



Treatment of tannery wastewater by electrocoagulation

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Abstract

Treatment of tannery wastewater by electrocoagulation with low cell current (≤ 1 A) and soluble electrodes (mild steel electrodes and aluminum electrodes) was studied. Compared with aluminum electrodes, mild steel electrodes were more effective for the removal of sulfide, with a removal efficiency of over 90%. But during the treatment process, black color precipitate typical to iron(II) sulfides was produced. While aluminum electrodes were effective to eliminate the colority of the effluent, the removal efficiency of sulfide was lower than 12%. The mechanisms of the removal of chemical oxygen demand, ammonia, total organic carbon, sulfide and colority with the two soluble electrodes (mild steel and aluminum electrodes) were discussed in detail. In order to exert the predominance of different types of electrodes, the tannery wastewater was treated using mild steel electrodes first followed by the filter and finally by the aluminum electrodes, the elimination rates of chemical oxygen demand, ammonia, total organic carbon, sulfide and colority were 68.0%, 43.1%, 55.1%, 96.7% and 84.3%, respectively, with the initial concentrations 2413.1 mg/L, 223.4 mg/L, 1000.4 mg/L, 112.3 mg/L and 256 dilution times, respectively. The absorbance spectra and energy consumption during electrocoagulation process were also discussed.

Key words: tannery wastewater; electrocoagulation; mild steel electrodes; aluminum electrodes

Introduction

It was reported that the total global quantity of bovine hides, sheep, goat and pigskins was nearly 8×10^6 t as wet salted weight a year and tanning workshop worldwide used 4×10^6 t of chemicals, produced over 3×10^8 t of wastewater and about 8×10^6 t of solid waste and dewatered sludge. Furthermore, these figures did not include the amount of salt used for preservation. Since possibly half of bovine hides were preserved by salt and hundreds of thousands tons of salt ended up in wastewater (Buljan, 2005).

Tannery wastewater, on the one hand, usually contained high concentrations of chlorides, aliphatic sulfonates, sulfates, aromatic and aliphatic ethoxylates, acrylic acid condensates, fatty acids, dyes, proteins, soluble carbohydrates and Na_2S (Murugananthan *et al.*, 2004a), on the other hand, the loadings of wastewater quality and quantity were very high posing a big problem for the treatment of tannery wastewater.

There were many processes for the treatment of tannery wastewater such as chemical coagulation (Bajza *et al.*, 2005; Song *et al.*, 2004), photodegradation (Sun *et al.*, 2006) and biodegradation (Suthanthararajan *et al.*, 2004; Ovez and Orhon, 2005; Lefebvre *et al.*, 2005; Murat *et al.*, 2003; Sui *et al.*, 2004). Chemical coagulation needed additional chemicals that caused a secondary pollution.

There were also disadvantages for the photodegradation of tannery wastewater because of the lower energy utilization efficiency. Although biodegradation process was cheaper than other methods, it was less effective because of the toxicity of the tannery wastewater that will affect the development of the bacteria.

Electrochemical methods for the treatment of wastewater have recently attracted great attention. It was found to be effective to treat dyes wastewater (Kim *et al.*, 2002; Gurses *et al.*, 2002; Kobya *et al.*, 2006a), arsenic-containing wastewater (Kumar *et al.*, 2004), phosphate-containing wastewater (Bektas *et al.*, 2004), electroplating wastewater (Adhoum *et al.*, 2004), metal finishing effluents (Khelifa *et al.*, 2005), poultry slaughterhouse wastewater (Kobya *et al.*, 2006b) and textile wastewater (Kobya *et al.*, 2003).

Recently many researches have been carried out on the electrolytic reduction of tannery wastewater. For example, Szpyrkowicz *et al.* (2001) studied the performance of electrochemical reactor for treatment of tannery wastewater by an undivided electrochemical reactor with parallel plate Ti/Pt-Ir anode and stainless steel cathode and suggested that the selectivity of the removal of different pollutants was affected by current density to a small extent. They also carried out electrochemical oxidation of tannery wastewater in an electrochemical reactor equipped with anodes based on noble metals and metal oxides (Ti/Pt-Ir, Ti/PbO₂, Ti/PdO-Co₃O₄ and Ti/RhOx-TiO₂) (Szpyrkowicz *et al.*,

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2005), and suggested that the rate of pollutant removal was significantly influenced by the type of anode material and electrochemical parameters.

However, the reports on the electrolytic decomposition contaminations in tannery wastewater by soluble electrodes, especially for the removal of ammonia in tannery wastewater using soluble electrodes, was relatively less. Only few works were published on the removal of tannery wastewater pollutants by electrocoagulation using soluble electrodes.

Murugananthan *et al.* (2004a) explained the electrocoagulation mechanism and kinetics of colloidal size suspended solids in tannery wastewater in detail. Zaroual *et al.* (2005) studied the removal effect of different pollutants with iron electrode used as a sacrificial anode during the treatment of tannery wastewater and several mechanisms for the pH variation in the electrolysis were suggested.

Compared with other methods, there were a few advantages for the treatment of tannery wastewater by electrocoagulation. Energy consumption could be decreased for the better conductivity due to the masses of salt and the reaction conditions could be easily controlled by changing the electro cell current or voltage. The fine bubbles and poly-nuclear hydroxy complexes produced by the electrocoagulation were effective to float and coagulate the pollutants (Mollah *et al.*, 2001; Chen, 2004).

In present study, the electrocoagulation effect and mechanisms of chemical oxygen demand (COD_{Cr}), total organic carbon (TOC), sulfide, colority and ammonia (NH₃-N) with low cell current (≤ 1 A) and different soluble electrodes (mild steel electrodes and aluminum electrodes) were compared in detail. The absorbance spectra, two-stage electrocoagulation and energy consumption during electrocoagulation process were also evaluated.

1 Materials and methods

1.1 Experimental device

The experimental device is depicted in Figs.1 and 2. As can be seen in Fig.1, a laboratory scale reactor consisted of an undivided electrocoagulation cell (0.1 m \times 0.15 m \times 0.2 m) made of organic glass with four anodes and three cathodes in parallel, all the electrodes were aluminum sheets (0.09 m \times 0.14 m, 2 mm thick) or mild steel sheets (0.09 m \times 0.14 m, 2 mm thick). The gap between anode and cathode was maintained at 10 mm to minimize the energy loss. In order to scoop out the floated material, a lip

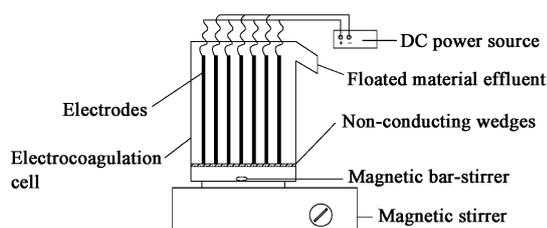


Fig. 1 Schematic diagram of the electrocoagulation cell.

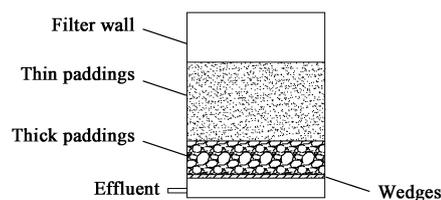


Fig. 2 Schematic diagram of the filter.

was provided on the front side of the cell. The filter (0.1 m \times 0.15 m \times 0.2 m) was also made of organic glass, which is shown in Fig.2. A sheet was placed above the bottom of the filter by 25 mm to underpin paddings. The thick paddings were made of carpolite (particle size 4–8 mm, thickness 30 mm), thin paddings consisted of quartzite (particle size 1–2 mm, thickness 90 mm). A DC stabilized power source was used to supply constant cell currents of 0–1 A at voltages 0–30 V (constant current source) (Hefei Yingdong Co., Ltd., China). All the experiments were carried out in static state.

1.2 Samples

Samples used in present study were collected from the first sedimentation tank of a tannery company in Ruji, Anhui Province, China. The typical qualities of the raw tannery wastewater are listed in Table 1.

Table 1 Qualities of the raw tannery wastewater

Parameter	Value	Parameter	Value
pH	7.0–8.5	Sulfide (mg/L)	100–120
TOC (mg/L)	900–1050	Colority (dilution times)	250–300
NH ₃ -N (mg/L)	200–230	Conductivity (mS/cm)	8–10
COD _{Cr} (mg/L)	2400–2600	Chloride (mg/L)	2700–2800
BOD ₅ (mg/L)	850–950		

1.3 Experimentation

For each experiment, 2.0 L sample was put in the electrocoagulation cell, pH and colority were measured at the end of the experiment, all the samples were centrifuged at 4000 r/min for 10 min before any analysis except pH and colority. The filter was used only in the two-stage electrocoagulation experiment. The solution was agitated with a magnetic stirrer (Jiangsu Ronghua Instrument Co., Ltd., China) during electrocoagulation process at 150 r/min. At the beginning of the experiment, the electrocoagulation cell was thoroughly washed and rinsed with de-ionized water followed by rinsing with the sample solution. All the experiments were repeated twice, and the experimental error was below 3%, the average data were reported.

1.4 Analysis

Standard methods were adopted for quantitative estimation of COD_{Cr}, TOC, NH₃-N, sulfide, BOD₅, pH and colority (State Environmental Protection Administration of China, 2002). Determination of COD was conducted by dichromate method. TOC determination was carried out with a TOC-5000A Shimadzu Total Organic Carbon Analyzer (Japan). Nessler's reagent colorimetric method

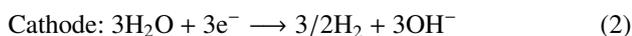
was used for the determination of ammonia. Determination of sulfide was carried out by methylene blue spectrophotometric method. Determination of BOD₅ was conducted by dilution and seeding method. The pH value was measured by pH monitor (Shanghai Kangyi Instrument Co., Ltd. China, PHS-2C). Colority was determined by dilution method. UV absorption scan at 190–350 nm was conducted by UV spectrophotometer (UV-2450, Shimadzu, Japan).

2 Mechanism of the electrocoagulation

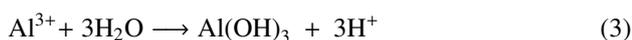
Electrocoagulation is a complex and interdependent process. A sacrificial metal anode is used to produce coagulating agent to dose the polluted water and electrolytic gases (mainly hydrogen at the cathode) are generated. Electrochemistry, coagulation and hydrodynamics form the basis of electrocoagulation (Holt *et al.*, 2002).

The most widely used electrode materials in electrocoagulation process are aluminum and iron, sometimes steel. The electrical current causes the dissolution of metal into wastewater. The metal ions, at an appropriate pH value, can form wide ranges of coagulated species and metal hydroxides that destabilize and aggregate the suspended particles or precipitate and adsorb dissolved contaminants (Daneshvar *et al.*, 2006).

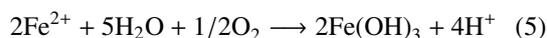
In the case of aluminum, main reactions are as (Daneshvar *et al.*, 2006):



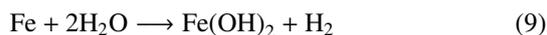
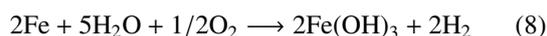
The generated Al³⁺ and OH⁻ react with each other to form Al(OH)₃.



While in the case of iron or mild steel electrodes, the mechanisms for the production of metal hydroxide are as (Zaroual *et al.*, 2006; Daneshvar *et al.*, 2003, 2004):



Overall reaction:

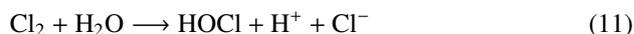


During electrocoagulation process, metal hydroxides formation occurs, these flocs have a large surface area, which are beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles. Finally, these flocs are removed easily from aqueous medium by sedimentation or flotation.

Because of the characteristic of the tannery wastewater, molecular chlorine generates during electrolysis (Daneshvar *et al.*, 2006; Kim *et al.*, 2005):



The generated molecular chlorine is hydrolyzed to form hypochlorous acid and hypochlorite ion.



The hypochlorous acid and hypochlorite ion can decompose organism because of their high oxidative potentials. Meanwhile, if the anode potential is high enough, other reactions such as direct oxidation of organic compounds may occur at the anode.

3 Results and discussion

3.1 Changes of pH values

The electrocoagulation treatment using aluminum electrodes induced an increase in the pH value when the initial pH value of the tannery wastewater was 7.85 (Fig.3), which could be explained by the excess of hydroxyl ions produced at the cathode and by the liberation of OH⁻ due to the occurrence of a partial exchange of Cl⁻ with OH⁻ in Al(OH)₃ (Vik *et al.*, 1984). While the solution pH stabilizes at nearly constant value around 8.7, which may be ascribed to the buffering capacity of complex nature of aqua Al³⁺/Al(OH)₃ system (Kobyta *et al.*, 2006a). In the case of mild steel electrodes, pH value increases gradually during the electrocoagulation process (Fig.3). This may be due to the formation of FeS, which was coincident with the literature (Muruganathan *et al.*, 2004b).

3.2 Effect of cell current on the efficiency of COD_{Cr} removal

It has been established that cell current is one of the important parameters to control the reaction rate in the electrochemical processes (Adhoum *et al.*, 2004). Fig.4 shows COD_{Cr} removal behavior when cell current was varied from 0.4 to 1.0 A. For a given time, the removal efficiency increased with the increasing of cell current. The COD_{Cr} removal process may involve electrochemical oxidation and adsorption by electrostatic attraction and physical entrapment (Zaroual *et al.*, 2006). The highest cell current produced the quickest treatment reduction occurring after 60 min. It may be the fact that the amount

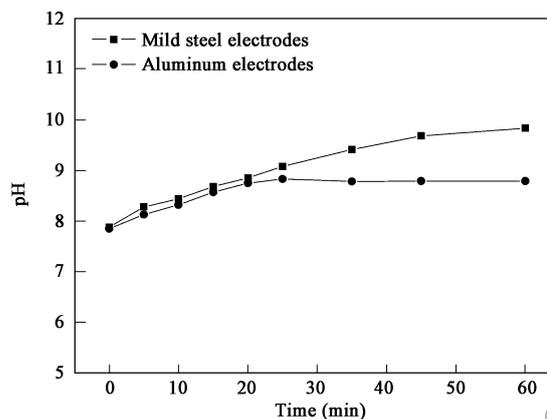


Fig. 3 Changes of pH values during electrocoagulation process.

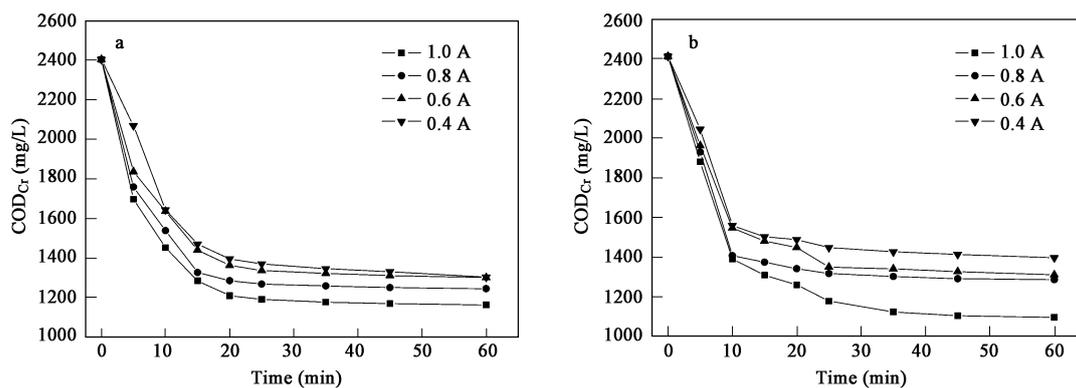


Fig. 4 Effect of cell current on the efficiency of COD_{Cr} removal. (a) anode and cathode are aluminum; (b) anode and cathode are mild steel.

of cell current determined the coagulant production rate, and adjusted the rate and size of the bubble production. At higher cell current, the amount of metal oxidized increased, resulting in a greater amount of hydroxide flocs for the removal of pollutants. Furthermore, the bubbles density increased and their size decreased with the increasing of cell current, resulting in a faster removal of pollutants (Adhoum and Monser, 2004; Carmona *et al.*, 2006). The efficiency of COD_{Cr} removal depended on the quantity of hydroxide flocs, which was bound with time and cell current of electrocoagulation. When one of the two parameters increased, the distribution of the coagulation agent density was more effective (Zaroual *et al.*, 2006). The concentration of COD_{Cr} decreased rapidly in the first 10 min of the electrocoagulation process, but with progress of treatment higher diffusional resistance came over to the surface of anode reduced the rate, consequently, high removal efficiency of COD_{Cr} were observed at high time and high cell current (Golder *et al.*, 2005). The lower removal efficiency at low time and cell current could be explained by the fact that the amount of precipitate formed was not enough and large part of COD_{Cr} in the tannery wastewater was soluble (Song *et al.*, 2004). There were no significant differences between mild steel electrodes and aluminum electrodes for the elimination of COD_{Cr} under the same condition.

3.3 Removal of TOC, sulfide, colority and NH₃-N

Obviously, the elimination rates of TOC improved with the extension of electrocoagulation time (Fig.5a). Under the same condition, the elimination rate of TOC using aluminum electrodes was higher than that of mild steel

electrodes. The removal of TOC by electrocoagulation could be due to the removal of suspended solids and precipitation of dissolved organic molecules. The TOC removal process may also involve electrochemical oxidation and adsorption by electrostatic attraction and physical entrapment (Muruganathan *et al.*, 2004b). As can be seen from Fig.5a, TOC concentration decreased in the first 15 min at a relatively high rate compared to that after 45 min of the reaction time. For example, the concentration of TOC decreased with a rate of 32.0 mg/(L·min) in the first 15 min at an initial concentration of 1007 mg/L using aluminum electrodes, while the rate fell to 0.5 mg/(L·min) in the last 45 min, which was similar to the removal of COD_{Cr}.

As shown in Fig.5b, the initial decomposition of sulfide was quite fast, the concentration of sulfide was reduced by 91.9% during the first 5 min of electrocoagulation using mild steel electrodes. It was an indication of the very fast rate of elimination, while the color of the solution became dark. In the case of aluminum electrodes, the elimination rate of sulfide was very low, less than 12%. However, the color of the solution became pale after electrocoagulation. The colority changes during electrocoagulation treatment are shown in Table 2.

Depending on the pH, sulfide exists as H₂S, HS⁻ and S²⁻. Because of the dissolving of the metal on the surface of the electrodes, in the case of mild steel electrodes, Fe²⁺ was released into the liquor (Reaction (4)) and converted to Fe³⁺ partly for the oxidation of the electrode or in the circumstance of oxidation (Reaction (12)).

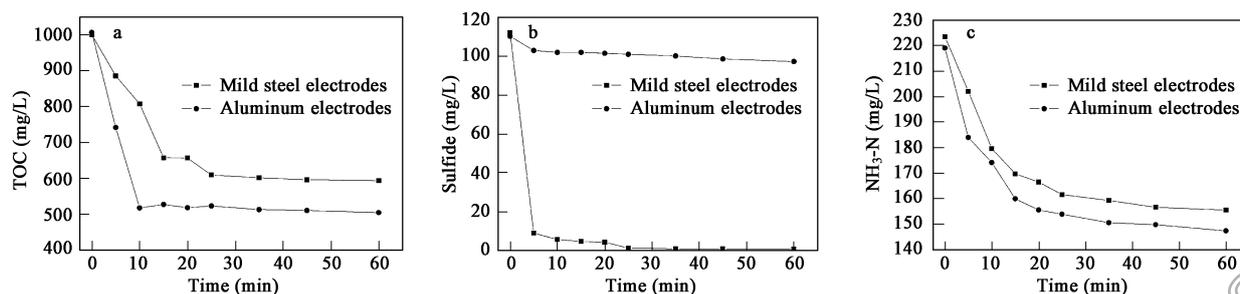


Fig. 5 Changes of the concentrations of TOC (a), sulfide (b) and NH₃-N (c) during electrocoagulation process (cell current: 1 A).

Table 2 Colority changes during electrocoagulation treatment (unit: dilution times)

Electrode material	Raw wastewater	Time (min)							
		5	10	15	20	25	35	45	60
Aluminum	256	80	50	40	20	20	20	20	20
Mild steel	256	1000	1200	1500	2000	2000	2000	2000	2000

Cell current was 1 A.

As a result of the reaction between Fe^{2+} , Fe^{3+} and H_2S , HS^- , S^{2-} species, black color FeS precipitate which was insoluble appeared and the color of the liquor became dark quickly, the concentration of sulfide dropped rapidly (Reactions (13), (14), (15)) (Muruganathan *et al.*, 2004a).



Furthermore, sulfide could be also partially oxidized by Fe^{3+} . Precipitates of ferric hydroxides formed were converted to FeS by sulfide ions by reductive dissolution mechanism (Poulton *et al.*, 2002). According to the literature (Muruganathan *et al.*, 2004b), the species pyrite, marcasite, elemental sulfur and FeS_2 could also be detected.

In the case of aluminum electrodes, different species formed, highly charged polynuclear hydroxy aluminum complexes, such as $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_7(\text{OH})_{17}^{4+}$, $\text{Al}_{13}(\text{OH})_{34}^{5+}$, $\text{Al}_3(\text{OH})_4^{5+}$, $\text{Al}(\text{OH})_6^{3-}$, $\text{Al}(\text{OH})_7^{4-}$ and AlO_2^- , were contained in the liquor (Muruganathan *et al.*, 2004a). At the same time interaction between Al^{3+} and sulfide led to the formation of Al_2S_3 , because of the instability of Al_2S_3 in the solution, Al_2S_3 was converted to $\text{Al}(\text{OH})_3$ ($K_{\text{sp}} = 2 \times 10^{-33}$) and sulfide was released again, which explained the low elimination rate of sulfide. These poly-nuclear hydroxy aluminum complexes could coagulate colloidal solids in the samples, which was helpful to removal the sample colority (Muruganathan *et al.*, 2004a). The colority removal may involve physically adsorption by these hydroxy aluminum complexes and altering some of the substituents which determine the color (Zaroual *et al.*, 2006).

As shown in Fig.5c the concentration of $\text{NH}_3\text{-N}$ was reduced from 223.4 to 155.5 mg/L using mild steel electrodes during the first 60 min, while in the case of aluminum electrodes from 219.1 to 147.4 mg/L, the corresponding elimination rates were 30.4% and 32.7%, respectively. The removal of $\text{NH}_3\text{-N}$ could probably be due to the generated chlorine, physical entrapment and hydrogen bubbles at higher pH. Hernlem and Tsai have observed the generation of molecular chlorine even at low cell current (0.8 A) (Hernlem and Tsai, 2000). Furthermore, there was an increase of pH value during electrocoagulation process (Fig.3), which was favorable to the $\text{NH}_3\text{-N}$ blow-off.

The electrodes used in the experiment were reactive leading to the erosion of the metal, thus the protective oxide film formed (Hu *et al.*, 2003). The film increased the potential and led to the discharge of chlorine ions,

chlorine gas generated during the electrolysis (Reaction (10)) (Daneshvar *et al.*, 2006; Kim *et al.*, 2005).

The generated molecular chlorine was hydrolyzed to form hypochlorous acid (Reaction (11)) which was consecutively changed to hypochlorite ion, depending on the pH. The hypochlorous acid and hypochlorite ion could decompose ammonia to nitrogen gas because of their high oxidative potentials (Reactions (16), (17)), and the overall reaction was analogous to the break-point chlorination (Eckenfelder and Argaman, 1991).



3.4 Absorbance spectra of the tannery wastewater

Figure 6 illustrates the adsorption spectra of the tannery wastewater before and after electrocoagulation process. There were several peaks in the spectra, which had the higher absorbance around 190–250 nm. It was interesting to note that the absorbance of the curve decreased when the electrocoagulation treatment was applied, which showed the removal of pollutants indirectly.

3.5 Effect of the two-stage electrocoagulation

In order to exert the predominance of different types of electrodes, tannery wastewater was treated using mild steel as electrodes first under the conditions of electrocoagulation time 20 min and cell current 1 A, followed by the filter and finally by the aluminum electrodes at electrocoagulation time 20 min and cell current 1 A. Results of the two-stage electrocoagulation are shown in Table 3. During the first stage, sulfide was converted to $\text{Fe}(\text{II})$ sulfides using mild steel electrodes, the concentrations of TOC, $\text{NH}_3\text{-N}$, COD_{Cr} also decreased, in the following

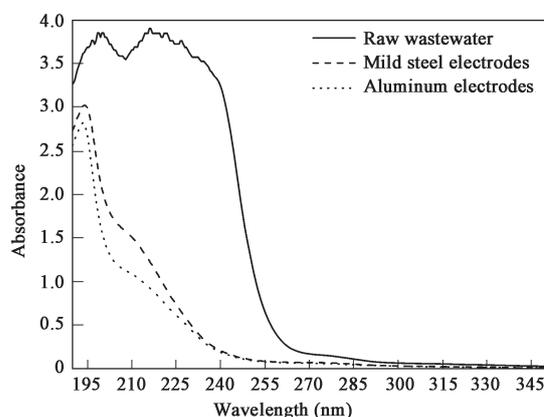


Fig. 6 Absorbance spectra of tannery wastewater before and after electrocoagulation. Electrocoagulation time: 60 min; cell current: 1 A.

Table 3 Effect of the two-stage electrocoagulation (cell current: 1 A)

Parameter	Conc. (initial) (mg/L)	Conc. (the 1st stage) (mg/L)	Conc. (the 2nd stage) (mg/L)	Removal rate (the 1st stage) (%)	Removal rate (the 2nd stage) (%)	Total removal rate (%)
TOC	1000.4	656.9	448.7	34.3	31.7	55.1
NH ₃ -N	223.4	166.5	127.2	25.5	23.6	43.1
BOD ₅	868.7	506.3	332.0	41.7	34.4	61.8
COD _{Cr}	2413.1	1259.7	772.2	47.8	38.7	68.0
Sulfide	112.3	4.1	3.7	96.3	9.8	96.7
Colority	256 dilution times	100 dilution times*	40 dilution times	60.9*	60	84.3

*Value after the filter. Conditions: electrocoagulation time 20 min; cell current 1 A.

aluminum sheets were used as electrodes to facilitate coagulation and float the contaminations. The removal rates of contaminations in the first stage were higher than those of the second stage. After the two-stage electrocoagulation the elimination rates of COD_{Cr}, NH₃-N, TOC, sulfide, and colority were 68.0%, 43.1%, 55.1%, 96.7% and 84.3%, respectively, with the initial concentrations 2413.1 mg/L, 223.4 mg/L, 1000.4 mg/L, 112.3 mg/L and 256 dilution times, respectively.

3.6 Energy consumption

The COD_{Cr} reduction efficiency was defined from the initial and final COD_{Cr} concentrations. The electrical energy consumed, expressed as kWh/m³ of the wastewater treated. COD_{Cr} reduction against power consumed has been plotted in Fig.7. Energy consumption in kWh/m³ of wastewater has been obtained from the data generated at cell current 1 A. The plot indicated a rapid initial reduction of COD_{Cr}, COD_{Cr} reduction of 1.12 kg was noted at the energy consumption of 0.25 kWh/m³ in the case of aluminum electrodes, the corresponding COD_{Cr} removal rate was 46.6%. At the same energy consumption, COD_{Cr} reduction of 1.10 kg was observed in the case of mild steel electrodes and the corresponding removal rate was 45.8%.

In the two-stage electrocoagulation experiment reaction time was 40 min, with the cell current 1 A, voltage 2 V (max.). According to the data above, the maximum power of the two-stages electrocoagulation system was 2.7 W (considering the energy loss of 25%), thus the average energy consumption was 0.89 kWh/m³ tannery wastewater.

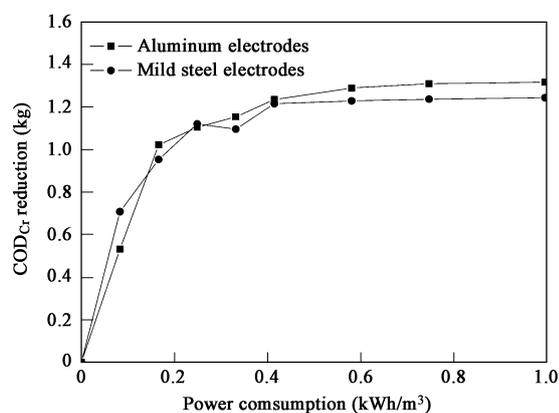


Fig. 7 COD_{Cr} reduction vs. power required during electrocoagulation process (cell current: 1 A).

4 Conclusions

The performance of a parallel-plate electrocoagulation system for the treatment of tannery wastewater was investigated. The experimental results revealed that the COD_{Cr}, NH₃-N, TOC, sulfide removal efficiency could be enhanced by increasing either the cell current or the electrocoagulation time. The concentration of each pollutant except the colority and sulfide decreased in the first 15 min at a relatively high rate compared to that after 45 min of the reaction time. The mild steel electrodes were more effective for the removal of sulfide compared with the aluminum electrodes, while the aluminum electrodes were more effective for the colority elimination of the effluent. The performance of the two-stage electrocoagulation was perfect, it could be used as the pretreatment of the biological processes for tannery wastewater treatment for BOD₅/COD_{Cr} was raised from 0.36 to 0.43 (after two-stage electrocoagulation) and the harmful matters to the bacteria were partly eliminated.

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