Korean J. Chem. Eng., **25**(4), 703-709 (2008)

Simultaneous removal of organic and inorganic pollutants in tannery wastewater using electrocoagulation technique

Sangkorn Kongjao, Somsak Damronglerd, and Mali Hunsom†

Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Phaya Thai Rd., Bangkok, 10330, Thailand
(*Received 22 November 2007 • accepted 14 January 2008*)

Abstract−Tannery wastewater can cause severe environmental problems related to its high chemical oxygen demand, high biochemical oxygen demand, high total suspended solids, high oil and grease contents together with the elevated chromium concentration and objectionable color. The one-step electrocoagulation process was carried out to simultaneously remove chromium and various pollutants from tannery wastewater at ambient temperature in the laboratory scale. Low-cost commercial iron plates were employed in this study as anodes and cathode materials. Effects of various parameters were investigated including types of electrode configuration, initial pH of wastewater (7-9), current density (15.7-24.6 Am^{-2}) and circulating flow rate of wastewater (0-3.67 $lmin^{-1}$). The optimum condition was found by applying the mono-polar electrode in a parallel connection at the current density of 22.4 Am^{-2}, flow rate of wastewater of 3.67 $lmin^{-1}$ and 20 min electrolysis time. The initial pH of wastewater ranging from 7-9 provided the similar removal efficiency. At optimum condition, more than 95% of chromium and pollutants except TKN and TDS were eliminated from the wastewater and the properties of the treated wastewater met the standard and permitted to discharge into the environment. The required energy consumption at optimum condition was less than 0.13 $kWhm^{-3}$ wastewater. In addition, the COD reduction was fit very well with the first-order kinetics model.

Key words: Tannery Wastewater, Electrocoagulation, Chromium, Oil and Grease, Current Efficiency

INTRODUCTION

Tannery wastewater is a powerful pollutant that can cause severe environmental problems related to its high chemical oxygen demand (COD), biochemical oxygen demand (BOD) together with elevated chromium concentration and deep color content. The strength parameters employed are COD, BOD, total suspended solids (TSS), total dissolved solid (TDS), total kjeldahl nitrogen (TKN), oil and grease. In Thailand, more than 14,000 ton $year^{-1}$ of leather are produced which generate more than 2.55×10^6 m^3 of wastewater $year^{-1}$. Many conventional processes were carried out to treat wastewater from tannery industry such as biological process [1-5], oxidation process [6-8] and chemical process [9-11], etc. One of the most interesting and effective processes for treating some pollutants in tannery wastewater is the electrochemical process because it can be applied in various techniques such as electrocoagulation, electrooxidation, electrodewatering, etc. [12-14]. The efficiency of this process is more sensitive to the type of electrodes used in the process. Ti/Pt-Ir anode is more efficient for treating the pre-treatment tannery wastewater than Ti/Pt and graphite [15]. For tannery wastewater without pre-treatment, however, a Ti/Pt-Ir anode was proved to have the electrocatalytic properties for NH_4^+ removals, but it resulted in being more sensitive to poisoning by H_2S contained in the wastewater [16]. The reaction was a pseudo first order reaction and the amount of chloride in the solution increased as a function of the electrolysis time [17,18]. Contamination of sulfides and organic compound in wastewater from liming and unhairing of the tannery process was reduced approximately 100% by using Ti/MnO_2 as the anode. However, only 50% of sulfides were removed from chrome-tanning [19]. Soluble anodes such as aluminum and iron were found to be very effective in eliminating pathogenic bacteria and color compared to stable anode such as Ti/Ir-Ta-Ru [20]. Focusing on chromium removal from tannery wastewater; trivalent chromium containing wastewaters were oxidized independently in alkaline conditions with aqueous oxidants to soluble chromate. Hydrogen peroxide was potentially a suitable oxidant as it could oxidize a suspension of $Cr(OH)_3$ to chromate to 98% (synthetic solution) and 88% (wastewater) [21]. A process named IERECHROM® has been developed based on the use of a weak electrolyte macroporous carboxylate resin, retaining the metal of reference together with other trace metals, including aluminum and iron [22]. The result indicated that this process allows the removal and separation of almost pure chromium (>99.9%) from other interfering metals, and the sludge production has less than 0.1% chromium content. Recovery of chromium by using a real-sized pilot plant was carried out by using a precipitation process with MgO and Na_2CO_3 [23]. The results showed that the MgO precipitation scenario was proven to be able to pay back economically within 3 years. Instead of using synthetic wastewater as in many previous works, the treatment of real wastewater from a tannery plant was carried out here by using the electrocoagulation technique. The effects of some parameters including current density, initial pH of solution and flow rate of wastewater were explored.

EXPERIMENTAL

The experiment was conducted in a bench-scale laboratory at ambient temperature (around 30 °C) by employing actual wastewater containing chromium and organic contaminants (Table 1) com-

†To whom correspondence should be addressed.
E-mail: mali.h@chula.ac.th

Table 1. Characteristics of wastewater from tannery industry in Thailand

Characteristics	Standard (Thailand)	Content (Before treatment)	Content (After treatment)
pH	5.5-9	7.0-8.7	8.22-8.24
Temperature (°C)	≤40	27-29	30
Conductivity (μscm^{-1})	-	2,480-2,840	2,900
TDS (mg l^{-1})	≤3,000	13,300-19,700	9,812
TSS (mg l^{-1})	≤150	600-955	30
COD (mg l^{-1})	≤400	4,100-6,700	352
TKN (mg l^{-1})	≤100	144-170	60
BOD (mg l^{-1})	<60	630-975	30
Cr (mg l^{-1})	≤0.5	11.5-14.3	0.019
Fe (mg l^{-1})	-	0.10-0.11	0.22
Color (Pt-Co unit)	Not objectionable	3,800-6,330	Not objectionable
Oil and grease (mg l^{-1})	≤15	638-780	7.92
Other components (Cl, S, N, Al, Ca, etc.)			

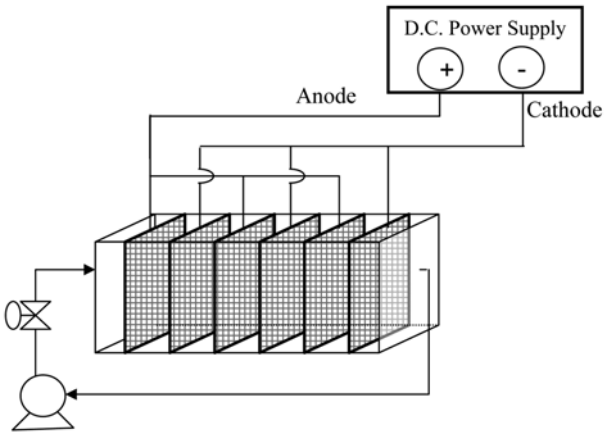

Fig. 1. Schematic view of electrocoagulation reactor.

ing from tannery plant in Thailand. The electrocoagulation cell was constructed with Plexiglas having a dimension of 0.12×0.21×0.15 m (Fig. 1). The total volume of wastewater in each experiment was approximately 0.003 m^3. Low-cost iron plate with total surface area of 0.0161 m^2 was used as the sacrificial electrodes. The electrodes rearrangement included both monopolar and dipolar configurations. In each batch, six iron plates were constructed in the electrochemical reactor and the distance between plates was fixed at approximately 0.05 m. To achieve good mass transfer in the system, a magnetic pump (Model NH-5PX type) was used to circulate the electrolyte in the reactor. A regulated DC power supply (ZS 3205-2X type) was employed to supply the external electricity. During the treatment, the properties of wastewater were analyzed at a time interval following the standard method [24], and the chromium concentration in the treated wastewater was analyzed by using an atomic absorption spectrophotometer (GBC Avanta Σ).

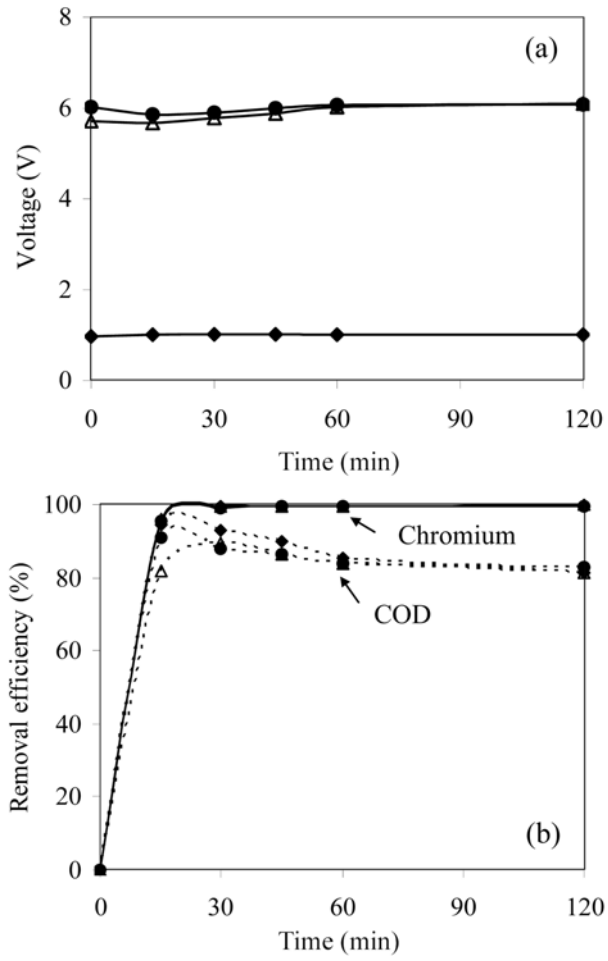

Fig. 2. Effect of electrode configuration as a function of electrolysis time at current density of 20.1 Am^{-2}. Monopolar electrodes in parallel (◆) and in series connections (●) and dipolar electrodes in parallel connections (△).

RESULTS AND DISCUSSION

1. Effect of Electrode Configuration

The experiments were performed in a bench-scale electrocoagulation reactor with three types of electrode configuration including the monopolar electrodes in series and parallel connections and dipolar electrodes in parallel connections with initial pH of wastewater of 7, flow rate of wastewater of 3.67 lmin^{-1}, and applied current

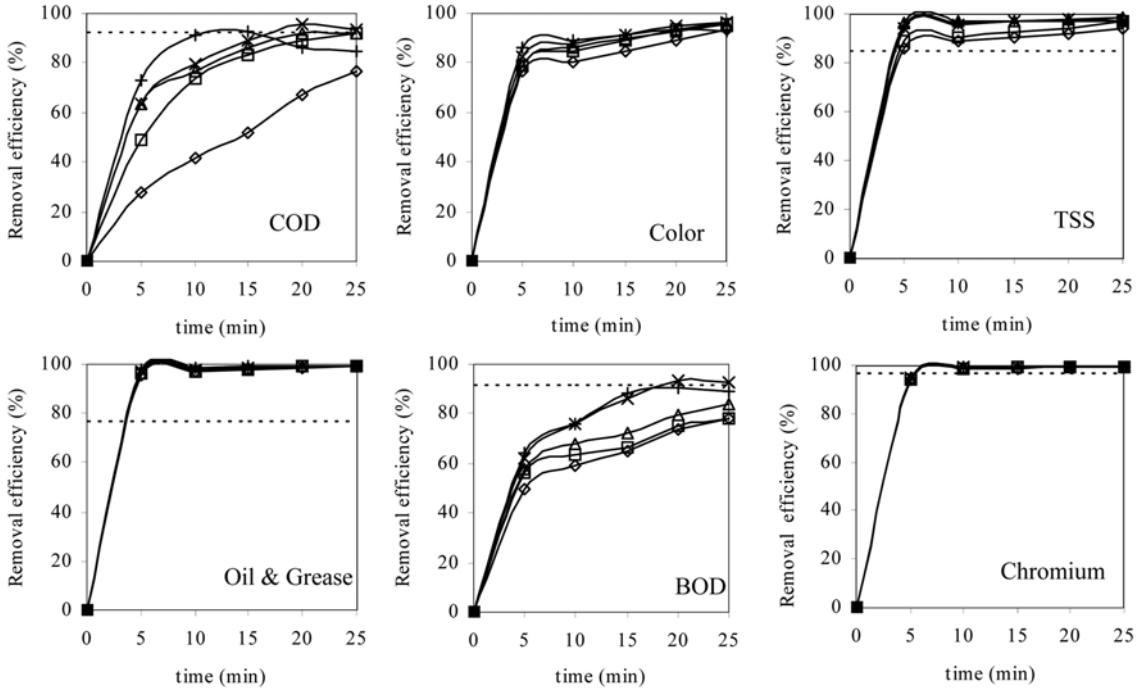

Fig. 3. Effect of current density on removal rate of COD, color, TSS, oil & grease, BOD and chromium at various current densities. 15.7 Am^{-2} (◇); 17.9 Am^{-2} (□); 20.1 Am^{-2} (△); 22.4 Am^{-2} (×); 24.6 Am^{-2} (+); the acceptable value of pollutants (---).

density of 20.7 Am^{-2}. The results demonstrated that high potential was required for driving the current to flow for the system having monopolar electrodes in series connections and in dipolar electrodes in parallel connections. Namely, they required an applied voltage approximately 6-times higher than that of the monopolar in parallel configuration as shown in Fig. 2(a). This can be explained as that the distance between anodes and cathodes in the parallel monopolar configuration was shorter than that of two others, which leads to lower electrolyte resistance. For the same amount of applied current density, the system with low electrolyte resistance required low voltage for driving the electricity flow through the system. Focusing on the removal efficiency of some contaminants in tannery wastewater, it was found that all electrode configurations provided more than 98% of chromium removal within 15 minutes as shown in Fig. 2(b). However, the configuration as the monopolar electrodes in parallel connections can promote the highest COD removal compared with two other configurations, namely, it was around 94% at the first 15 minutes. This is because the distance between electrodes in the parallel monopolar configuration was shorter as recommended above, leading to a good attractive force between the monomeric or polymeric species generated in the system and the molecules of pollutant. However, for all cases, the removal efficiency of COD decreased slowly when electrolysis time increased. This is because the generated ferrous species can react with the dissolved oxygen as expressed by Eq. (1) leading to the decrease of the amount of dissolved oxygen in the treated wastewater [25].

$$4Fe^{2+}+O_2+10H_2O \rightarrow 4Fe(OH)_3+8H^+ \quad (1)$$

2. Effect of Current Density

The effect of current density was also investigated in this type of wastewater because the supply of current indicates the amount of ferrous ions produced from the respective electrodes. A large current means a small electrocoagulation unit; however, there is a huge chance of wasting electrical energy in heating up the water [14]. The experiments were carried out with the wastewater at initial pH of 7 and flow rate of wastewater of 3.67 $lmin^{-1}$ with the applied current density in the range of 15.7-24.6 Am^{-2}. Fig. 3 shows the removal efficiency of various contaminants as a function of operating time, and the dashed line indicates the acceptable limit set by the Thai government calculated from the initial concentration of each value. It was found that the removal percentage of all pollutants increased as a function of current density. This is because when high current was supplied to the system, a large amount of monomeric and polymeric species were produced according to Faraday's law, leading to the decrease of pollutants in the system. According to the results of this part, for removal of chromium together with all pollutants, the optimum current density was found to be at 22.4 Am^{-2} and electrolysis time greater than 20 min. The charge loading indicating the amount of metal produced in the process was also calculated. It was found that approximately 967 $mgA^{-1}\ h^{-1}$ was obtained at this condition. This value was close to the recommended value (1,041 $mgA^{-1}\ h^{-1}$) of the previous work [14].

3. Effect of Circulating Flow Rate

Fig. 4 displays the effect of circulating flow rate of wastewater in the reactor ranging from 0-3.67 $lmin^{-1}$ on the removal efficiency of various pollutants at current density of 22.4 Am^{-2}, initial pH of wastewater of 7 and electrolysis time of 20 min. It was found that the removal percentage increased as a function of flow rate. Namely, high flow rate provided high removal efficiency for all pollutants. This is because high circulating flow rate can promote either turbulent flow or collision occasion between active species and pollutant molecules.

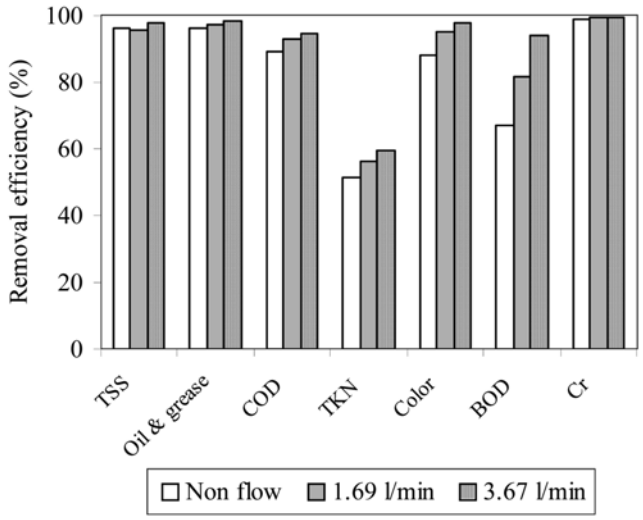

Fig. 4. Plot of removal efficiency of various pollutants at different flow rates.

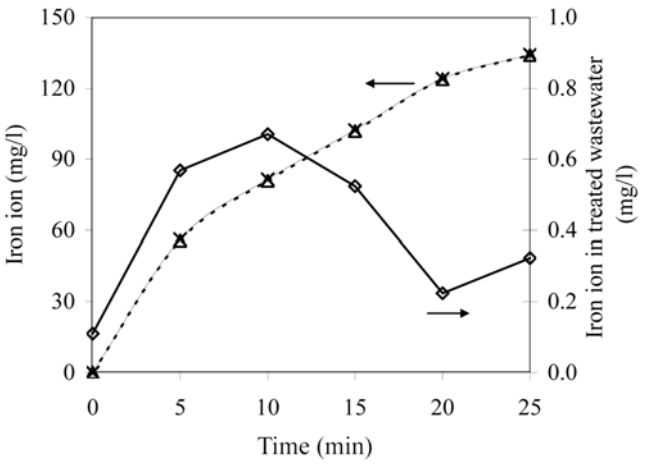

Fig. 6. Amount of iron ions generated from anode (×); iron ions in sludge (△) and iron ions in the treated wastewater (◇).

4. Effect of Initial pH of Wastewater

Fig. 5 displays the removal efficiency of all investigated pollutants as a function of initial pH of wastewater at current density of 22.4 Am^{-2}. It seemed to be that the initial pH in the range of 7-9 provided a similar effect on the removal efficiency of all pollutants. This can be explained as that the structures of ferrous in the system in the pH range of 7-9 were the monomeric ($Fe(OH)_3$) and the polyhydroxyl iron (III) complexes such as $Fe(OH)^{2+}$, $Fe(OH)_2^+$, $Fe(H_2O)_5OH^{2+}$ and $Fe(H_2O)_4(OH)_2^+$ which can be combined with the pollutant molecules causing the coagulation [26]. According to all the above results, it can be concluded that the optimum condition for treating tannery wastewater containing either chromium or various kinds of pollutant was found at a current density of 22.4 Am^{-2}, circulating flow rate of wastewater in the reactor of 3.67 $lmin^{-1}$, initial pH of 7-9, and 20 min electrolysis time by employing the monopolar electrode in parallel configuration.

Fig. 6 shows the quantity of iron ions generated from the oxidation reaction at anode, iron ions in sludge and iron ions remaining in the treated wastewater by using the electrocoagulation process at optimum condition. It can be seen that the amount of iron ions generated from anode and in sludge increased as a function of electrolysis time and they were equal. This phenomenon indicated that the iron ions generated from anode could be combined with the pollutant species leading to the coagulation process for all electrolysis time. Nevertheless, a small amount of iron ions remained in the treated wastewater. Namely, approximately 0.22 mgl^{-1} remained in the treated wastewater at 20 min electrolysis time, but this value is permitted to discharge into the environment.

The current efficiency (CE), which is the ratio of amount of liberated iron over the theoretical amount of liberated iron, was calculated according to Faraday's law as expressed by Eq. (2). As seen clearly from Fig. 7, the current efficiency was greater than 100% at

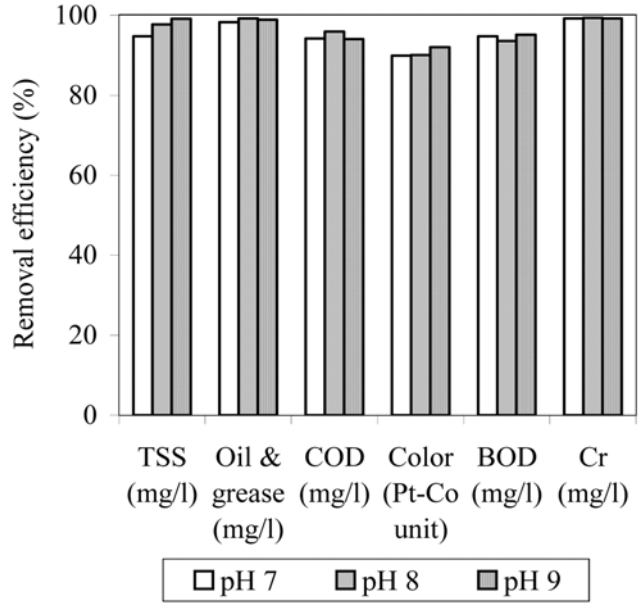

Fig. 5. Plot of removal efficiency of various pollutants at different initial pH.

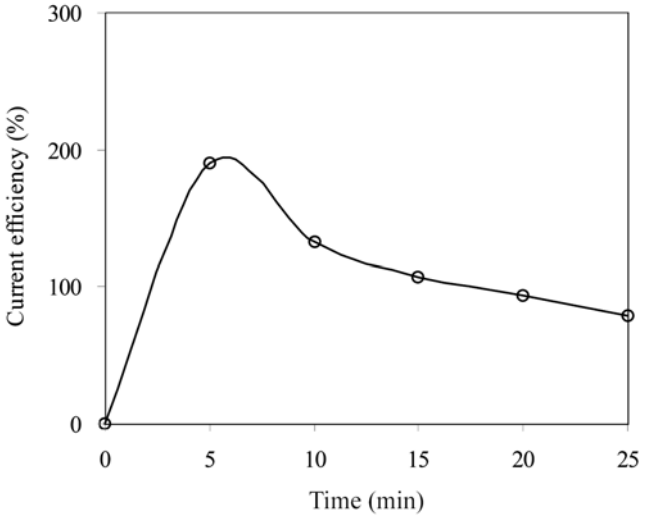

Fig. 7. Current efficiency as a function of electrolysis time at current density of 22.4 Am^{-2}.

early electrolysis time similar to many previous works [27,28]. This may be attributed to two reasons. The first one is the effect of pitting corrosion especially observed when chloride ions are present in the wastewater [14]. The second one is due to the applied current being the sum of partial currents due to anodic oxidation and cathodic reduction of dissolved oxygen [28]. The current efficiency, however, decreased dramatically when electrolysis time increased, namely, it decreased from around 190% at 5 min to 78% at 25 min. This is because the trapping or bridging of colloidal particles formed as a result of the coagulation process on the electrode surface, leading to lower the effective surface area of electrode. Consequently, the energy consumption (EC), i.e., the electricity used in this process, was also calculated by using Eq. (3). It was found that the energy consumption increases as a function of electrolysis time. At optimum condition, it was around 0.13 $kWhm^{-3}$ wastewater. Furthermore, the operating cost related to costs of electrode cost, electricity cost and landfill cost of the generated sludge of this treatment process were also investigated. They were around 0.34 $US\$m^{-3}$ wastewater (1 US$=39.5 Baht) which is lower than that of the conventional process used in tannery industry in Thailand (0.36-0.44 $US\$m^{-3}$).

$$CE = \frac{nFm}{M_w It} \quad (2)$$

$$EC = \frac{ItV}{36Q} \quad (3)$$

The kinetics of the COD removal calculated by using a macro-kinetics model was also explored. The kinetics rate law for explaining the reduction of COD concentration was the first-order kinetics model. Fig. 8(a) demonstrates the series plot of $\ln[COD]_t/[COD]_0$ as a function of current density. Very good agreement between the first-order model and the experimental results was obtained with a coefficient of determination, R^2, greater than 0.95. The rate constant was directly proportional to the applied current density as displayed in Fig. 8(b), namely, it increased when the current density increased similar to the results of Kim et al. [29].

$$[COD]_t = [COD]_0 \exp(-kt) \quad (4)$$

Table 2 displays the comparison of the removal efficiency obtained from this work and other works. It can be seen that the electrocoagulation process provides a higher removal efficiency of pollutants

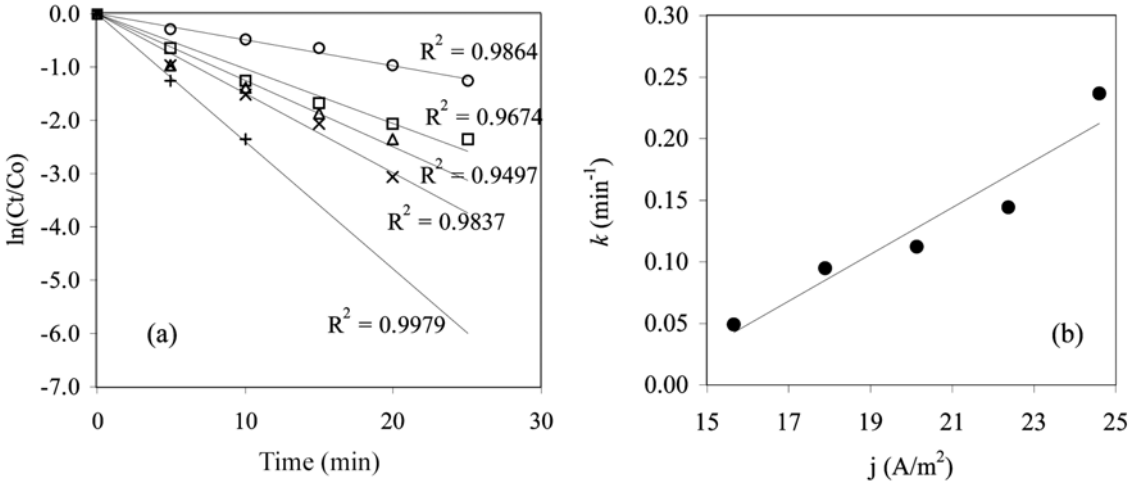

Fig. 8. (a) Plot of first-order kinetics of COD as a function of current density; 15.7 Am^{-2} (○); 17.9 Am^{-2} (□); 20.1 Am^{-2} (△); 22.4 Am^{-2} (×); 24.6 Am^{-2} (+); and (b) the obtained rate constant as a function of current density.

Table 2. Comparison of removal efficiency of all pollutants in this work and that in other works

Authors	Treatment process	COD		BOD		Cr		TSS		TKN		TDS		Oil & grease	
		(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
Ram et al. [31]	Chemical	3,714	58	1,126	42	8.3	58	1,147	25	-	-	11,737	−12	-	-
Di Iaconi et al. [9]	Biological	3,790	93	-	-	-	-	2,200	99	294	91	-	-	-	-
Balakrismsn et al. [32]	Ozone	737	811	601	60	-	-	-	-	-	-	-	-	-	-
Maruganuthan et al. [20]	Electroflotation	3,092	52	1,750	53	3	99	3,036	92	-	-	-	-	-	-
Kongjao et al. [33]	Electroprecipitation	17,600	82	3,540	74.6	19.5	99	8,200	59.8			18,680	−61	680	86
This work	Electrocoagulation	6,758	95	780	96	12.59	100	848	96	158	62	19,644	−50	774	99

(a) Initial concentration of pollutants in wastewater before treatment (mg l^{-1}).
(b) Removal efficiency of each pollutant after treatment (%).

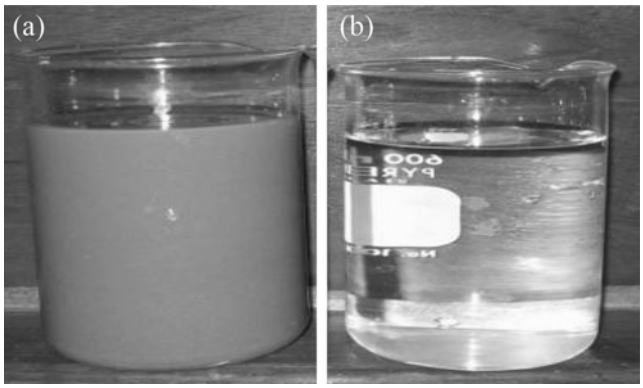

Fig. 9. Tannery wastewater (a) before and (b) after treatment by electrocoagulation technique.

than that of other processes. The chemical process, for example, can remove merely 58% of COD and 42% of BOD, respectively, whereas they were around 98% and 97% by using the electrocoagulation process. In addition, adding chemical reagent in the chemical treatment process led to the increase of TDS around 12%, while this process can remove such pollutants around 50%. Although the biological process can provide similar removal efficiency of COD and TSS compared with that of the electrocoagulation process, it requires a large treatment area and generates a large amount of low-density sludge, which leads to a disposal problem [30]. The characteristics of wastewater after treatment are already demonstrated in Table 1. All pollutants were markedly reduced to the level of discharge permission of the government except TDS. It was still higher than the standard around 3-fold. Fig. 9 shows an example of tannery wastewater before and after treatment by using electrocoagulation at our optimum condition. The color of wastewater after treatment is clear and unobjectionable in comparison with that before treatment.

CONCLUSION

The electrocoagulation process was performed to remove the pollutants in tannery wastewater. The results demonstrated that the electrode configuration in the parallel monopolar connections was more suitable in the treatment process than the other configurations because it required low applied voltage for driving the same amount of current in the system. The optimum condition for treating tannery wastewater was found at current density of 22.4 Am^{-2}, circulating flow rate of wastewater in the reactor of 3.67 $lmin^{-1}$, initial pH of 7-9, and 20 min electrolysis time. According to this condition, approximately 95% of COD, 96% of BOD, 100% of Cr, 96% of TSS, 62% of TKN, 50% of TDS and 99% of oil & grease were removed. In addition, a small amount of iron ions remained in the treated wastewater. Low energy consumption around 0.13 $kWhm^{-3}$ wastewater was obtained in this process, leading to the low operating cost of approximately 0.34 US$$m^{-3}$ wastewater. The rate of COD reduction was a direct function of the applied current density.

ACKNOWLEDGMENT

The author would like to thank the Ratchadaphisaksomphot Foundation of Chulalongkorn University for financial support for our project.

NOMENCLATURE

CE : current efficiency [%]
$[COD]_t$: concentration of COD at time t
$[COD]_0$: initial concentration of COD
EC : energy consumption [$kWhm^{-3}$]
F : Faraday's constant [96,485 C]
I : applied current [A]
k : the first order rate constant [min^{-1}]
M_w : molecular weight of iron [g]
m : mass of iron dissolved into the solution [g]
n : number of electron involved in the reaction
Q : volume of wastewater [m^3]
t : time [min]
V : voltage [V]

REFERENCES

1. D. H. Ahn, Y. C. Chung, Y. J. Yoo, D. W. Pak and W. S. Chang, *Biotechnol. Let.*, **18**(8), 917 (1996).
2. K. Vijayaraghvan and D. V. H. Murthy, *Bioprocess Eng.*, **16**(3), 51 (1997).
3. M. Wiemann, H. Schenk and W. Hegemann, *Water Res.*, **32**(3), 774 (1998).
4. C. Di Iaconi, A. Lopez, R. Ramadori and R. Passino, *Environ. Sci. Technol.*, **37**, 3199 (2003).
5. G. Farabegoli, A. Carucci, M. Majone and E. Rolle, *J. Environ. Manage.*, **71**, 345 (2004).
6. S. G. Schrank, H. J. Jos, R. F. P. M. Moreira and H. Fr. Schröder, *Chemosphere*, **50**, 411 (2003).
7. G. Sekaran, K. Chitra, M. Mariappan and K. V. Raghavan, *J. Environ. Sci. Health A*, **31**, 579 (1996).
8. S. Dogruel, G. E. Ates, B. F. Germirli and D. Orhon, *J. Environ. Sci. Health A*, **39**, 1705 (2004).
9. C. Di Iaconi, A. Lopez, G. Ricco and R. Ramadori, *J. Anal. Environ. Cultur. Herit. Chem.*, **91**, 587 (2001).
10. D. Orhon, S. Sözen, E. Ubay Cokgšr and E. Ates, IAWQ 19th Biennial International Conference, 256 (1998).
11. Z. Song, C. J. Williams and R. G. J. Edyvean, *Desalination*, **164**, 249 (2004).
12. H. S. Shin and J. K. Lee, *Korean J. Chem. Eng.*, **23**, 188 (2006).
13. S. H. Shin, Y. H. Kim, S. K. Jung, K. H. Suh, S. G. Kang, S. K. Jeong and H. G. Kim, *Korean J. Chem. Eng.*, **21**, 806 (2004).
14. G. Chen, *Separ. Purif. Technol.*, **38**, 11 (2004).
15. J. Naumczyk, L. Szpyrkowicz, R. De Faveri and F. Zillio Grandi, *T. I. Chem. Eng. B*, **74**, 59 (1996).
16. L. Szpyrkowicz, J. Naumczyk and F. Zilio-Grandi, *Water Res.*, **29**, 517 (1995).
17. A. G. Vlyssides and C. J. Israilides, *Environ. Pollut.*, **97**, 147 (1997).
18. L. Szpyrkowicz, H. Geoffery, N. Santosh and M. De Faveri, *Chem. Eng. Sci.*, **56**, 1579 (2001).
19. G. Rajalo and T. Petrovskaya, *Environ. Technol.*, **17**, 605 (1996).
20. M. Murugananthan, R. G. Bhaskar and S. Prabhakar, *Separ. Purif. Technol.*, **40**, 69 (2004).

21. M. Ali Awan, M. A. Baig1, J. Iqbal, M. R. Aslam and N. Ijaz, *Electron. J. Environ. Agr. Food. Chem.*, **2** (2003).
22. G. Tiravanti, D. Petruzzelli and R. Passino, *Water Sci. Technol.*, **36**, 197 (1997).
23. T. Panswad, O. Chavalparit and C. Chandung, *Waste Manage. Res.*, **19**, 450 (2001).
24. APHA, AWWA, WEF. Standard Methods for the Examination of Water and Wastewater, 20th ed. Part 3111 B (1998).
25. S. Kongkao, A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science Program in Chemical Technology, Department of Chemical Technology, Faculty of Science, Chulalongkorn university, Bangkok, Thailand (2005).
26. M. Y. A. Mollaha, P. Morkovskyb, J. A. G. Gomesc, M. Kesmezc, J. Pargad and D. L. Cockec, *J. Hazard. Mater. B*., **114**, 199 (2004).
27. C. Y. Hu, S. L. Lo and W. H. Kuan, *Water Res.*, **37**, 4513 (2003).
28. J. Q. Jiang, N. Graham, C. Andre, G. H. Kelsall and N. Brandon, *Water Res.*, **36**, 4064 (2002).
29. T. H. Kim, C. Pak, E. B. Shin and S. Kim, *Desalination*, **150**, 165 (2002).
30. M. Hunsom, H. Vergne, P. Duverneuil, K. Pruksathorn and S. Damronglerd, Proceeding of 6th World Congress of Chemical Engineering, Melbourne, Australia (2001).
31. B. Ram, P. K. Bajpai and H. K. Parwana, *Proc. Biochem.*, **35**, 255(1999).
32. P. A. Balakrishman, A. Arunagiri and P. G. Rao, *J. Electrostat.*, **56**, 77 (1999).
33. S. Kongjao, S. Damronglerd and M. Hunsom, *Korean J. Chem. Eng*., **24**, 730 (2007).