

Application of the electrocoagulation technique for treating heavy metals containing wastewater from the pickling process of a billet plant

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Abstract—This work was carried out to study the removal of various heavy metals, including Cu, Cr, Pb and Zn, from billet industry wastewater by the electrocoagulation process in both batch and continuous experiments at a laboratory scale and ambient temperature (30 °C). In the batch experiment, the effect of various parameters including the current density, initial wastewater pH and electrolysis time, on the metal removal efficiency was examined. Optimal metal ion depletion was attained with a current density of 98 A/m², an initial wastewater pH of 5 and a 30 min electrolysis time. Under these conditions, greater than 99% of Cu, Cr and Zn was removed, whilst the outlet wastewater contained Cu, Cr, Pb and Zn at less than 0.02, 0.01, 0.07 and 0.05 mg/l, respectively. For the continuous process, the results indicated that the treatment system reached its steady state condition within 120 min, and the optimum condition for the continuous treatment was found at an initial wastewater pH of 3 and flow rate of 55 ml/min. At this condition, a complete removal of Cu and Pb and greater than 99% removal of Cr and Zn were achieved.

Key words: Electrocoagulation, Metal Removal, Current Efficiency, Pickling Process

INTRODUCTION

The pickling process, which is used to remove oxide scales from the surface of raw metal specimens prior to processing, is a hydro-metallurgical process that typically uses hydrochloric, sulfuric, nitric and hydrofluoric acids for the surface etching [1]. Effluents from this process are typically characterized by highly concentrated solutions of heavy metal ions such as chromium (Cr), copper (Cu), nickel (Ni), zinc (Zn), etc., and the leaching acids, depending on the production process. Discharging such wastewater to the environment without proper remedial treatment is forbidden due to its hazardous properties to both humans and the environment. Many management concepts of such wastewater have been carried out, such as spent acid minimization and spent acid recovery [2-6]. However, due to the large quantity of such waste production each year, in the past decade, some new approaches have been investigated for the treatment of spent pickling liquors, including absorption [7,8], chemical precipitation [9,10], extraction [11,12] and nanofiltration [13]. However, all these schemes on their own are either incomplete, impractical or unviable. Precipitation, for example, requires a large amount of chemical treatment and also produces a considerable volume of low-density sludge. Nanofiltration is a pressure-related process that requires a specific membrane type and high-pressure pump leading to high investment costs. In addition, it requires the chemical pre-treatment of wastewater to prevent scaling and precipitation of insoluble solids on the membrane surface.

Considering the economics and scale of wastewater purification operations, the electrochemical procedure has been found to be the

most suitable process [14] due to its fast reaction rate, versatility, simplicity and ease of operation. Application of this process for treating industrial wastewater can be performed in different ways. By employing electrooxidation, Vlyssides et al. [15] demonstrated that the types of anode used and the presence of an oxidizing agent had a significant influence on the treatment process. Greater than 92% of the color from a distillery effluent was reduced by using titanium substrate insoluble anodes (RuO₂-Ti) [7], or by using a voluminous electrode or graphite [16]. Chou et al. [17] demonstrated a novel electro-Fenton method, using an applied H₂O₂ and electrogenerated ferrous ion, and reported that this was the most effective method compared with H₂O₂/Fe²⁺, H₂O₂/Fe³⁺ and direct electrolysis. For COD removal, Zhang et al. [18] reported that the COD removal efficiency increased as the current density, ferrous ion and hydrogen peroxide dosages were increased. However, further (extreme) increases in any of these three variables above an optimal level then led to a significant decrease in the metal removal efficiency. In addition, they reported that the stepwise or continuous addition of hydrogen peroxide was more effective than a single step addition. By using the electro-Fenton system containing a polypyrrole/anthraquinone-disulphonate (PPy/AQDS) composite film modified graphite cathode, Zhang et al. [19] showed that their system can degrade amaranth azo dye efficiently in various acidic solutions and the amount of doping AQDS in PPy matrix did not significantly influence the dye decay rate.

Among the possible uses of the electrochemical process for wastewater remediation, electrocoagulation has recently attracted considerable attention due to its variety of applications for various kinds of industrial wastewater containing both organic and inorganic substances. For wastewater containing heavy metal ions, Adhoum et al. [20] reported that the most effective metal removal capacity was

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by using an aluminum electrode in the pH range between 4 and 8, whereas by using a iron electrode, wastewater with an initial pH of 7-9 provided a similar removal efficiency [21]. Nevertheless, the iron electrode was found to be more efficient than the aluminum electrode in terms of COD and TOC removal efficiencies and operating costs [22]. The plausible reason for less metal removal, such as arsenic, by aluminum in comparison to iron electrodes could be that the adsorption capacity of hydrous aluminum oxide for As(III) is much lower in comparison to hydrous ferric oxides [23]. By using combination of electrodes between aluminum and iron for treating arsenic wastewater, Gomes et al. [24] demonstrated the substitution of Fe^{3+} ions by Al^{3+} ions in the solid surface indicating an alternative removal mechanism of arsenic in these metal hydroxides and oxyhydroxides. Al^{3+} substitution during formation of crystalline and/or amorphous/poorly crystalline Fe hydroxide/oxyhydroxides resulted in a product that might be more stable against transformation to well crystalline iron oxides.

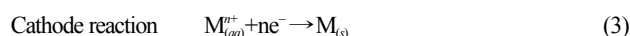
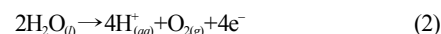
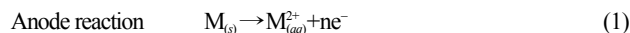
In the studies reported here, importantly, real wastewater containing Cu, Cr, Pb and Zn from a billet plant pickling bath, instead of using synthetic wastewater as in many of the previous works, was remediated by the electrocoagulation technique, both in batch and continuous processes. The effects of various parameters on each metal removal were explored.

2. A Brief Description of the Electrocoagulation Mechanism with Fe Electrodes

Electrocoagulation is a complicated process involving many chemical and physical phenomena. Its basics involve the generation of coagulants *in situ* by electrically dissolving some of the sacrificial electrode, typically aluminum or iron. In this process, the coagulating ions are produced with three successive stages including the formation of coagulants by electrolytic oxidation of the sacrificial electrode, the destabilization of the contaminants, particulate suspension and breaking of emulsions and the aggregation of the destabilized phases to form flocs. The destabilization mechanism of the contaminants, particulate suspension, and breaking of emulsions have been described in broad steps and may be summarized in the following three stages [25]. First is the compression of the diffuse double layer around the charged species by the interactions of ions

generated by oxidation of the sacrificial anode. Next is the charge neutralization of the ionic species present in wastewater by counterions produced by the electrochemical dissolution of the sacrificial anode. These counterions reduce the electrostatic interparticle repulsion to the extent that the van der Waals attraction predominates, thus causing coagulation. Last is floc formation as a result of coagulation creating a sludge blanket that entraps and bridges colloidal particles still remaining in the aqueous medium.

Besides the formation of coagulants, during the treatment process, hydrogen gas is released from the cathode which can help to float the flocculated particles out of the water, a process which is sometimes called electroflocculation [26]. The main reactions are:



In the presence of iron electrodes, the ferric ions generated by the electrochemical oxidation of the iron electrode, according to Eq. (1), may form monomeric species, such as $\text{Fe}(\text{OH})^{2+}$, $\text{Fe}(\text{OH})_2^+$, $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$, $\text{Fe}(\text{H}_2\text{O})_4\text{OH}_2^+$, $\text{Fe}(\text{OH})_3$, and $\text{Fe}(\text{OH})_4$, and polymeric species, such as $\text{Fe}_2(\text{H}_2\text{O})_8\text{OH}_2^{4+}$ and $\text{Fe}_2(\text{H}_2\text{O})_6\text{OH}_4^{2+}$, depending on the pH of the aqueous medium in the electrocoagulation process [22,24]. These complex molecules can act as adsorbents and/or traps for metal ions and so eliminate them from wastewater.

3. Experimental

The experiments were performed at a laboratory bench-scale and ambient temperature, both in batch (Fig. 1(a)) and continuous experiments (Fig. 1(b)), by employing actual wastewater from a billet plant (Table 1). The electrocoagulation cell was constructed from Plexiglas with dimensions of $0.12 \times 0.21 \times 0.15$ m (3 liters capacity). The low-cost iron grids with a total surface area of 0.0322 m^2 and rearranged in monopolar configurations were used as the sacrificial electrodes with the distance between each plate fixed at approximately 0.03 m. To achieve a good mass transfer in the system, a magnetic pump (Model NH-5PX type) was used to circulate the

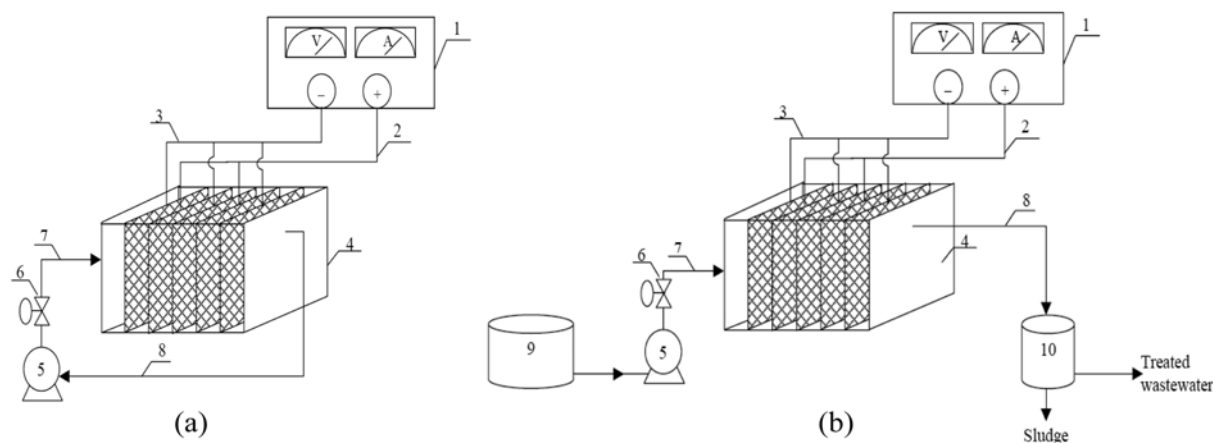


Fig. 1. Experimental set up for batch (a), and continuous experiments (b) electrocoagulation.

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|-----------------|------------|----------|------------------|------------------------------|
| 1. Power supply | 3. Cathode | 5. Pump | 7. Inlet stream | 9. Wastewater reservoir tank |
| 2. Anode | 4. Reactor | 6. Valve | 8. Outlet stream | 10. Filtration tank |

Table 1. Chemical and physical properties of wastewater from the pickling process of a billet plant in Thailand, and after both batch and continuous electrocoagulation treatments

Properties	Thai standard	Values (Before treatment)	Values (After treatment) Batch	Values (After treatment) Continuous ^a
pH	5.5-9	2.8-4.3	4.4-5.7	5-8
Cu (mg/l)	<2.0	110-230	0.02	0
Cr (mg/l)	<0.25	190-500	0.01	0.04
Pb (mg/l)	<0.2	0.1-2	0.07	0
Zn (mg/l)	<0.05	66-140	0.05	0.01
Fe (mg/l)	NA	7.38-8.85	0.02	<0.01
Conductivity (mS/cm)	NA	1.25	NA ^b	NA
Cl ⁻ (mg/l)	<1.0	<1.0	NA	NA

^aData obtained at optimum condition of batch treatment with a feed rate of wastewater of 55 l/min after 1.0 h start-up time

^bNA not applicable

electrolyte in the treatment system. A regulated DC power supply (GPS-3030DD) was employed to supply the external electricity. In the continuous experiment, a peristaltic pump (Model Masterflex77200-60) was used to carry wastewater from the reservoir to the electro-chemical reactor. During the experiment, wastewater was sampled at time intervals and passed through the filtration system to remove the sludge, and consequently, the concentration of all investigated metals was analyzed by atomic absorption spectroscopy (AAS, GBC Avanta Σ). The pH of the system was monitored by using the pH

meter (Type Horiba, Model F-22). The data are reported as the means obtained from duplicate experiments and with standard errors of the mean being less than 3% of the mean.

RESULTS AND DISCUSSION

1. Batch Experiment

The effect of current density on metal removal was first explored in the range of 47-109 A/m², with wastewater of an initial pH of

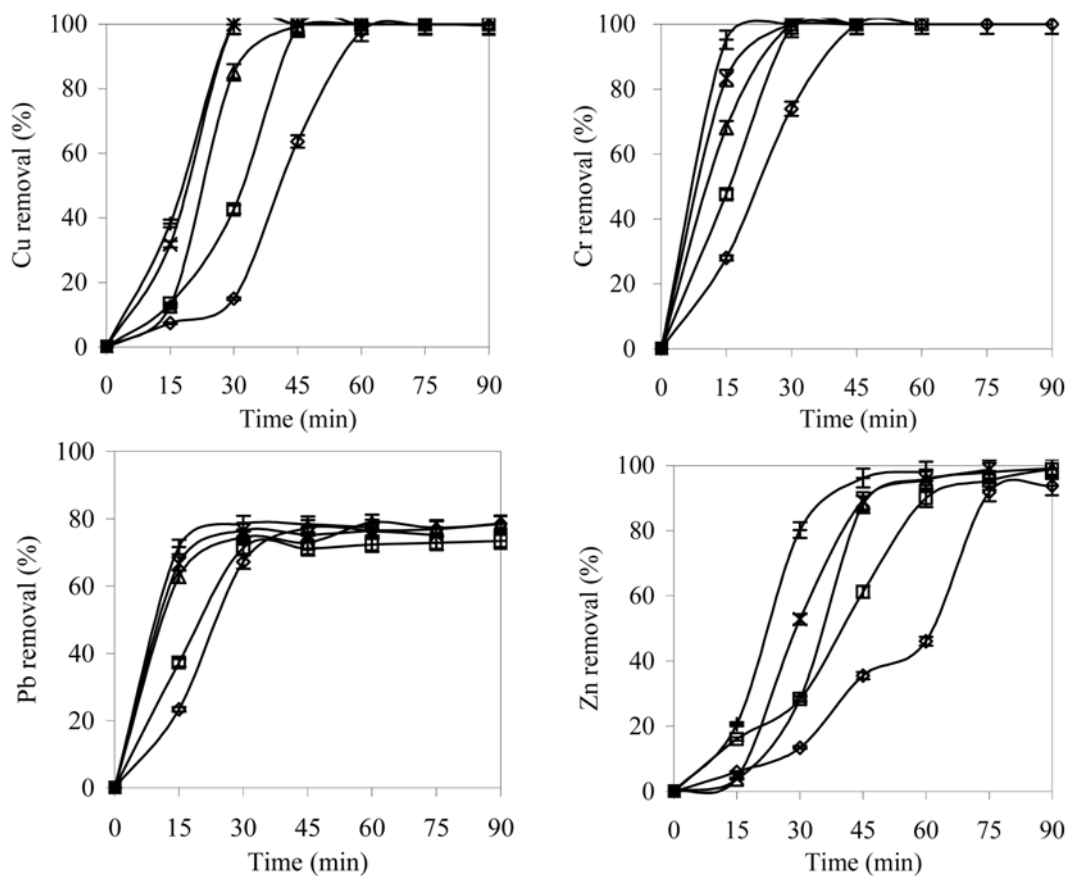


Fig. 2. Removal percentages of metals as a function of times at various current densities of 47 A/m² (◇); 62 A/m² (□); 78 A/m² (△); 98 A/m² (×) and 109 A/m² (+) at initial pH of 3.83.

3.83, and a circulating flow rate of 0.08 m³/min. The initial concentration of Cu, Cr, Pb and Zn was 120, 196, 1 and 66 mg/l, respectively. The removal of these heavy metals increased with increasing current density and electrolysis time. This is expected since a high-applied current density over a long electrolysis time will generate a large amount of coagulant according to Faraday's law, leading to lower amount of heavy metals in the treated wastewater. However, increasing the current density to levels greater than 98 A/m² did not result in a higher removal percentage for Pb (Fig. 2). In the case of Cu, Cr and Zn removal, almost total removal was already attained with a current density of 98 A/m² negating any ability for further increases in the current density to increase the removal efficiency. This might be attributed to the difference in removal mechanisms of each heavy metal in the treatment process. Namely, for Cu, Pb and Zn, the dominant removal mechanism might be electrodeposition because the wastewater pH at a current density of 98 A/m² fluctuated in the range of 4.4-5.7 (Fig. 3), which is lower than the pH required to induce precipitation of Cu, Pb and Zn. However, the removal of Zn was lower than that of Cu at the same operating conditions, presumably due to its low standard reduction potential (-0.76 V/SHE) compared with that of Cu (0.34 V/SHE). For Pb, although it had very low initial concentration compared to the other heavy metals, its low removal efficiency was observed. This might be explained by two reasons: first, the low accuracy of heavy metals measurement apparatus at very low metal concentration, and second, the

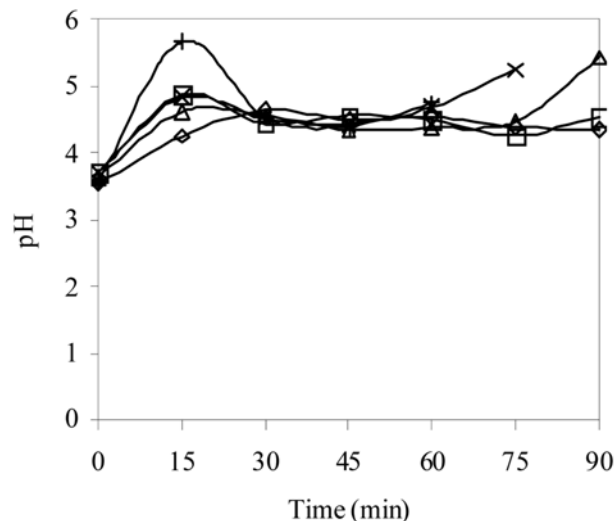


Fig. 3. Variation of pH in the electrochemical reactor during electrolytic treatment at various current densities of 47 A/m² (◇); 62 A/m² (□); 78 A/m² (△); 98 A/m² (×) and 109 A/m² (+).

phenomenon of metal removal and the treatment condition. Namely, the metal removal occurred with two mechanisms: the electrodeposition at early period of electrolysis time (low pH condition) and

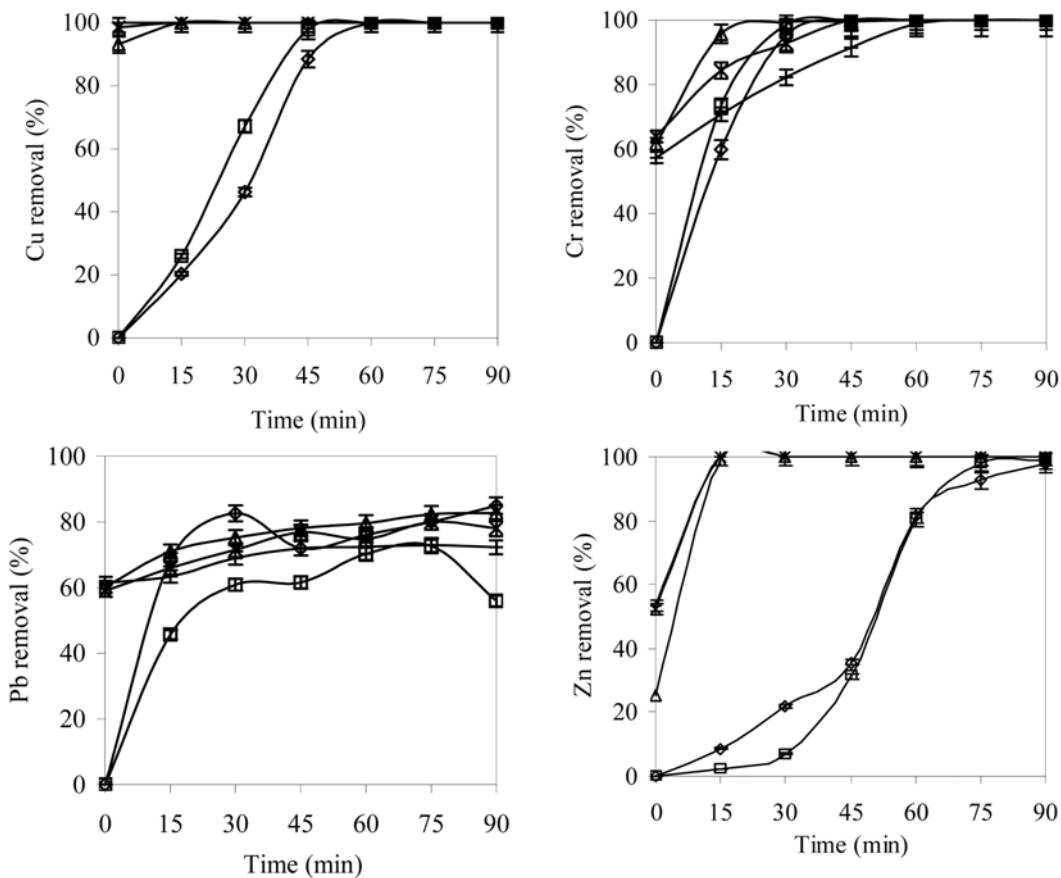


Fig. 4. Removal percentages of metals as a function of time at different pH of 3.2 (◇); 4.0 (□); 5.1 (△); 6.0 (×) and 7.0 (+) at current densities of 98 A/m².

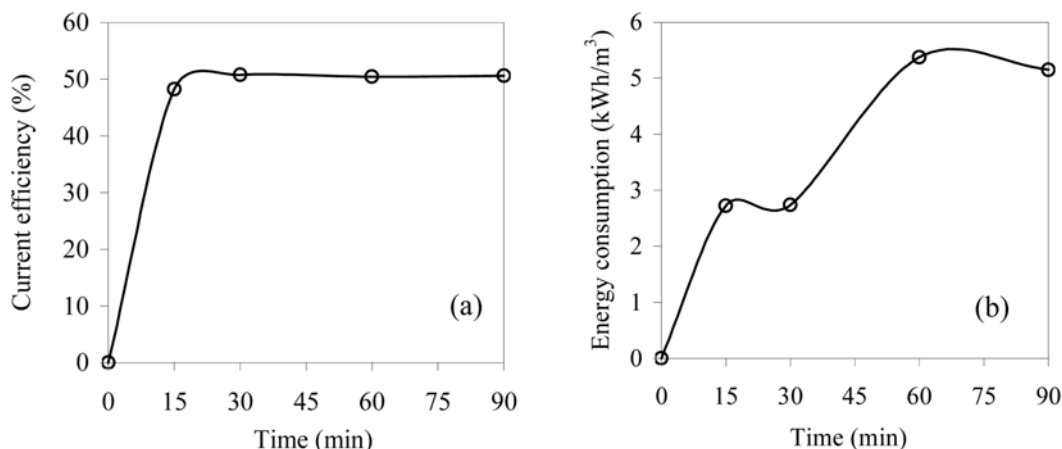


Fig. 5. Variation of current efficiency (a) and energy consumption (b) at optimum condition of batch experiment (current density 98 A/m^2 and initial pH of 5).

the deposition on Pb can occur slightly due to its low standard potential (-0.1263 V/SHE). In addition, due to the slight increase of pH of wastewater in the range of 4.4-5.7, the precipitation of Pb in this condition occurs slightly resulting in low Pb removal efficiency. On the other hand, the removal process for Cr is likely to have occurred with two steps: the reduction of Cr^{6+} to Cr^{3+} , which is effective in acid solution [27], and then the coagulation with the monomeric or polymeric ions produced by electrolysis. Thus, the optimum current density was 98 A/m^2 , which led to removal of nearly all Cu and Cr, some 70% of Pb, but only 50% of Zn within 30 min.

To improve the efficiency of metal removal, the effect of the initial wastewater pH was also explored in the range of 3.2-7.0, with an applied current density of 98 A/m^2 , a circulating wastewater flow rate of $0.08 \text{ m}^3/\text{min}$, and an initial concentration of Cu, Cr, Pb and Zn of 226, 448, 1 and 139 mg/l , respectively. Adjusting the initial wastewater pH by 0.1 M NaOH to $\text{pH} > 5$, but not when $\text{pH} < 5$, before the electrochemical treatment increased the removal level attained to 93-99, 57-61, 59-62 and 25-53% for Cu, Cr, Zn, and Pb, respectively (Fig. 4), and is likely to be due to the chemical precipitation of heavy metals under these conditions. Subsequently, when electrocoagulation was applied to the wastewater with a high initial pH, the degree of removal of all metals increased rapidly to their maximum because, at high initial wastewater pH values, the structures of ferrous ions in the system were in the monomeric ($\text{Fe}(\text{OH})_2$) form and polyhydroxyl iron (III) complexes such as $\text{Fe}(\text{OH})_2^{2+}$, $\text{Fe}(\text{OH})_3^+$, $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ and $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^+$ which can combine with the metal ion molecules causing the coagulation [20] and the reduction of heavy metals in the wastewater. Taken together, the optimum condition for treating wastewater from the billet plant in batch experiment was a current density of 98 A/m^2 and an initial wastewater pH of 5. The treated wastewater contained Cu, Cr, Pb and Zn levels of less than 0.02, 0.01, 0.07, and 0.05 mg/l , respectively, which is acceptable for discharge into the environment according to current legislation of Thailand. At this condition, the dry sludge production and the electrode consumption was around 0.192 g/l and 0.176 g/l wastewater, respectively.

The current efficiency (η) and energy consumption (EC) of the electrocoagulation in batch experiment at the optimum condition were then respectively calculated by Eq. (5) and Eq. (6) and the

obtained results were plotted in Fig. 5.

$$\eta = \frac{M_d}{M_r} \times 100 \quad (5)$$

$$\text{EC} = \frac{1000(\text{ItP})}{V} \quad (6)$$

It can be seen that the current efficiency increased rapidly as a function of electrolysis time within the first 15 min to a plateau at 50% at which it remained with increasing time. In contrast, the energy consumption increased slightly as a function of electrolysis time over 60 min, whereupon it may have become constant but further time points are required for confirmation.

2. Continuous Experiment

The treatment process was also evaluated in a continuous experiment using a current density of 98 A/m^2 with a circulating flow rate of $0.08 \text{ m}^3/\text{min}$, but with different feed rates of fresh wastewater in range of 35-100 ml/min equal to the retention time of 85.7-30 min pre-adjusted to one of two different pH values (pH 3 and 5). The initial concentration of Cu, Cr, Pb and Zn of the actual wastewater used was around 115, 428, 0.14 and 191 mg/l , respectively. In each experiment, to accumulate the coagulant in the system, the treatment process was run as a batch electrocoagulation for the first operating hour and then fresh wastewater was supplied continuously thereafter at the indicated flow rate. The complete removal of Cu was achieved for all treatment conditions, whereas complete removal of Cr, Pb and Zn was only accomplished under some conditions (Fig. 6). For Cr removal, the removal efficiency decreased with increasing fresh wastewater feed rates, presumably due to the effect of a short resident time at a high feed rate. However, treatment of wastewater with a pH of 3 resulted in a higher level of Cr removal compared with that of pH 5, which is attributed to the acid-dependent two-step treatment mechanism of Cr as mentioned previously. For Pb and Zn removal, a feed rate of 100 ml/min and an initial pH of 3 provided lower removal levels, particularly in the case of Zn, because Pb and Zn removal under these conditions was predominantly conducted by electrodeposition due to slight changes in the wastewater pH during the treatment process (Fig. 7(a)). The concentration of residual Fe ions in the treated wastewater as a func-

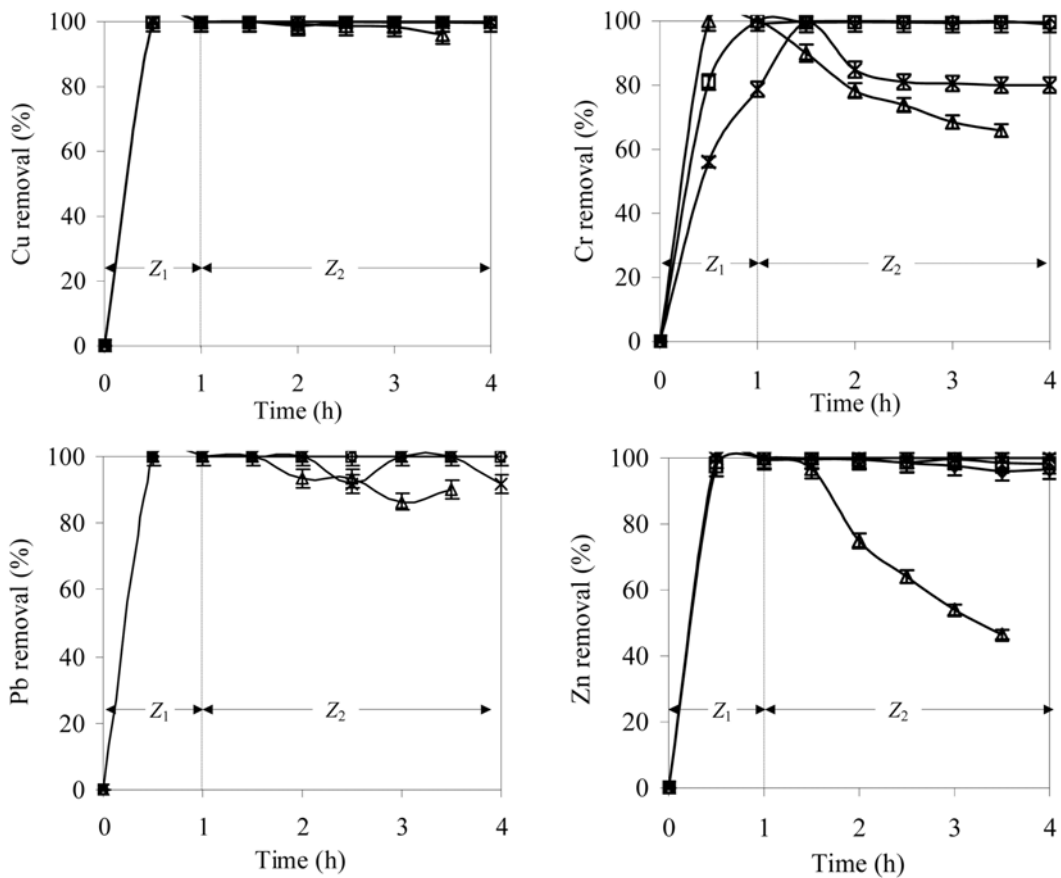


Fig. 6. Variation of metal removal as a function of electrolysis time during the batch start up period (Z_1) and continuous treatment periods (Z_2) at various operating conditions of 35 ml/min, pH 3 (\diamond); 55 ml/min, pH 3 (\square); 100 ml/min, pH 3 (\triangle) and 55 ml/min, pH 5 (\times) and current densities of 98 A/m².

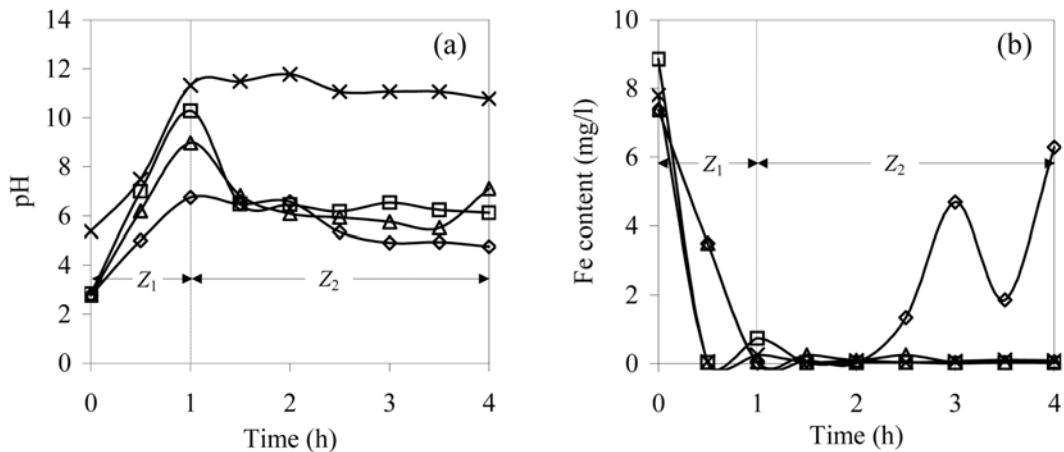


Fig. 7. Variation of pH values in the electrochemical reactor (a), and the residual concentration of Fe ions in the treated wastewater (b), during the batch start up period (Z_1) and continuous treatment periods (Z_2), at various operating conditions of 35 ml/min, pH 3 (\diamond); 55 ml/min, pH 3 (\square); 100 ml/min, pH 3 (\triangle) and 55 ml/min, pH 5 (\times).

tion of time during the treatment process is summarized in Fig. 7(b), where a small concentration of Fe ions was found during the treatment process under all operating conditions except that using a flow rate of 35 ml/min and a pH of 3, which is likely due to high dissolution of Fe ions in acid solution at long residence times.

According to all these results, for simultaneous removal of all

metals, the optimum conditions would be a feed rate of 55 ml/min and an initial wastewater pH of 3. Under these conditions, the system reached steady state within 120 min and greater than 99% of all heavy metals were removed with a residual iron concentration of less than 0.01 mg/l and a final pH of the treated wastewater within the range of 5-8. In addition, the color of wastewater after treat-

Table 2. Heavy metal removal efficiencies from industrial wastewater using different treatment techniques

Authors	Treatment process	Cu		Cr		Zn		Pb		Ni	
		(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
Jai et al. [28]	Precipitation			451	99.00			20.6	100		
Panayotova et al. [29]	Ion exchange	50	99.9	100	99.95						
Congeevaram et al. [30]	Biosorption			100	92.00					50	90
Feng et al. [31]	Electrodeionization	35.6-98.5	>99.8	46.8-98.4	>99.8	56.5-80.3	>99.8			22.9-87.9	>99.8
Kumbasar [32]	Liquid extraction			100	99.00						
Beauchesne et al. [33]	Electrocoagulation							2.2	98.8		
Thella et al. [34]	Electrocoagulation			15	99.2						
This work	Electrocoagulation (Batch)	226	99.99	448	99.99	139	99.96	1.00	93.00		
	Electrocoagulation (Continuous)	115	100	428	99.90	191	99.94	0.14	100		

(a) Initial concentration range of heavy metals in the wastewater before treatment (mg/l)

(b) Removal efficiency of each metal after treatment (%)

ment was clear and not objectionable in comparison with that before the treatment. The characteristics of wastewater after batch and continuous treatments are summarized in Table 1. It can be seen that in both the batch and the continuous process all heavy metals were markedly reduced to below the current maximum allowed levels for discharge permission by the Thai Government.

Table 2 displays the comparison of the metal removal efficiencies obtained from this and previous studies and reveals that the electrocoagulation processes both reported here and previous reports provide a removal efficiency equal or better than that of the other treatment processes, despite the fact that this study used much higher (and realistic being actual wastewater) initial metal concentrations in the wastewater. In addition, some of the other processes had their individual drawbacks not present in this electrocoagulation approach. The precipitation process, for example, is as good as this study and it does not have energy consumption, which makes it more attractive for users. However, it required a large amount of chemical agent, large amount of treatment area and, in addition, it generated a large amount of low-density sludge which further adds to the disposal problem. The electrodeionization and the ion exchange processes require a strong base or acid to regenerate the exchanged resin and, consequently, the release of the basic or acid effluent containing a high concentration of heavy metal ions up to 10 g/l requires a further treatment process [29]. The bioadsorption process provided a relatively low metal removal rate and required a long operating time of up to 18 h for chromium and 20 h for nickel removal [30].

CONCLUSION

The results presented here are consistent with the notion that, at least at a laboratory bench scale, the electrocoagulation process is currently the most effective process for treating wastewater containing heavy metal ions, but its removal efficiency was significantly affected by various parameters including the current density, initial wastewater pH and electrolysis time. By employing this process

with the billet plant pickling process wastewater, it was found that the optimum conditions for treating such wastewaters in batch experiment were a current density of 98 A/m², an initial wastewater pH of 5 and a 30 min electrolysis time. Under these conditions, all investigated heavy metals, except Pb, were markedly reduced up to 99% with a current efficiency of 50% and energy consumption lower than 3 kWh/m³ wastewater. For the continuous experiment, the treatment system reached its steady state condition within 120 min and optimum conditions were not that different being a current density of 98 A/m², a feed rate of wastewater of 55 ml/min and an initial pH of 3. The continuous experiment also attained a greater than 99% removal of all heavy metals assayed after 1 hr of start up time, and with a residual concentration of iron ions lower than 0.01 mg/l. Overall, if the electrocoagulation process reported here can be scaled up to commercial levels without significant changes in its parameters, it provides the best removal efficiency of all four tested metals, but requires careful evaluation of the economic and environmental costs of the electricity consumption. The cost of this treatment process has not estimated here because this work was carried out at a bench-scale, and it is difficult to estimate the real treatment cost in this situation. In addition, in order to apply this process to the billet industry, a proper design of a continuous process in pilot-scale experiment together with the sludge management should first be performed and characterized.

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NOMENCLATURE

η	: current efficiency [%]
EC	: energy consumption [kWh/m ³]
I	: current intensity [A]
M_A	: actual mass of Fe loss from anode by weighting
M_T	: theoretical mass of Fe loss from anode calculated by Faraday's law
P	: electrical potential [Volt]
t	: operation time [hr]
V	: volume of wastewater [m ³]

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