Thammasat Int. J. Sc. Tech., Vol. 13, No. 4, October-December 2008

Heavy Metals Removal from COD Wastewater by Electrochemical Treatment Process

Anawat Pinisakul and Chinapong Kritayakornupong
Department of Chemistry, Faculty of Science, King Mongkut's University of Technology Thonburi,
126 Pracha-utis Rd., Bangmod, Thung-kru, Bangkok, 10140, Thailand.
Email : ianaakul@kmutt.ac.th

Abstract

The COD wastewater, containing initial concentrations of chromium, iron, mercury and silver were in ranges of 280-317, 4828-6312, 2871-3342 and 910-1408 mg/L, respectively, with high acid content, was treated by electrochemical treatment (ECT) process. The reactor was made of acrylic plastic and was installed with 6 iron plates as electrodes to be a bipolar system, applying DC electrical current. The suitable conditions were found as follows: initial pH was approximately 3.0-3.5, electrical potential was 10 volts and an operation time of 4 hours, which the concentrations of chromium and iron were very low after applying electricity less than 1 hour. But the concentration of mercury in the effluent was still higher than the standard effluent in Thailand. The water in a sludge sample was evaporated if the sample was kept for 1 day. The sludge was further treated by stabilization and solidification process which the heavy metals were not found after extraction. From the mass balance study of mercury and chromium removal, it was found that chromium and mercury in sludge were in the range of 97-98% incorporated and absorbed in the sludge. The operation cost by electrochemical treatment process was lower than that by the chemical precipitation process.

Keyword : COD Wastewater, Electrochemical Treatment Process, Heavy Metals, Mass Balance

1. Introduction

There are two major parameters for measurement of oxygen demand to stabilize organic substance in water and wastewater which are biochemical oxygen demand (BOD) and chemical oxygen demand (COD). The BOD is a measure of the quantity of oxygen used by microorganisms for stabilizing organic substances, while the COD is a measure of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant [1]. The COD measurement may not be replaced by the BOD determination, but the COD measurement was used in some treatment systems such as anaerobic treatment [2-6]. Moreover, BOD is analyzed in about 5 days whereas COD is measured within 3 hours [7]. Thus, the COD measurement is used in terms of short time determination and correcting the treatment system immediately.

In COD determination, there were some heavy metals, consisting of chromium (Cr), mercury (Hg), iron (Fe) and silver (Ag). Chromium (from potassium dichromate, $K_2Cr_2O_7$) which are used as oxidizing agents to stabilize organic substances in wastewater. Mercury (from mercury (II) sulfate, $HgSO_4$) was used for the protection of interferences from chloride ion. Iron (from ferrous ammonium sulfate, FAS, $Fe(NH_4)_2(SO_4)_2.6H_2O$) was used as titrant to determine the remaining dichromate ion. Silver (from silver sulfate, Ag_2SO_4) was used for digestion of straight-chain aliphatic compounds by dichromate ion effectively. Moreover, the condition for digestion was acidic by adding sulfuric acid (H_2SO_4). Thus, the wastewater from COD determination consisted of heavy metals and high acid content [7].

Heavy metals can be removed from water by chemical precipitation in basic conditions as the hydroxide form. Chromium in hexavalent form (Cr(VI)) cannot be precipitated easily in basic conditions. Chromium (VI) ion must be reduced to chromium (III) ion in acidic condition, then, precipitated as the hydroxide form in basic conditions. [8, 9]. For some heavy metals such as arsenic, a coagulant such as ferric chloride must be used to co-precipitate and remove it from the contaminated water [10].

The Electrochemical Treatment (ECT) process is a method that can be used to remove heavy metals from contaminated water [10]. Direct current (DC) was applied to a cell consisting of electrodes (anode and cathode). The electrodes were made of iron. The oxidation of iron occurred to form ferrous ions (Fe^{2+}) or ferric ions (Fe^{3+}) at the anode and the reduction of water occurred to form hydroxide ions (OH^-) at the cathode. The precipitates of ferrous hydroxide ($Fe(OH)_2$) or ferric hydroxide ($Fe(OH)_3$) formed were coagulants to remove heavy metals from the contaminated water. The development of these coagulants had an advantage in their price over the use of iron compounds such as ferric chloride or ferrous sulfate. The usage of water to be the source of OH^- is lower priced than chemicals such as sodium hydroxide (NaOH).

From the Notification of the Ministry of Science, Technology and Environment, No. 3, B.E.2539 (1996) [11], it was found that the heavy metals consisting of chromium and mercury were treated to be less than 1 mg/L and 0.005 mg/L, respectively. Thus, this research aimed to study suitable conditions for chromium and mercury removal from COD wastewater, to study the mass balance of chromium and mercury removal, and to determine the operation cost of COD wastewater treatment by ECT process.

2. Materials and Methods

The ECT experiments were conducted at the Department of Chemistry, Faculty of Science, King Mongkut's University of Technology (KMUTT), Bangkok, Thailand, at which the ambient temperatures were 25-33 °C.

2.1 Experimental Setup

The ECT reactor, consisting of an electrolytic cell and electrolyte solution (COD wastewater), was made of an acrylic plate with a dimension of 5×30×10 cm^3 (width×length×depth) and the effective volume was 1.5 L. Six iron electrode plates were installed along the reactors length, each with a size of 0.2×30×10 cm^3, to be a bipolar system, and they were fixed at 1 cm from each other. The first and sixth iron electrode plates (anode and cathode) were connected to an AC/DC converter in which the electrical potential was controlled by a variable transformer. The ECT experimental setup for treatment of the COD wastewater is shown in Figure 1. The COD wastewater was collected from the Department of Environmental Engineering, Faculty of Engineering, KMUTT and Division of Environmental Technology, School of Energy and Materials, KMUTT.

The electrode plates were prepared by etching the iron plates with hydrochloric acid (HCl, 1:10), steel brushed to remove scale, rinsed with tap-water, dried at 103 °C for 1 hour, cooled in a desiccator, and weighed.

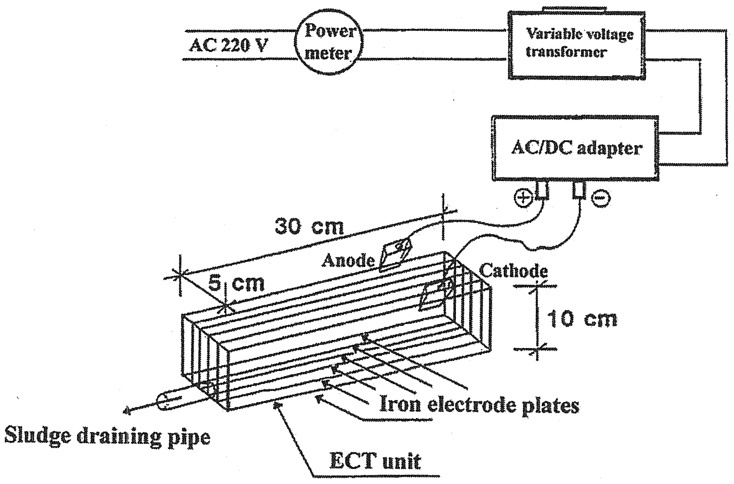


Figure 1 ECT Experimental Set-up for treatment of COD Wastewater

2.2 Determination of Suitable Conditions for Heavy Metals Removal from COD Wastewater

The experimental conditions to achieve the determination of suitable conditions for chromium and mercury removal from COD wastewater were shown in Table 1. The chromium, mercury, iron and silver removal efficiencies were determined by analysis of initial and residual concentrations at various operation times, as shown in Table 1. The initial pH of the COD wastewater was adjusted by NaOH. During the experiments, the residual chromium, mercury, iron and silver concentrations, electrical current, total suspended solids (TSS) concentration, pH, conductivity and temperature were monitored at the various operation time as shown in Table 1. The volume of COD wastewater for each batch was 300 mL.

Table 1 Parameters Variation during the ECT Experiments

Heavy metal	Electrical Potential Applied (volts)	Operation Time	Initial pH
Chromium and Iron[a]	4^{b}, 6, 8^{c}	0, 10, 20, 30, 40, 50, 60, 90, 120, 150 and 180 min	Not adjusted and adjusted to 3.0-3.5
Mercury and Silver[d]	6, 8, 10	0, 1, 2, 3 and 4 hours	Not adjusted and adjusted to 3.0-3.5

Note [a] Use AC/DC converter no. 1.

[b] When initial pH values were adjusted to 3.0-3.5 and using the electrical potential of 4 volts, the electrochemical reaction could not take place.

[c] When initial pH values were adjusted to 3.0-3.5, the AD/DC converter no. 1 could not be adjusted to 8 volts, then, an electrical potential of 10 volts had to be used instead.

[d] Use AC/DC converter no. 2 because AC/DC converter no. 1 was damaged. The above electrical potentials were adjusted.

The suitable conditions of the ECT reactor for heavy metals removal from the COD wastewater were based on the conditions that could result in the highest chromium and mercury removal efficiency, or the chromium and mercury concentration remaining in the supernatant to be less than 1 mg/L and 0.005 mg/L, respectively [11]. The iron and silver concentration in the supernatant was not compared because there was no standard [11]. The suitable conditions for chromium and mercury removal in the ECT reactors were determined by varying the following operating parameters : electrical potential and initial pH.

Because the mercury concentration in supernatant cannot be decreased to be less than 0.005 mg/L and the water in the sludge sample was evaporated to be dried if the sample was kept for 1 day to increase the solid content, the stabilization and solidification process should be performed in which cement and sand are used as the stabilization agents [12]. The extraction of heavy metals from unstabilized (ECT sludge) and stabilized sludge were done to compare to the standard of the Ministry of Industry [13]. The compression test of stabilized sludge was also performed to compare to the standard of the Ministry of Industry for disposal in a secure landfill [13].

2.3 Determination of Mass Balance of Chromium and Mercury Removal

The mass balance of chromium and mercury removal in the ECT process was determined using Eq. (1).

$$HM_{Inf} = HM_{Eff} + HM_{Slu} + HM_{un} \qquad (1)$$

Where

HM_{Inf} = Initial chromium and mercury content, mg

HM_{Eff} = Residual chromium and mercury in the supernatant, mg

HM_{Slu} = Chromium and mercury incorporated in and adsorbed on the ECT sludge, mg

HM_{Un} = Unaccounted for chromium and mercury, mg

HM_{Slu} was determined from the percent content of chromium and mercury in ECT sludge using X-ray fluorescence (XRF) analysis.

2.4 Determination of Operation Cost of COD Wastewater Treatment by ECT Process

The operation cost of COD wastewater treatment by the ECT process was determined using Eq. (2). The cost from the ECT process was used to compare to the cost from the chemical precipitation process [8] for chromium and mercury removal from COD wastewater.

$$C_{Total} = C_{NaOH} + C_{Fe} + C_I \qquad (2)$$

Where

C_{Total} = Total operation cost (Baht/L)

C_{NaOH} = Cost of NaOH (Baht/L)

C_{Fe} = Cost of iron (Baht/L)

C_I = Cost of electricity (Baht/L)

2.5 Method of Analysis

Chemical and physical parameters were analyzed according to the methods described in "Standard Methods for the Examination of Water and Wastewater" [7] as shown in Table 2.

Table 2 Chemical and Physical Parameters and Analytical Methods

Parameters	Analytical Methods
Chromium, Iron and Silver (mg/L)	Atomic Absorption Spectroscopy (AAS)
Mercury (mg/L)	AAS (Cold Vapor Technique)
pH	Glass Electrode Method
TSS (mg/L)	Filtered and Dried at 103 °C
Percent Content of Chromium and Mercury in ECT sludge	X-ray Fluorescence Spectrometer
Conductivity (mS/cm)	Conductivity Meter
Temperature (°C)	Thermometer
Electrical Current (amp)	Digital Multi-meter
Electrical Potential (volts)	Digital Multi-meter

Table 3 Some Characteristics of COD Wastewater

Parameters	Values
Chromium (mg/L)	280-317[a]
Iron (mg/L)	4,828-6,312[a]
Mercury (mg/L)	2,871-3,342[a]
Silver (mg/L)	910-1,408[a]
pH	ND[b]
Conductivity (mS/cm)	15.1-122.4[a]

Note [a] Number of sample (n) = 3 were analyzed from the taken samples mentioned in section 2.1.
[b] ND = Non-detectable

3. Results and Discussion

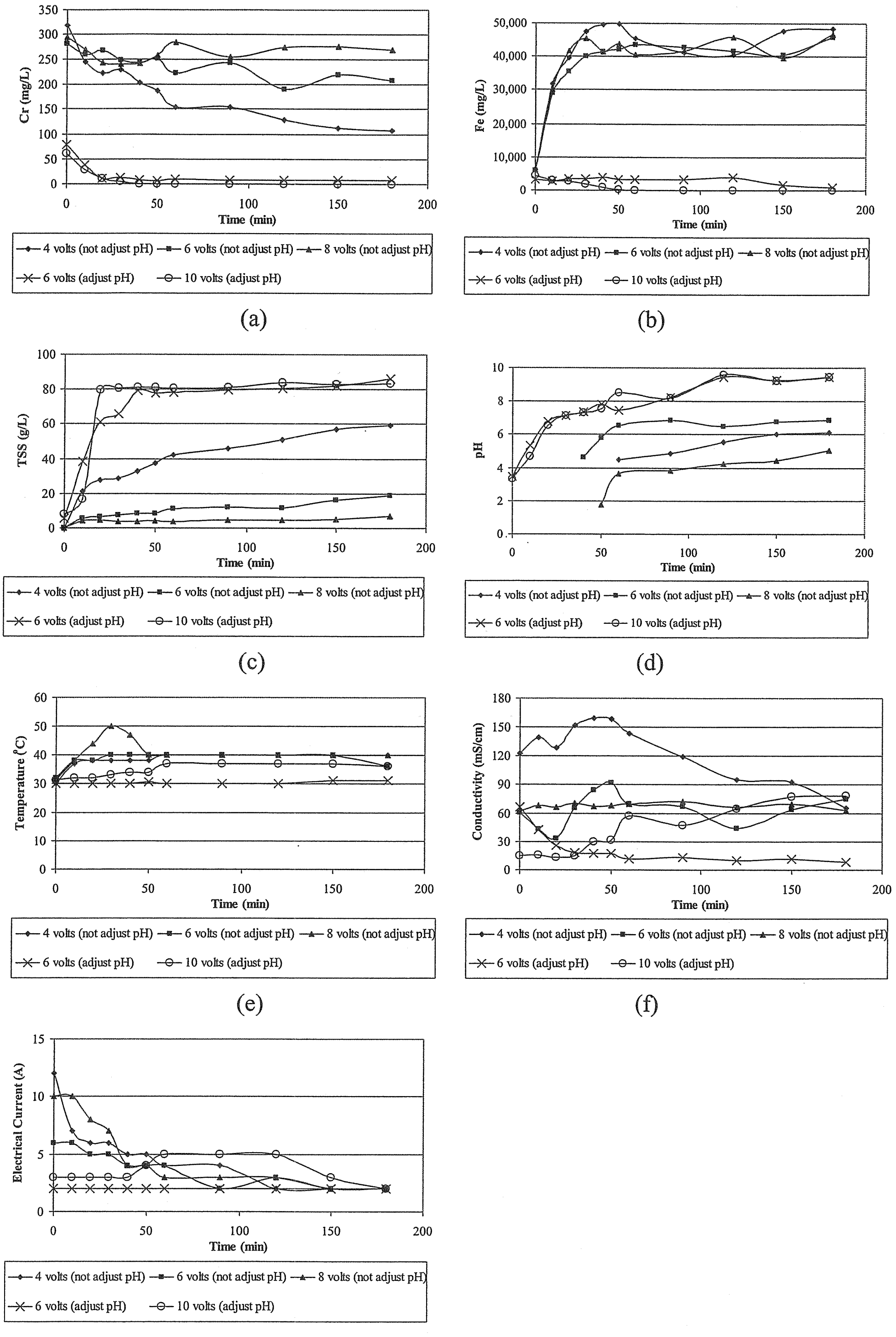
3.1 Characteristics of COD Wastewater

The characteristics of COD wastewater are shown in Table 3.

The COD wastewater contained high concentration of chromium, mercury, iron and silver because there were usage of $K_2Cr_2O_7$, $HgSO_4$, FAS and Ag_2SO_4. The COD wastewater was acidic and the pH values cannot be detected because a high concentration of sulfuric acid was used during digestion. Due to the high concentration of heavy metals and acidic conditions, the proper treatment should be performed before discharging wastewater to a public water body.

3.2 Determination of Suitable Conditions for Heavy Metals Removal from COD Wastewater

Figures 2 and 3 were used to determine the suitable conditions for chromium and mercury removal from COD wastewater by ECT process.



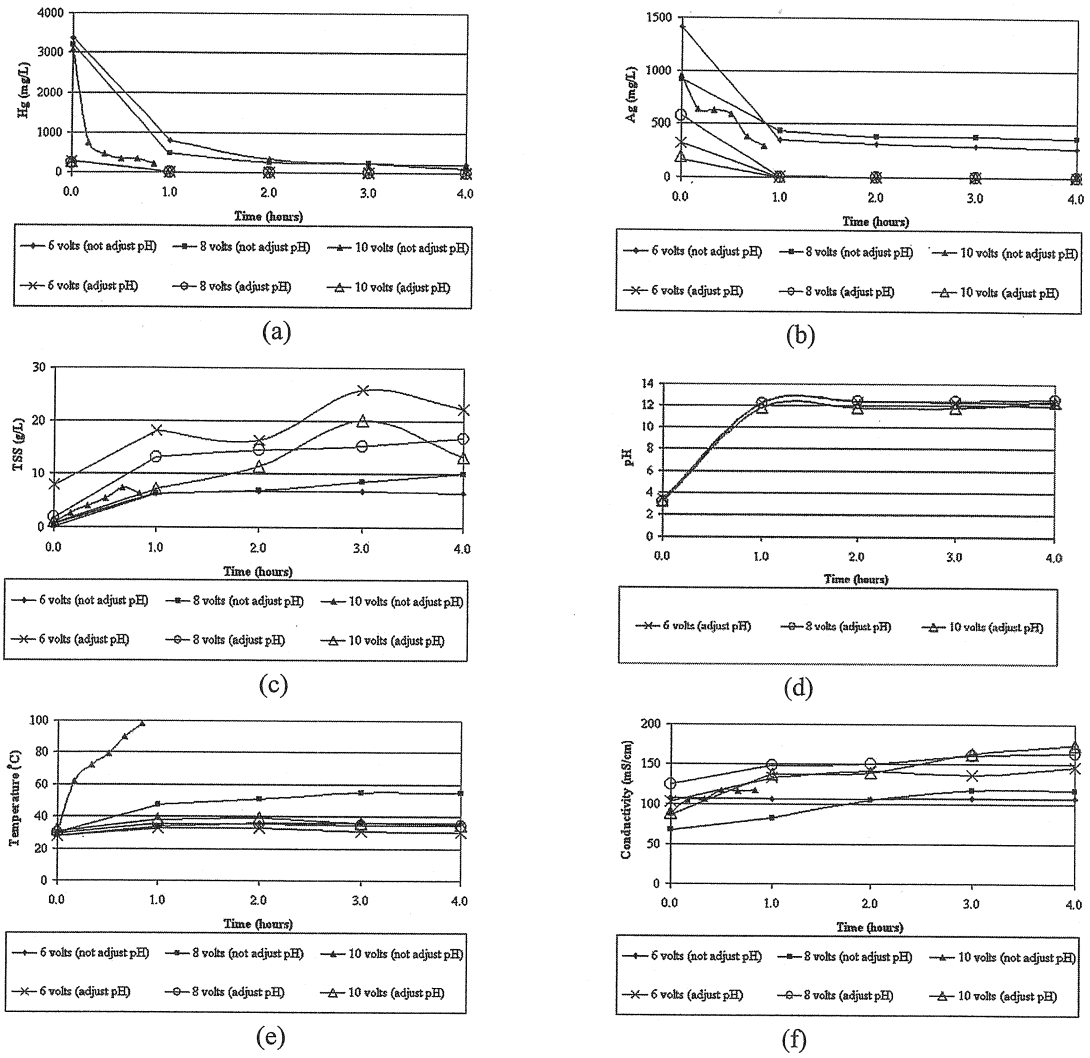
(a) (b)

(c) (d)

(e) (f)

(g)

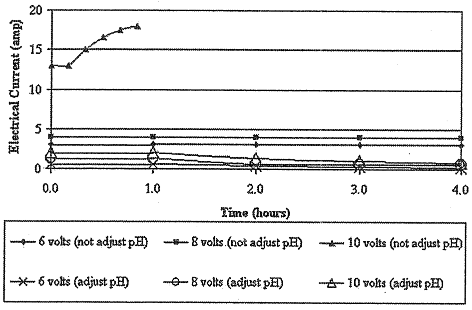
Figure 2 Parameters Variation for Chromium and Iron Removal during the ECT Experiments
(a) Chromium Content (b) Iron Content (c) TSS Content
(d) pH Value (e) Temperature (f) Conductivity
(g) Electrical Current



(a) (b)

(c) (d)

(e) (f)



(g)

Note :
At an electrical potential of 10 volts when the pH was not adjusted, it cannot be operated until 4 hours because the temperature (98°C) and current (17 amp) were very high. It may be dangerous. The operation time at this condition was only 50 minutes.

Figure 3 Parameters Variation for Mercury and Silver Removal during the ECT Experiments
(a) Mercury Content (b) Silver Content (c) TSS Content
(d) pH Value (e) Temperature (f) Conductivity
(g) Electrical Current

From Figures 2(a), 2(b), 3(a) and 3(b), after adjusting pH by NaOH, the initial chromium, iron, mercury and silver concentrations were decreased from 280-317 mg/L, 4828-6312 mg/L, 2871-3342 mg/L and 910-1408 mg/L (all n=3) to approximately 60-80 mg/L (n=2), 3000-4000 mg/L (n=2), 220-270 mg/L (n=3) and 200-600 mg/L (n=3), respectively, because some chromium, iron, mercury and silver contents may be precipitated as hydroxide forms because of low solubility product constants [8, 14]. The advantages of adding NaOH to adjust pH were the decreasing of acidic content leading to the reaction of hydrogen ion (H^+) to react with hydroxide ion (OH^-) to make water. The water can be dissociated to hydrogen gas and OH^- at the cathode while the oxidation of iron occurs at the anode to be Fe^{2+} and some Fe^{3+} from air oxidation to produce a precipitate of $Fe(OH)_2$ or $Fe(OH)_3$, which is a coagulant, resulting in the precipitation of heavy metals as the Equations (3), (4) and (5).

Anode :

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^- \quad (3)$$

Cathode :

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \quad (4)$$

Overall :

$$Fe(s) + 2H_2O(l) \rightarrow H_2(g) + Fe(OH)_2(s) \quad (5)$$

Using only NaOH added, cannot be used to remove all of chromium content, because Cr(VI) or dichromate ion cannot be completely precipitated in basic conditions. During ECT process, Cr(VI) was reduced to Cr(III) by the reduction at the cathode, and Fe(II) from the anode can also reduce Cr(VI) to Cr(III), which precipitates as hydroxide forms in basic conditions such as $Cr(OH)_3$ which resulted in non-detection of chromium in the supernatant in the conditions of adjusting initial pH to 3.0-3.5, electrical potential of 10 volts and operation time of 15 min.

All iron content can be removed from the wastewater at the same conditions as chromium removal (electrical potential of 10 volts and initial pH of 3.0-3.5), except using the operation time of 60 min.

The mercury and silver concentrations were decreased during ECT process because of the continuous production of OH^- and precipitation of hydroxide forms as shown for the removal efficiencies at the operation time of 4 hours in Table 4.

The not-adjusted pH process gave lower removal efficiencies than the adjusted pH process because the reaction may occur very difficultly at the electrodes, which was due to a lot of ions that moved to the electrodes and protected the reaction from occurring (from the polarization of ions near the electrodes). Comparing to the adjusted pH to 3.0-3.5 process, it was found that the removal efficiencies were higher than the values from the not-adjust pH process because the ions in the solution were diluted by water to reduce the polarization of ions which resulted from reaction between OH^- from NaOH and H^+ in the COD wastewater. The additional water acted as a reactant to produce more OH^- in the ECT process, leading to higher removal efficiencies of mercury and silver.

Table 4 Removal Efficiencies of Mercury and Silver at various Conditions

Electrical Potential (volts)	Mercury Removal Efficiency (%)	Silver Removal Efficiency (%)
6 (not adjusted pH)	93.14	80.89
8 (not adjusted pH)	97.03	59.89
10 (not adjusted pH)[a]	93.40	69.81
6 (adjusted pH to 3.0-3.5)	99.98	99.83
8 (adjusted pH to 3.0-3.5)	99.98	99.92
10 (adjusted pH to 3.0-3.5)	99.99	99.96

Note : [a] The operation time was 50 minutes because the temperature was 98°C and the electrical current was 17 amps, which may be dangerous. The other operation times were 4 hours.

The TSS concentrations increased with increasing of time as Figures 2(c) and 3(c) because the $Fe(OH)_2$ or $Fe(OH)_3$ occurred along the operational time to increase the removal efficiency. For the adjusted pH process, the pH values of the system (Figures 2(d) and 3(d)) increased because of the continuous production of OH^- from the cathode. The final pH at 4 hours was higher than 12.0 because there was a usage of NaOH to raise the pH to 3.0-3.5 and OH^- production from additional water from the reaction between OH^- and H^+. The system temperatures (Figures 2(e) and 3(e)) increased in the range of 30-60°C because there was some accumulation of heat from the current flowing through the ECT reactor which had resistance. Only with the conditions of not adjusted pH and electrical potential of 10 volts (Figure 3(e)), the temperature increased to 98°C because of a higher concentration of ions in the COD wastewater, which may be dangerous to researchers. This condition should not be selected. The conductivity of solutions (Figures 2(f) and 3(f)) were high because the COD wastewaters contain high concentration of salt, leading to high electrical current after applying electricity (Figure 2(g) and 3(g)).

The Suitable Conditions

From Figure 2(a), at the electrical potential of 4, 6 and 8 volts without adjusting pH to 3.0-3.5, the chromium concentrations after the ECT process were higher than the standard effluent in Thailand [11]. After adjusting the pH to 3.0-3.5, the ECT reaction cannot occur at a electrical potential of 4 volts. It may be the dilution of water by adding NaOH. The electrical potential of 8 volts cannot be adjusted, but 10 volts was used and all contents of chromium and iron can be removed at this electrical potential. It was found that the electrical potential of 4 volts was not suitable for the following experiments.

For mercury and silver removal experiments, the highest removal efficiencies were found with the conditions of adjusted pH to 3.0-3.5, electrical potential of 10 volts and operational time of 4 hours, which showed the highest removal efficiencies of chromium and mercury. Thus, this was the suitable conditions for heavy metals removal by the ECT process.

Although the mercury removal efficiency was 99.99%, the mercury concentration in the supernatant was 0.2 – 0.4 mg/L, which was still higher than a standard effluent in Thailand [11]. The water in a sludge sample was evaporated to be dried if the sample was kept for 1 day to increase the solid content. The extraction of heavy metals of unstabilized sludge (ECT sludge) are shown in Table 5.

From Table 5, it was found that the extracted mercury concentrations were higher than the standard. The stabilization and solidification process should be performed which cement and sand are used as the stabilization agents at a ratio of sand : cement : sludge of 80 : 20: 0.2 [12]. The results of extraction of stabilized sludge and compression test are shown in Table 6.

From Table 6, it was found that the heavy metals were fixed by stabilization agents. The stabilized sludge was suitable for disposal in secured landfill with the compression test in the safety range. The COD wastewater was completely treated by the ECT process and stabilization and solidification process.

Table 5 Heavy Metals Extraction from ECT Sludge

Heavy Metals	Concentration (mg/L)	Standard [a] (mg/L)
Chromium	0.245 – 0.352	≤ 5.0
Iron	0.287 – 0.491	No Standard
Mercury	0.314 – 0.326	≤ 0.2
Silver	0.290 – 0.937	≤ 5.0

Note [a] Notification of Ministry of Industry No. 6 (B.E. 2540)

Table 6 Heavy Metals Extraction from Stabilized Sludge and Compression Test

Incubation Period (days)	Chromium (mg/L)	Iron (mg/L)	Mercury (mg/L)	Silver (mg/L)	Compression Test (kg/cm^2)
7	ND	ND	ND	ND	11.87 – 12.09
14	ND	ND	ND	ND	118.59 – 157.67
21	ND	ND	ND	ND	136.81 – 139.76
28	ND	ND	ND	ND	174.14 – 179.22
Standard [a] (mg/L)	≤ 5.0	No Standard	≤ 0.2	≤ 5.0	≥ 3.5

Note [a] Notification of Ministry of Industry No. 6 (B.E. 2540) and ND = Non-detectable

3.3 Determination of Mass Balance of Chromium and Mercury Removal

From XRF analysis, the chromium and mercury contents in sludge were 0.33 g Cr and 2.54 g Hg in 100 g sludge, respectively. The chromium and mercury contents in the components according to Eq. (1) of the ECT reactors and the mass balance for chromium and mercury removal in the ECT process are shown in Table 7.

At the suitable conditions, it was found that the major mechanism for chromium and mercury removal was the chromium and mercury incorporated in and adsorbed on ECT sludge (97-98%). The low chromium and mercury contents in effluent (or supernatant) (ND-0.004%) indicated the high removal efficiency of chromium and mercury from the COD wastewater.

3.4 Determination of Operation Cost of COD Wastewater Treatment by ECT Process

The comparison of operational cost of COD wastewater treatment between ECT process and chemical precipitation process (reduction and precipitation)is shown in Table 8.

From Table 8, it was found that the heavy metal removal by the chemical precipitation process [8] had higher operation cost than the cost from the ECT process. Moreover, the chemical precipitation process required the 10-fold dilution of wastewater before treatment, leading to increase in the volume of wastewater. In the ECT process, the lower cost may be from the lower content of NaOH usage because some OH^- from water dissociation can be used instead of NaOH. The remaining mercury concentration of the ECT process was lower than the values in chemical precipitation, which resulted in higher removal efficiency. There was no dilution in the ECT process. The ECT process may be an alternative method for removing heavy metals from COD wastewater.

Table 7 Mass Balance for Chromium and Mercury Removal in the ECT Process

Mass Balance for Chromium Removal			Mass Balance for Mercury Removal		
Cr_{Eff}	Cr_{Slu}	Cr_{un}	Hg_{Eff}	Hg_{Slu}	Hg_{un}
ND	98.04	1.96	0.004	97.37	2.63

Note Cr_{Eff} = Chromium content in effluent
Cr_{Slu} = Chromium content in ECT sludge
Cr_{un} = Unaccount for Chromium
Hg_{Eff} = Mercury content in effluent
Hg_{Slu} = Mercury content in ECT sludge
Hg_{un} = Unaccount for chromium
ND = Non-detectable

Table 8 Cost Comparison between the Chemical Precipitation and the ECT Processes

Chemical Precipitation Process [8]			ECT Process (This study)			
$FeSO_4.7H_2O$ (Baht/L)	NaOH (Baht/L)	Total (Baht/L)	NaOH (Baht/L)	Iron (Baht/L)	Electricity (Baht/L)	Total (Baht/L)
0.003	15.18	15.18	12.00	1.17	0.60	13.77

Note The price of chemical and electricity as follows :

1. $FeSO_4.7H_2O$ (commercial grade) : 5.50 Baht/kg
2. NaOH (99%, commercial grade) : 20 Baht/kg
3. Iron (plate) : 25 Baht/kg
4. Electricity cost : 2.61 Baht/unit

4. Conclusion

This study demonstrates the following conclusions :

1. The suitable conditions for removal of heavy metals in the COD wastewater by theECT process were the following : adjusting pH to 3.0-3.5, electrical potential of 10 volts and operation time of 4 hours. The chromium and iron cannot be detected after treatment. The efficiencies of mercury and silver removal were higher than 99.9%. After stabilization and solidification process of the ECT sludge, the stabilized sludge was safe for disposal in a secure landfill.
2. The major mechanism for chromium and mercury removal was the mercury incorporated in and adsorbed in the ECT sludge (97-98%).
3. The operational cost for ECT process (13.77 Baht/L) was lower than that of chemical precipitation process (15.18 Baht/L).

Acknowledgement

This research was supported by King Mongkut's University of Technology Thonburi (KMUTT) Research Fund for financial support. The Department of Chemistry, Faculty of Science, KMUTT is acknowledged for laboratory analysis. The authors are grateful to Assoc. Prof. Naraporn Hanvajanawong for her valuable suggestions, Mr. Winyu Pibanwong, Ms. Arissara Thatpitak, Mr. Pichate Satjanurakwong and Ms. Jiraporn Yodkaew for their laboratory analysis.

5. References

[1] Sawyer, N.C., McCarty, P.L. and Parkin, G.F., Chemistry for Environmental Engineering and Science, 4th ed., McGraw-Hill, Inc, Boston, 2003.

[2] Rao, A.G. and Bapat, A.N., Anaerobic Treatment of Pre-Hydrolysate Liquor (PHL) from a Rayon Grade Pulp Mill: Pilot and Full-Scale Experience with UASB Reactors, Bioresource Technology, Vol. 97, No. 18, pp. 2311-2320, 2006.

[3] Luostarinen, S., Sanders, W., Kujawa-Roeleveld, K. and Zeeman, G., Effect of Temperature on Anaerobic Treatment of Black Water in UASB-Septic Tank Systems, Bioresource Technology, Vol. 98, No. 5, pp. 980-986, 2007.

[4] Boubaker, F. and Ridha, B. C., Anaerobic Co-Digestion of Olive Mill Wastewater with Olive Mill Solid Waste in a Tubular Digester at Mesophilic Temperature, Bioresource Technology, Vol. 98, No. 4, pp. 769-774, 2007.

[5] Gohil, A. and Nakhal, G., Treatment of Tomato Processing Wastewater by an Upflow Anaerobic Sludge Blanket–Anoxic–Aerobic System, Bioresource Technology, Vol. 97, No. 16, pp. 2141–2152, 2006.

[6] Ramakrishnan, A. and Gupta, S. K., Anaerobic Biogranulation in a Hybrid Reactor Treating Phenolic Waste, Journal of Hazardous Materials Vol. 137, No. 3, pp. 1488–1495, 2006.

[7] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater. 20th Edition, American Public Health Association, Washington D.C., 1998.

[8] Kumdee, K. and Kumngao, P., Heavy Metal Treatment of Mixed Wastewater from DO, BOD, COD and Solids Analysis of Chemical and Applied Chemical Laboratory, Research in Bachelor of Science, Department of Chemistry, Faculty of Science, KMUTT, 1999.

[9] Almeida, M.A.F. and Boaventura R. A. R., Chromium Precipitation from Tanning Spent Liquors using Industrial Alkaline Residues : A Comparative Study, Waste Management , Vol. 17, No. 4, pp. 201-209, 1997.

[10] Pinisakul, A., Polprasert, C., Parkpian P. and Satayavivad J, Arsenic Removal Efficiency and Mechanisms by Electro-Chemical Precipitation Process, Wat. Sci. and Tech., Vol. 46, No. 9, pp. 247-254. 2002.

[11] Notification of the Ministry of Science, Technology and Environment, No. 3, B.E.2539 (1996), issued under the Enhancement and Conservation of the National Environmental Quality Act B.E.2535 (1992), the Royal Government Gazette, Vol. 113 Part 13 D, dated February 13, B.E.2539 (1996).

[12] Kijchainukul, V., Characteristic of Moulding Sand Waste from Steel Melting

Industry Using as Cementitious Binder in Solidification, Thesis in Master of Science, Division of Environmental Technology, School of Energy and Material, KMUTT, 1998.

[13] Notification of the Ministry of Industry, No. 6, B.E.2540 (1997), issued under the Factory Act B.E.2535 (1992), the Royal Government Gazette, Vol. 114 Part 106 D, dated November 13, B.E.2540 (1997).

[14] Speight, J. G., Lange's Handbook of Chemistry, 16th ed, McGraw-Hill, New York, 2005.