Simultaneous removal of chromium and organic pollutants in tannery wastewater by electroprecipitation technique

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Abstract−The simultaneous removal of chromium and other organic pollutants from tannery wastewater was investigated in a batch electrochemical membrane reactor. This reactor, having a total capacity of 1 liter, was separated into two compartments (anodic and cathodic compartments) by using an anionic membrane. A stainless steel sheet with the square holes having total surface area of $0.0215 \ m^2$ and a Ti/RuO_2 grid was used as the cathode and anode, respectively. The results indicated that the optimum condition for removal of chromium from tannery wastewater was found at the current density of $60.5 \ A/m^2$ at initial pH of 4.5. At this condition, more than 98% of chromium was removed within 60 min. Some organic pollutants contained in wastewater such as oil and grease, color and the level of biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total kjeldahl nitrogen (TKN) were also markedly reduced.

Key words: Tannery Wastewater, Electroprecipitation, Chromium, Organic Pollutants, Removal

INTRODUCTION

The tannery industry represents an important economic sector in many countries, but in parallel, it generates large amounts of heavy metals such as chromium, high levels of BOD, COD, total suspended solids (TSS), total dissolved solids (TDS), TKN, grease and oil, salt, color and, worst of all, odor. In Thailand, more than 14,000 tons/year of leather is produced which generates more than $2.55 \times 10^6 \ m^3$/year of wastewater. There are many conventional processes used to treat wastewater from industries such as biological process [1-6], oxidation process [7-12], chemical process [13-15], etc. One of the most interesting and effective processes for treating some pollutants in tannery wastewater is the electrochemical process. The efficiency of this process is more sensitive to the types of electrodes used in the process. Ti/Pt-Ir anode is more efficient to treat the pre-treatment tannery wastewater than Ti/Pt and graphite [16]. For tannery wastewater without pre-treatment, however, a Ti/Pt-Ir anode was proved to have the electrocatalytical properties for NH_4^+ removal, but it was more sensitive to poisoning by H_2S contained in the wastewater [17]. The reaction was a pseudo first order reaction and the amount of chloride in the solution increased as a function of electrolysis time [18,19]. Soluble anode, 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 can be oxidized independently in alkaline conditions with aqueous oxidants to soluble chromate. Hydrogen peroxide is a potentially suitable oxidant as it can 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 results 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 in 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 able to pay-back economically within three years.

In this paper, 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 electroprecipitation technique. Effects of current density, initial pH and circulating flow rate of wastewater in the system were explored. In addition, the mechanism of organic pollutants reduction in the presence of chromium was also proposed.

EXPERIMENTAL

Wastewater containing chromium (III) and various kinds of organic pollutants from the tannery industry in Thailand (Table 1) were employed in this study. The experiments were carried out in an electrolytic cell constructed with Plexiglas having a dimension of $0.10 \times 0.10 \times 0.11 \ m^3$ (1 liter capacity) as shown in Fig. 1. The cell was separated into two compartments, anodic and cathodic compartments, by using an anionic membrane (IONAC type). The volume of both anode and cathode compartments was set equal to 0.5 liters. A stainless steel grid with surface area of $0.0215 \ m^2$ and a titanium grid coated with ruthenium oxide (Ti/RuO_2) were used as cathode and anode, respectively. They were placed at the center of each compartment, and the distance between them was fixed at around 0.05 m. To achieve good mass transfer in the system, two magnetic pumps (Model NH-5PX type) were used to circulate the electrolyte in both compartments. The regulated DC power supply (Model ZS 3205-2X type) was used to supply the current in the galvanostatic mode. The electrolysis time was fixed at 300 min and the solution was sampled every 30 min. All physical properties of wastewater were

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Table 1. Characteristics of wastewater from tannery industry in Thailand

Characteristics	Content	Standard (Thailand)
pH	9.5-9.8	5.5-9
Conductivity (μs/cm)	2,640-2,680	-
Chromium (III) (mg/l)	18-20	≤ 0.5
TDS (mg/l)	18,400-21,050	$\leq 3,000$
TSS (mg/l)	10,980-11,480	≤ 150
Oil & grease (mg/l)	650-765	≤ 5
COD (mg/l)	17,240-17,860	≤ 400
Temperature (°C)	26.5-29.0	≤ 40
TKN (mg/l)	185-190	≤ 100
Chromium (mg/l)	19.1-20.0	≤ 0.5
Color (Pt-Co unit)	1,249-1,430	Not objectionable
BOD (mg/l)	3,000-3,600	< 60
Other compounds (SO_4^{2-}, Na^+, Cl^-, Ca^{2+}, NH_4^+)		
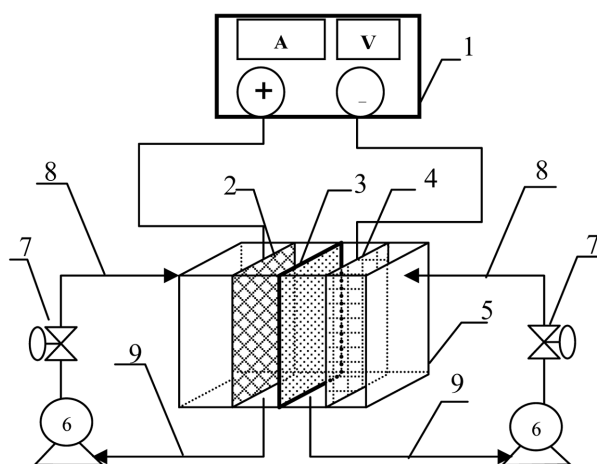
Fig. 1. Schematic view of electrolysis cell with plane electrode.
1. DC Power supply   6. Pump
2. Anode   7. Valve
3. Anionic membrane   8. Inlet stream
4. Cathode   9. Outlet stream
5. Reactor
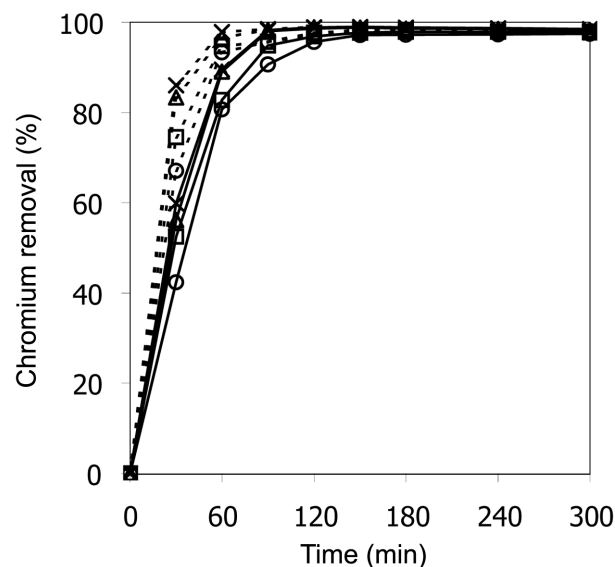
Fig. 2. Chromium removal percentage versus electrolysis time. pH =3.0 (—), pH=4.5 (---); j=51.2 A/m² (○), j=60.5 A/m² (□), j=69.8 A/m² (△); j=81.4 A/m² (×).

analyzed by following the standard method [24].

RESULTS AND DISCUSSION

1. Effect of Current Density and Initial pH

In this part, the treatment will first focus on chromium elimination because the presence of chromium in wastewater interferes with the treatment of other organic pollutants. This is because of its high standard potential [25]. Fig. 2 shows the percentage of chromium removal as a function of electrolysis time at pH=3.0 and 4.5 at current densities of 51.2, 60.5, 69.8 and 81.4 A/m². The results indicated that the percentage of chromium removal increased as a function of electrolysis time. At the same current density, the percentage of chromium removal at high initial pH was higher than that at low initial pH, whereas at the similar initial pH, the tendency of chromium removal increased when high current density was applied to the system. According to the results, more than 98% of chro-

mium was removed within 120 min at all current densities at initial pH of 4.5, and more than 98% of chromium was removed within 150 min for all conditions. When the electrolysis time was over, the concentrations of chromium were less than 0.18 mg/l.

2. Effect of Flow Rate of Wastewater

Effect of wastewater flow rate on the chromium removal by electroprecipitation was also investigated by using different flow rates of 0, 2.3 and 4.5 l/min at current density of 69.8 A/m² and initial pH of 4.5. The results as plotted in Fig. 3 demonstrated that the flow rate of wastewater had only a slight effect on chromium removal. High flow rate provided a high percentage of chromium removal because a greater collision frequency of Cr^{3+} and OH^- can be achieved. For example, a 2-fold increase of flow rate leads to a increase of about 10% of chromium removal.

3. Removal Percentage of other Pollutants

Besides the successful removal of chromium from tannery waste-
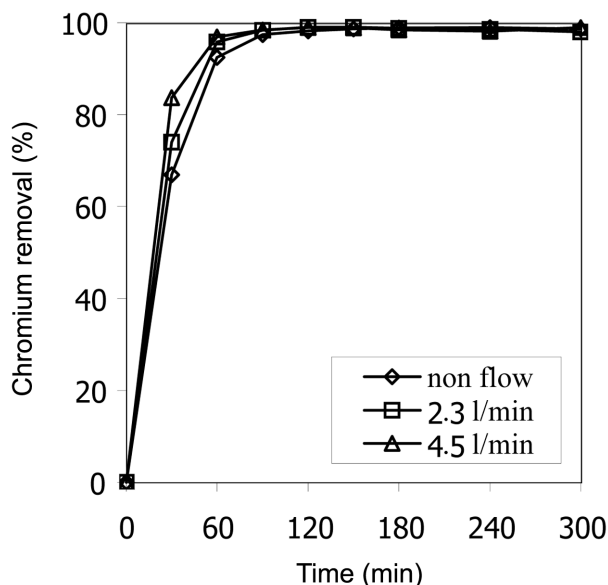
Fig. 3. Effect of flow rate of electrolyte as a function of electrolysis time.
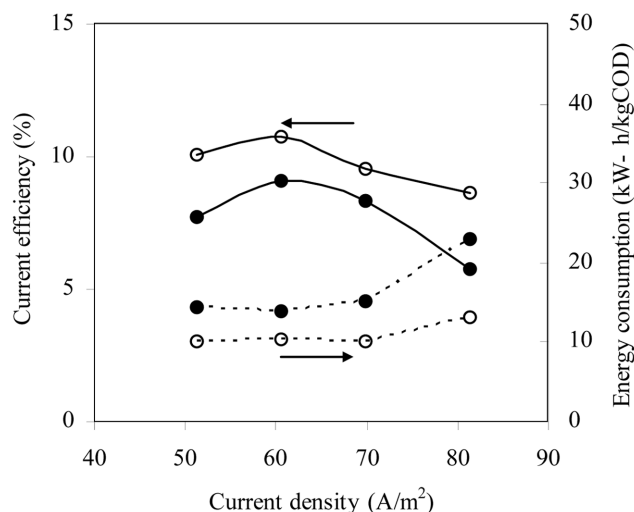

Fig. 5. Variation of current efficiency (—) and energy consumption (----) as a function of current density at 300 min operating time at pH=3.0 (●) and pH=4.5 (○).
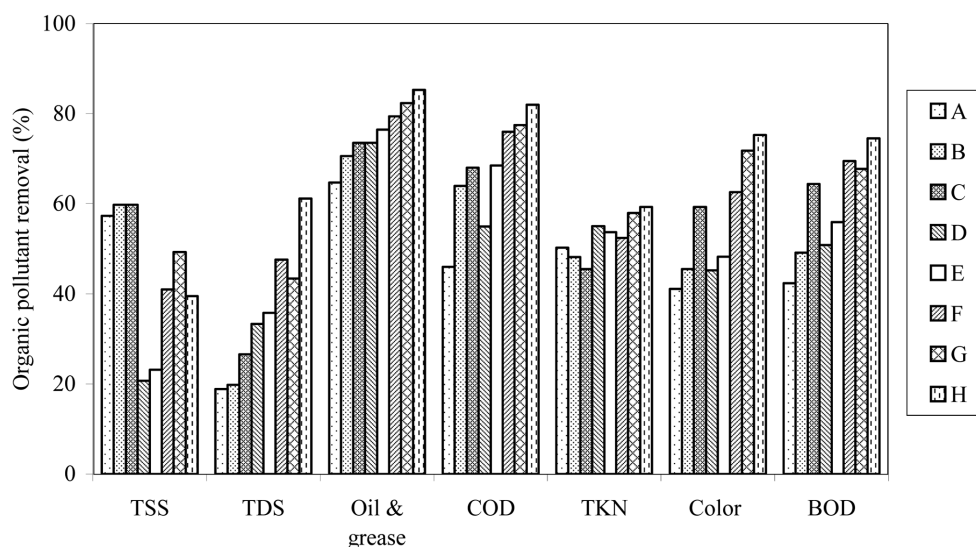

Fig. 4. Plot of organic pollutant reduction at various experimental conditions and 300 min electrolysis time. A: j=51.2 A/m², pH=3; B: j=60.5 A/m², pH=3; C: j=69.8 A/m², pH=3; D: j=81.4 A/m², pH=3; E: j=51.2 A/m², pH=4.5; F: j=60.5 A/m², pH=4.5; G: j=69.8 A/m², pH=4.5; H: j=81.4 A/m², pH=4.5.

water by using this technique, the concentrations of all organic pollutants were markedly reduced as demonstrated in Fig. 4. It can be seen that, at the same initial pH, the removal percentage of organic pollutants had a tendency to increase when the current density was increased. In addition, at a similar current density, high initial pH demonstrated high percentage of organic pollutant removal. For all conditions, more than 65% of oil and grease was removed from the wastewater, and the maximum removal was observed at around 85% at initial pH of 4.5 and current density of 81.4 A/m². In addition, more than 45% of COD and TKN was removed at all conditions, particularly at high current density and high initial pH. Merely high initial pH condition (pH=4.5) was more effective to remove color and BOD, namely more than 50% of them was removed. For

TDS, increasing initial pH and current density led to the increase of removal percentage, and the maximum percentage was obtained at initial pH of 4.5 and current density of 81.4 A/m². The fluctuation of removal percentage of TSS was observed for all conditions, particularly at high initial pH conditions because a large amount of colloidal particles were produced during the process and suspended in the solution. The higher the production of fine colloidal particles, the larger amount of TSS was observed.

4. Current Efficiency (CE) and Energy Consumption (EC)

To monitor the efficiency of the treatment process, the current efficiency and energy consumption were then calculated at a particular current density by Eqs. (1) and (2), respectively [26]. The results exhibit that the current efficiency of high initial pH solution

Table 2. Comparison of various parameters between this work and previous works

Author (Year)	COD		BOD		Chromium		TSS		TDS		Oil & Grease	
	A	B	A	B	A	B	A	B	A	B	A	B
Di Iaconi et al. [4][a]	3,790	92.6	-	-	-	-	2,200	99.0	-	-	-	-
Maruganuthan et al. [20][b]	3,092	52.0	1,750	53.0	2.50	99.2	3,036	91.5	-	-	-	-
Ram et al. [29][c]	3,714	57.8	1,126	42.4	8.3	57.8	1,147	25.4	11,737	−12.2	-	-
Balakrismsn et al. [30][d]	737	81.0	60.0	59.7	-	-	-	-	-	-	-	-
This work[e]	17,600	82.0	3,540	74.6	19.5	98.5	8,200	59.8	18,680	61.2	680	85.7

[a]Biological process.
[b]Electroflotation process.
[c]Chemical process.
[d]Ozone process.
[e]Electroprecipitation process.
A=concentration of pollutants in wastewater before treatment (mg/l), B=Percentages of pollutant removal (%).

was higher than that at low initial pH solution (Fig. 5). This is because, at the same operating time, the amount of hydroxide ions contained in solution at high initial pH was higher than that at low initial pH solution, thus leading to a large amount of pollutant removal. Less than 20% of current efficiency, however, was obtained for all conditions. This might be attributed to the adsorption of a polymeric material generated by the electroprecipitation reaction. In addition, the energy consumption of high initial pH solution was lower than that of low initial pH solution at approximately 1.5-1.8 times. According to the results of this part, the optimum current density and initial pH of wastewater were found at 60.5 A/m^2 and pH= 4.5, respectively. The current efficiency and energy consumption at such condition were 10.77% and 10.31 kW-h/kgCOD.

$$CE(\%) = \frac{(COD)_t - (COD)_{t+\Delta t}}{8I\Delta t}FL\,100 \qquad (1)$$

$$EC = \frac{1000(ItV)}{L[(COD)_t - (COD)_{t+\Delta t}]} \qquad (2)$$

Table 2 shows a comparison of various parameters of this work and some previous works. It can be seen that the wastewater used in this work contained high concentration of pollutants. Namely, the concentrations of COD, BOD, chromium, TSS and TDS were higher than that of other wastewaters, up to 23.9, 59.0, 7.8, 7.2 and 1.6 times, respectively. From the results, the electroprecipitation process provided a higher removal efficiency of pollutants than that of many processes. The chemical process, for example, can remove merely 57.8% and 42% of COD and BOD, respectively, whereas they were around 82.0% and 74.6% by using the electroprecipitation process. In addition, adding chemical reagent in the chemical treatment process led to an increase of TDS removal at around 12.2% while this process can remove such pollutants at around 61.2%. Although the biological process can provide similar removal efficiency for COD and TSS compared with that of our process, it requires a large treatment area and generates large amounts of low-density sludge, which leads to a disposal problem. The electroprecipitation process, though, has a lower removal percentage of some pollutants, such as TSS, than that of the electroflotation process. However, the amount (weight per unit volume) of those pollutants removed by this method was higher.

5. Mechanism of Chromium and other Pollutants Removal

In the presence of merely chromium in wastewater, the removal of chromium by the electroprecipitation technique occurred in the cathodic compartment [27]. Chromium in the solution presented in hexavalent forms ($Cr_2O_7^{2-}$ and/or $HCrO_4^-$) is usually observed at pH 1-6 [28], This hexavalent chromium in wastewater was reduced to trivalent chromium as expressed by Eqs. (3)-(4), when the current was applied to the system. Simultaneously, the reduction of H^+ and H_2O to H_2 and OH^- occurred as Eqs.(5)-(6) which led to the increase of pH in the cathodic compartment. As the electrolysis time proceeded, large amounts of OH^- were produced in the solution and they consequently attached to the trivalent chromium and precipitated in the forms of $Cr(OH)_3$ as Eq. (7). The chromium precipitation can occur at pH around 5.5 or higher, depending on its concentration in the wastewater. However, in the presence of both chromium and organic species such as tannery wastewater, the removal
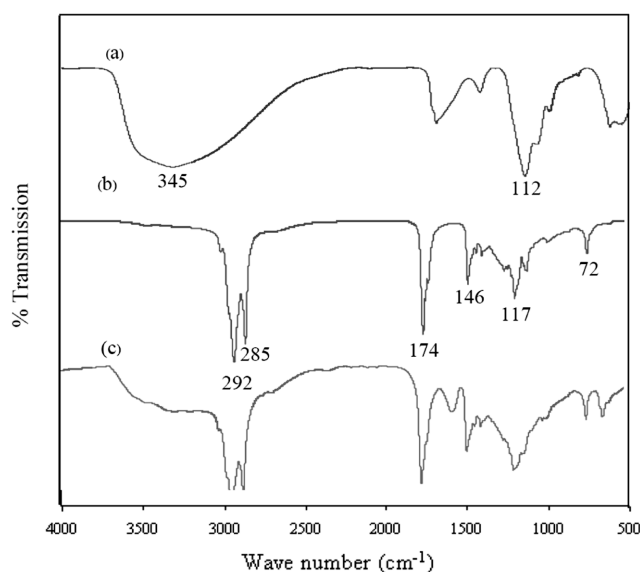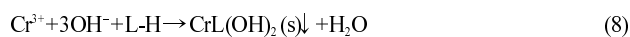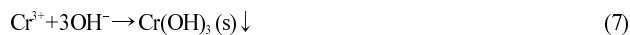

Fig. 6. FTIR spectra of various kinds of sludge: (a) dried synthetic sludge (contains only chromium), (b) dried synthetic sludge (contains both chromium and pollutants, Tristearin) and (c) dried sludge from tannery wastewater (contains both chromium and pollutant).

of pollutants (L-H) occurred by the surface complex or electrostatics attractions as expressed by Eq. (8).

$$Cr_2O_7^{2-}+14H^++6e^-\rightarrow 2Cr^{3+}+7H_2O \tag{3}$$

$$HCrO_4^-+7H^++3e^-\rightarrow Cr^{3+}+4H_2O \tag{4}$$

$$2H^++2e^-\rightarrow H_2\ (pH<5.5) \tag{5}$$

$$H_2O+e^-\rightarrow OH^-+1/2H_2\ (pH\geq 5.5) \tag{6}$$

$$Cr^{3+}+3OH^-\rightarrow Cr(OH)_3\ (s)\downarrow \tag{7}$$

$$Cr^{3+}+3OH^-+L\text{-}H\rightarrow CrL(OH)_2\ (s)\downarrow +H_2O \tag{8}$$

Organic pollutants such as oil and grease can precipitate as colloidal particles in the treated wastewater. Fig. 6 shows the FTIR spectra of various kinds of dried sludge including the dried synthetic sludge containing only chromium prepared from $Cr_2(SO_4)_3$ solution (a), the dried synthetic sludge containing both chromium and animal fat (Tristearin, $C_{51}H_{140}(CO)_3$) (b) and the dried sludge from tannery wastewater containing both chromium and pollutants (c). It can be observed that, for (a), the -OH peak was strongly observed during the wavelength of 2,500-3,600 cm^{-1}. The main functional groups observed in the spectra of the dried synthetic sludge containing both chromium and animal fat, (b), were the main functional groups observed in the animal fat. Namely, it included the C-H of aliphatic stretching vibration (λ=2,920 and 2,850 cm^{-1}), C=O of ester stretching vibration (λ=1,745 cm^{-1}), C-H bending (scissoring) vibration at (λ=1,465 cm^{-1}), C-O of ester stretching vibration (λ=1,175 cm^{-1}), and C-H bending (rocking) vibration (λ=720 cm^{-1}). It can be confirmed that organic pollutants such as oil and grease precipitated as colloidal particles in the treated wastewater. For real sludge from the tannery wastewater, (c), it had peaks nearly similar to that of the dried synthetic sludge prepared from animal fat.

CONCLUSIONS

From all of these results, the hexavalent chromium in tannery wastewater was successfully removed by using the electroprecipitation technique in a membrane reactor. The optimum condition for chromium removal was found at 60.5 A/m^2, and pH=4.5. At this condition, more than 98% of chromium was removed within 60 min with a current efficiency greater than 10.77% and energy consumption of 10.31 kW-h/kgCOD. The concentration of chromium in wastewater was lower than the acceptable limit set by the Thai Government. High flow rates of wastewater can achieve high percentage of chromium removal. Besides chromium, by using this technique, the amount of some organic pollutants such as oil and grease, BOD, COD, TKN, and color was markedly reduced as a chromium-organic pollutant complex in the forms of fine colloidal particles. Although the concentration of all pollutants was significantly reduced during the treatment process, it were still higher than the acceptable limit set by the Thai Government, specifically, TKN and color. The removal of these organic pollutants was further performed, but the results are not presented here because it is out of scope of this article.

ACKNOWLEDGMENT

NOMENCLATURE

$(COD)_t$: chemical oxygen demands at time t $[gO_2/l]$
$(COD)_{t+\Delta}$: chemical oxygen demands at time t+Δt $[gO_2/l]$
F : Faraday constant [26.8 Ah]
I : current intensity [A]
L : volume of electrolyte [l]
t : electrolysis time [h]
V : cell voltage [V]

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