates were separated after each experiment for water quality determination.

2.3. EC process

First, the effects of different electrode combinations on the removal efficiency of Cr^{3+} and Cr^{6+} were compared to explore the optimal electrode. Then, the reaction voltages of 1, 2, 3, 4 and 5 V were tested with a reaction time of 30 min. After the confirmation of optimal reaction voltage, the initial pH values of 3.00, 4.00, 5.00, 5.85, 6.00, 7.00, 8.00 and 9.00 were assessed. Finally, the batch test of Cr removal was carried out by the optimal electrode under the optimal reaction voltage and initial pH value. The water was sampled after 5, 10, 15, 20, 25 and 30 min of reaction to detect the total Cr and COD. The change in current efficiency was studied. The mass balance of Cr was calculated and the transformation form and fate of Cr were explored.

2.4. Analytical methods

The concentration of total chromium was determined by atomic absorption spectrometry (AA7003F, East & West Analytical Instruments Inc., China). The concentration of hexavalent chromium was determined by diphenylcarbazide colorimetry with a spectrophotometer (TU-1810, Beijing Purkinje General Instrument Co. Ltd., China) [19]. The COD was measured by the Potassium Dichromate method. The pH of the water was measured by a pH meter (STARTER3100, Shanghai Ohaus International Trading Co. Ltd., China). The color index of the actual tannery waste water was determined by the dilution factor method [20]. The concentration of total Cr in the sludge was determined in a digester (SK-312, Tianjin Ze Qing electric furnace industry and Trade Co. Ltd., China) [21].

The Cr^{3+} concentration was calculated by subtracting total Cr concentration with Cr^{3+} concentration. The calculation formula for the removal efficiency of total Cr, Cr^{3+}, and Cr^{6+} is as follows:

$$R = \frac{(\mathrm{Cr}_0 - \mathrm{Cr}_t)}{\mathrm{Cr}_0} \times 100\% \tag{1}$$

where Cr_0 is the mass concentration of original solution Cr, mg/L; Cr_t is the mass concentration of effluent Cr at time t, mg/L; R is Cr removal efficiency, %.

2.5. Kinetic modeling

The EC processes of Cr and COD were evaluated by quasi-first-order kinetic equations (Eq. (2)) and quasi-second-order kinetic equations (Eq. (3)).

$$\frac{1}{q_t} = \frac{k_1}{(q_e \cdot t)} + \frac{1}{q_e} \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{(k_2 \cdot q_e^2)} + \frac{t}{q_e} \tag{3}$$

where k_1 is primary reaction rate constant, 1/min; k_2 is secondary reaction rate constant, g/(mg min); t is adsorption time, min; q_t is adsorption capacity at time t, mg/g; q_e is adsorption capacity at equilibrium, mg/g.

2.6. Energy and electrodes consumptions

In the EC process, the electrical energy consumption and amount of electrode dissolved in solution exhibit significant economic factors. Regarding the electrode consumption, the dissolved amounts of Al or Fe electrodes were estimated theoretically using Faraday's law in Eq. (4) [10]:

$$m_{\mathrm{Al/Fe}} = \frac{I \cdot T \cdot M_{\mathrm{Al/Fe}}}{Z_{\mathrm{Al/Fe}} \cdot F \cdot V} \tag{4}$$

where $m_{\mathrm{Al/Fe}}$ is the specific amount of dissolved Al or Fe (g/m^3), I is the direct electrical current (A), T is the EC time (s), $M_{\mathrm{Al/Fe}}$ is the molecular weight (Al = 27 g/mol, Fe = 56 g/mol), $Z_{\mathrm{Al/Fe}}$ is the chemical equivalence ($Z_{\mathrm{Al}} = 3$, $Z_{\mathrm{Fe}} = 2$), F is the Faraday constant (F = 96,500 C/mol), V is the volume of the treated wastewater (m^3).

Besides, the electrical energy consumption was calculated by Eq. (5) [22]:

$$E = \frac{U \cdot I \cdot t}{V \cdot (C_0 - C)} \tag{5}$$

where E is the specific energy consumption (kW h/g), U is the voltage (V), I is the electric current (A), t is EC time (h), V is the volume of the treated wastewater (L), C_0 is the initial COD concentration (mg/L), C is the final COD concentration after the reaction (mg/L).

3. Results and discussion

3.1. Selection of electrode materials

3.1.1. Cr^{3+} removal in synthetic wastewater

The synthetic Cr^{3+} wastewater was used to select electrode materials. The concentration of Cr^{3+} wastewater was 50 mg/L under the voltage of 5 V and the reaction time of 30 min. The experimental results show that the total Cr removal efficiencies of anodes with Ti were higher (more than 98.00%) than those without Ti (less than 96.00%) (Table 2), which could be due to the reduction function of Ti. The total Cr in the raw water was Cr^{3+}, whereas Cr^{6+} was found in the effluent (0.004–0.009 mg/L). The accumulation of Cr^{6+} was aroused by the oxidation during EC, and Ti in electrodes of (Al + Ti)–C and (Fe + Ti)–C reduced Cr^{6+} to Cr^{3+} that finally precipitated as $Cr(OH)_3$. The $Cr(OH)_3$ was likely to co-precipitate with $Al(OH)_3$ or $Fe(OH)_3$.

Al anode can achieve a good chromium flocculation effect. However, the Al anode is likely to be inactive and difficult to dissolve, contributing to its inferior flocculation effect compared to (Al + Ti) anode. The reason for the good

Table 2
Results of Cr^{3+} removal for synthetic wastewater by different electrodes

Electrode	$R_{\text{total Cr}}$	R_{Cr}^{3+}	pH	Color index
	%	%		
Al–C	95.97	95.95	6.54	–
Fe–C	95.73	95.71	6.12	20
(Al + Ti)–C	98.15	98.17	6.29	–
(Fe + Ti)–C	99.15	99.16	7.54	10

flocculation effect of (Al + Ti) might be that the Ti shares a part of the current and weakens the current density of the Al anode, allowing the Al anode dissolving and generating flocs to adsorb the chromium.

It should be pointed out that a rise in color occurred for the electrodes with Fe. Almost all the electrodes with Fe resulted in the color index of effluent, ranging from 10 to 20 (Table 2). The reason is that the electrodes with Fe performed as sacrificial anode iron to produce Fe^{2+} during the reaction. Overall, the titanium was suggested to replace iron to avoid color index increase.

3.1.2. Cr^{6+} removal in synthetic wastewater

The synthetic Cr^{6+} wastewater was used to select electrode materials. The concentration of Cr^{6+} wastewater was 50 mg/L under the voltage of 5 V and the reaction time of 30 min. In Table 3, it could be seen that the removal efficiency of total Cr varied between 78.35% and 89.49%, and EC treatment of Cr^{6+} was more difficult than that of Cr^{3+}. It was found that (Al + Ti)–C and (Fe + Ti)–C electrodes performed better in removing Cr^{6+} than other electrodes, and their removal efficiencies of total Cr reached 89.49% and 84.84%, respectively. The combinations of Al–C and Fe–C without adding titanium electrodes did not perform well, whose removal efficiencies of total Cr reached only 79.08% and 78.35%, respectively. This is due to the reduction of titanium electrodes. The Cr^{6+} was firstly converted to Cr^{3+} by titanium and then $Cr(OH)_3$ was precipitated with $Al(OH)_3$ or $Fe(OH)_3$.

For the color problem, Fe–C electrodes had a high color index of 25, probably due to the dissolved Fe^{2+}. However, the use of titanium electrodes instead of iron electrodes could achieve the same reduction effect and also reduce the color of effluent, whose color index arrived at 10. Although it was difficult to remove the color for Cr^{6+} wastewater, the (Al + Ti)–C electrode could still effectively get rid of the watercolor problem.

3.1.3. Treatment of real tannery wastewater

The real tannery wastewater was treated with different electrodes by setting the voltage of 5 V and a reaction time of 30 min. The pH of effluent was monitored to investigate the effect of chemical precipitation. The results are shown in Table 4.

The pH value of raw water was 5.85. The experimental results clearly show that the pH values of effluent after EC increased for all electrodes, although the augmentation extents were different. In the reaction system, the appropriate alkaline conditions resulted in the metal hydroxides and precipitation of metal ions.

Table 3
Results of Cr^{6+} removal for synthetic wastewater by different electrodes

Electrodes	$R_{\text{total Cr}}$	R_{Cr}^{6+}	Con. $_{\text{Cr}}^{3+}$	Color index
	%	%	mg/L	
Al–C	79.08	83.28	2.083	10
Fe–C	78.35	83.68	2.154	25
(Al + Ti)–C	89.49	91.50	1.046	–
(Fe + Ti)–C	84.84	89.54	1.510	10

Table 4
Results of different electrodes for treating real tannery wastewater

Electrodes	Al–C	Fe–C	(Al + Ti)–C	(Fe + Ti)–C
$R_{\text{total Cr}}$, %	97.16	95.41	98.88	98.31
Con. $_{\text{Cr}}^{6+}$, mg/L	0.009	0.024	0.006	0.009
R_{Cr}^{6+}, %	83.64	56.36	89.10	83.64
R_{COD}, %	75.82	62.92	90.33	85.49
pH	8.02	6.16	6.96	8.81
Color index	–	10	–	5

According to Table 4, it could be concluded that the removal efficiencies of total Cr for the electrodes modified by Ti (more than 98%) was higher than the electrodes without Ti (ranging from 95.41% to 97.16%), and the (Al + Ti)–C electrode performed the optimal. Meanwhile, the lowest concentration of Cr^{6+} in the effluent was achieved by the (Al + Ti)–C electrode to be 0.006 mg/L, followed by the Al–C and (Fe + Ti)–C electrodes, being both 0.009 mg/L. The reason is that titanium increased the reduction effect with the transformation of Cr^{6+} to Cr^{3+} in the system. Regarding Al–C or Fe–C electrodes, the removal efficiencies of Cr were reduced due to the formation of a passive film, contributing to the low dissolution efficiency, uneven dissolution and high operating voltage [23].

To the COD removal, its efficiency stayed higher for electrodes with Ti than those without Ti (Table 4), probably resulted from the enhancement of dissolved metal ions by Ti. After the combination of the Al or Fe electrode and titanium electrode, titanium will share a part of the current and reduce the current density of the metal anode. As a result, the metal anode will activate and dissolve more metal ions to enhance the effect of coagulation. Yadav et al. [24] used an aluminum electrode to remove 83.94% of COD and an iron electrode to remove 54.83% of COD from the wastewater. In our study, the removal efficiency of COD reached 90.33% by using the Al + Ti electrode. Regarding the effluent color, the color of effluent is mainly caused by the Fe electrode rather than the Al electrode. Aghdam et al. [25] used EC to remove the color index of pulp wastewater and reported that EC was an effective, fast and economical method for industrial wastewater treatment.

3.2. Optimizing EC parameters

3.2.1. Effect of voltage

The voltages were separately set to 1, 2, 3, 4 and 5 V. The pH was 5.85 and the reaction time was 30 min. The real tannery wastewater was treated with (Al + Ti)–C electrode. It could be seen that the voltage increased from 1 to 5 V contributed to the removal efficiency of the total Cr, which gradually rose from 79.14% to 98.88% (Fig. 2). The total Cr concentration of effluent met the national discharge standard under the voltage of 5 V. The reason is that the voltage determines the amount of Al^{3+} and Fe^{3+} dissolved in the reaction system. The greater the voltage, the more Al^{3+} and Fe^{3+} were dissolved. Then, Al^{3+} and Fe^{3+} were hydrolyzed into $Al(OH)_2^+$, $Al(OH)^{2+}$, $Al_2(OH)_2^{4+}$, $Al(OH)_4^-$ and other hydrolysate serving as flocculants in the solution. The COD removal efficiency also increased from 78.54% to 90.46% along with the augmentation of voltage. The reason could be that great amounts of $^\bullet OH$ were produced along with the increase in voltage.

3.2.2. Effect of initial pH

The initial pH values were separately set to be 3.00, 4.00, 5.00, 5.85, 7.00, 8.00 and 9.00. The voltage was 5 V and the reaction time was 30 min. The real tannery wastewater was treated with (Al + Ti)–C electrode. Fig. 3 shows that the removal efficiencies of total Cr were always more than 90%. When the pH range was between 3.00 and 5.85, the removal efficiency augmented along with the increase of pH. When the pH ranged from 5.85 to 8.00, the removal efficiency tended to be stable that decreased at pH greater than 8. Experimental results were similar to those obtained by Jin et al. [26], which showed that the removal efficiencies of Cr were nearly 99% at the pH value in the range of 5.00–8.00.

Besides, the pH of effluent was measured at different initial pH values as shown in Fig. 3. It is suggested that the pH value of effluent was higher than that of raw real tannery wastewater (5.85). The amount of OH^- increased was favorable for the formation of precipitates, such as $Al(OH)_3$ and $Cr(OH)_3$. When the initial pH value rose from 3.00 to 5.00, the removal efficiency of the total Cr also increased. For the initial pH value of 5.85, 7.00 and 8.00, the pH of effluent was 6.96, 7.35 and 8.04, respectively. The highest removal efficiency of total Cr was reached at an initial pH of 5.85. Because $Al(OH)_3$ was more likely to precipitate at pH of about 6.5, while $Cr(OH)_3$ mostly precipitated at pH of about 8.5 [27]. The condition of pH between 6.5 and 8.5 was likely to generate the precipitation of $Cr(OH)_3$. However, when the initial pH was adjusted to 9.00, the removal efficiency of total Cr was decreased due to the conversion of Cr ions to CrO_4^{2-} that weakened the Cr removal efficiency. Meanwhile, $Al(OH)_4^-$ and $Cr(OH)_4^-$ was generated in the EC process at high pH value [28], and the precipitation of $Al(OH)_3$ and $Cr(OH)_3$ began to dissolve resulting in a reduction of total Cr removal. Therefore, it was considered that the precipitation amounts of $Al(OH)_3$ and $Cr(OH)_3$ were large in the pH between 6.00 and 8.00 [29]. So the raw tannery wastewater did not need to adjust the pH value for the treatment.

3.2.3. Effect of current density

The current density was set to be 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 A/cm² separately. The reaction time was 30 min under the conditions of application of (Al + Ti)–C electrode treating real tannery wastewater. The removal performances of COD, total Cr, and Cr^{6+} were shown in Fig. 4. It could be seen that the removal efficiencies of total Cr and Cr^{6+} fluctuated because the temperature of the reaction system might affect the solubility of chromium in the solution [30]. The removal efficiencies of total Cr and Cr^{6+} greatly increased when the current density was larger than 600 A/m². The removal efficiencies of COD always increased with the rise of current density.

The magnitude of the current density determines the amount of coagulant produced and the size of the bubbles which affect the formation of the flocs [31]. So the current density is assumed to be an important factor directly affecting the reaction efficiency. When the current density increased, the amount of Al^{3+} and the number of formed flocs grew [32]. At a low current density, there was a long time to accumulate enough hydroxide for the EC process [29].

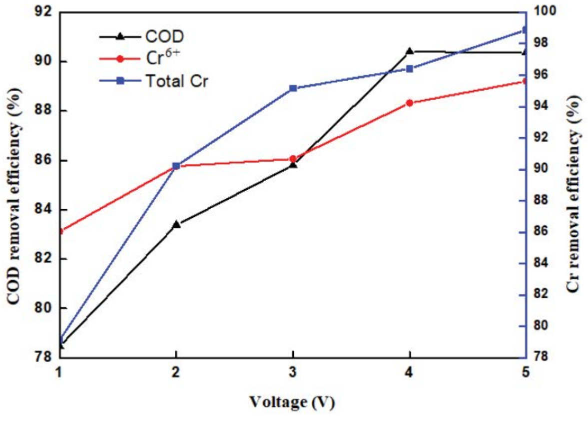

Fig. 2. Effects of voltage on the removal efficiencies of COD, total Cr and Cr^{6+}.

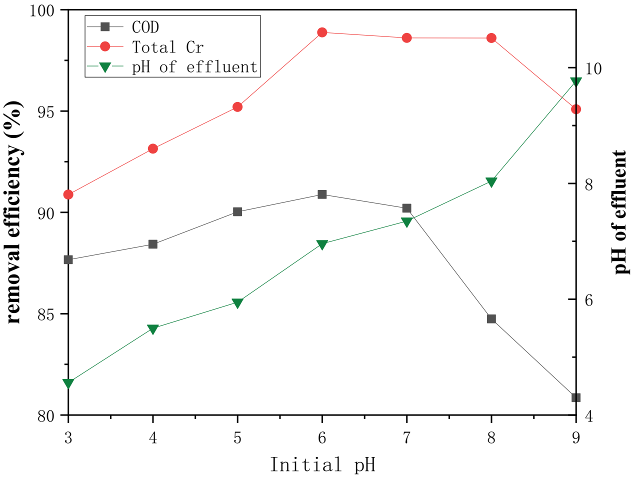

Fig. 3. Effects of initial pH on the removal efficiencies of COD and total Cr and pH of effluent.

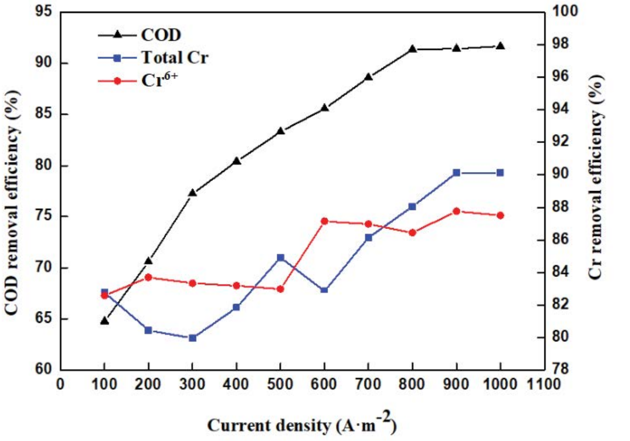

Fig. 4. Effects of current density on the COD, total Cr and Cr^{6+} removal efficiency.

When the current density increased to 900 A/cm², the change of EC efficiency was not observable. The reason may be that the current density not only determines the amount of flocculant produced, but also the efficiency of bubble generation [33]. The excessive current enlarged the diameter of the bubble and reduced the mass transfer efficiency between the pollutants and electrodes. Also, the increase of current density caused the augmentation of the volume of aluminum flocs. Consequently, the shortened contact time of flocs and contaminants was not conducive to the promotion of electric flocculation efficiency [34].

3.3. Morphology of removed Cr

The total Cr concentration of raw tannery wastewater was 10 mg/L in 100 mL of water. The total Cr concentrations of solution and sludge after EC were analyzed. As shown in Table 5, there was a slight error in the experiment that led to differences between the sum of total Cr after EC and the total Cr in raw tannery wastewater. The electrolytes produced sludge after treatment and different morphologies of removed Cr were detected in detail. It is proved that the EC mainly transferred the soluble Cr into the precipitated sludge because of most amounts of Cr accumulated in the sludge produced by EC. The results indicate that the Cr was removed by the formation of precipitation.

It is important to investigate the morphology of dissolved Cr^{3+} that includes four hydroxide forms ($[Cr^{3+}]$, $[Cr(OH)_2^+]$, $[Cr(OH)^{2+}]$ and $[Cr(OH)_4^-]$). The reaction equilibrium constant was used to calculate the yield of the various products of the reaction [35]. The concentration of the hydroxide form could be expressed in the form of $[H^+]$ and $[Cr^{3+}]$ by the expression of the equilibrium constant (Eqs. (6)–(8)).

$$\left[\mathrm{Cr}\left(\mathrm{OH}\right)^{2+}\right]=\frac{K_1\times[\mathrm{Cr}^{3+}]}{[\mathrm{H}^+]} \tag{6}$$

$$\left[\mathrm{Cr}\left(\mathrm{OH}\right)_2^{+}\right]=\frac{K_2\times[\mathrm{Cr}^{3+}]}{[\mathrm{H}^+]^2} \tag{7}$$

Table 5
Cr content in solution and sludge after electrocoagulation

Electrodes	Total Cr in solution, mg/L	Total Cr in sludge, mg/L	Sum
			mg/L
Al–C	0.284	9.668	9.952
Fe–C	0.459	9.541	10.00
Al + Ti–C	0.112	9.818	9.930
Fe + Ti–C	0.169	9.811	9.980

Table 6
Concentration and ratio of each substance in the form of Cr^{3+}

	Concentration$_{\text{initial}}$ [a]	Ratio$_{\text{initial}}$ [b]	Concentration$_{\text{final}}$ [c]
	mol/L	%	mol/L
$[Cr^{3+}]$	0.0014	0.73	1.4323×10^{-7}
$[Cr(OH)^{2+}]$	0.0704	36.80	9.2744×10^{-5}
$[Cr(OH)_2^+]$	0.1195	62.47	1.9061×10^{-3}
$[Cr(OH)_4^-]$	1.0854×10^{-7}	0.00005	2.8535×10^{-7}
Sum	0.1913		0.0020

[a] Concentration$_{\text{initial}}$ represents initial concentrations of different Cr^{3+}
[b] Ratio$_{\text{initial}}$ represents ratio of different Cr^{3+}
[c] Concentration$_{\text{final}}$ represents final concentrations of different Cr^{3+}

$$\left[\mathrm{Cr}\left(\mathrm{OH}\right)_4^{-}\right]=\frac{K_3\times[\mathrm{Cr}^{3+}]}{[\mathrm{H}^+]^4} \tag{8}$$

where $K_1 = 7.1 \times 10^{-5}$ $K_2 = 1.6 \times 10^{-10}$ $K_3 = 2.88 \times 10^{-28}$

The solution pH leads to the different concentrations of hydroxide Cr^{3+}. The pH of raw tannery wastewater and the effluent were 5.85, 6.96, respectively. Table 6 shows that the Cr^{3+} concentration correspondingly changed from 0.1913 to 0.0020 mol/L by the process of EC. It can be seen that the complex composition $[Cr(OH)_2^+]$ and $[Cr(OH)^{2+}]$ dominated in four morphologies. The Cr^{3+} in the real tannery wastewater was mainly in the form of complexes formed by the combination of Cr and hydroxide. Only free Cr^{3+} ions were removed by the pretreatment chemical precipitation, but the complex ions were not completely removed. The EC method is needed to remove the Cr complex including the hydroxide form of Cr^{3+}.

3.4. Kinetic of Cr and COD removal

The kinetic analysis tests were carried out under the total Cr initial mass concentration of 10 mg/L, the current density of 800 A/m², pH of 6 and reaction time ranging between 0–30 min. The reaction time was set to 5, 10, 15, 20, 25 and 30 min under the condition of voltage was 5 V with the initial pH of raw tannery wastewater. The analysis of Cr removal kinetic was carried out. The fitting results of Cr removal kinetics are shown in Table 7. It can be seen that the correlation coefficient R^2 of the quasi-first-order kinetic equation was higher than that of the quasi-second-order kinetic equation. It is indicated that the EC process was preferably

Table 7
Comparing kinetic parameters of Cr and COD removal through quasi-first-order and quasi-second-order kinetic equations

	Cr_{1st}[a]			Cr_{2nd}[b]			COD_{1st}[c]			COD_{2nd}[d]		
	K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (g/(mg min))	q_e (mg/g)	R^2	K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (g/(mg min))	q_e (mg/g)	R^2
This study	0.0846	0.3930	0.9999	0.1320	0.5390	0.9970	0.2700	87.9600	0.9400	0.0046	96.9700	0.9880
Wang [37]	–	–	–	–	–	–	0.0412	13.2964	0.8925	0.0026	37.8645	0.9989
Lin [36]	0.0110	4.4520	0.9420	0.0110	14.706	0.9990	–	–	–	–	–	–

[a]represents fitting results of quasi-first-order kinetic equation for removal of Cr;
[b]represents fitting results of quasi-second-order kinetic equation for removing Cr;
[c]represents fitting results of quasi-first-order kinetic equation for removal of COD;
[d]represents fitting results of quasi-second-order kinetic equation for removing COD

explained by the quasi-first-order kinetic model for Cr removal. According to the removal efficiency of Cr, the q_e in this study was 0.5390 mg/L, and the q_e in the study of Lin was 14.706 mg/L [36], which indicates that the removal of Cr by the dried algae of Sargassum performed better. The reason could be that the removal effect of seaweed on heavy metals is mainly related to carboxyl groups.

Furthermore, the analysis of COD removal kinetic was conducted and the fitting results of COD removal are shown in Table 7. It can be seen that the correlation coefficient R^2 of the quasi-second-order kinetic equation was higher than that of the quasi-first-order kinetic equation, demonstrating that the process is mainly a chemical reaction process. At the same time, it can be seen from Table 7 that the maximum q_e in this study was 96.97 mg/L, and the maximum q_e in the study of Wang [37] was 37.86 mg/L. The phenomenon indicates that the effect of removing COD by EC is remarkable in this study. In the study of Wang [37], the adsorption of COD resulted from straw biochar owning abundant pore structure and a large number of folds that contained acidic functional groups. Thus, the adsorption effect of biochar was affected by four factors: pH, initial concentration, time and dosage, so the adsorption capacity of COD was difficult to control.

3.5. Evaluation of electrode and power consumption

The electrode and power consumption were evaluated by treating 18 L real wastewater in a time of 30 min at a current density of 800 A/m^2. The dissolved amounts of Al and Fe electrodes, obtained through Eq. (4), arrived at 6.267 and 19.498 g/m^3, respectively. Besides, in the process of EC, electrical energy consumption is an important economic indicator calculated according to Eq. (5). The calculated electrical energy consumption of Al–C electrode and (Al + Ti)–C electrode reached 0.123 W h/g$_{\text{(COD)}}$ and 0.103 W h/g$_{\text{(COD)}}$, respectively The calculated electrical energy consumption by using Fe–C and (Fe + Ti)–C composite electrode was 0.148 W h/g$_{\text{(COD)}}$ and 0.109 W h/g$_{\text{(COD)}}$. The results show that the use of (Al + Ti)–C composite electrode has the greatest economic benefit. Overall, by adding the titanium, the color index of the effluent and consumption of anode were both reduced, making the EC reaction economically feasible.

4. Conclusions

The optimal electrode combination was (Al + Ti)–C electrode with the removal efficiency of Cr^{3+} and Cr^{6+} over 98% and 91%, respectively. The optimal reaction parameters include the voltage of 5 V, the initial pH of raw wastewater and a reaction time of 30 min. When the current density increased, the removal efficiency of Cr grew up. The removal efficiency total of Cr, Cr^{6+}, and COD for the real tannery wastewater reached 98.88%, 89.10% and 90.15%, respectively. The Cr ions were indeed removed by the precipitation and accumulated in sludge after EC. The Cr^{3+} in wastewater was mainly formed by the combination of Cr and hydroxide e.g. [Cr(OH)$_2^+$] and [Cr(OH)$^{2+}$]. According to the fitting of reaction kinetics, the process of removing Cr by EC is in accordance with the quasi-first-order kinetic, and the process of removing COD accords with the quasi-second-order kinetic.

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