

การฟื้นฟูตะกั่วในตะกอนดินที่มีการปนเปื้อนโดยกระบวนการอิเล็กโทรโคแอกกูเลชัน



นางสาวกาญจนา โลกคำลือ

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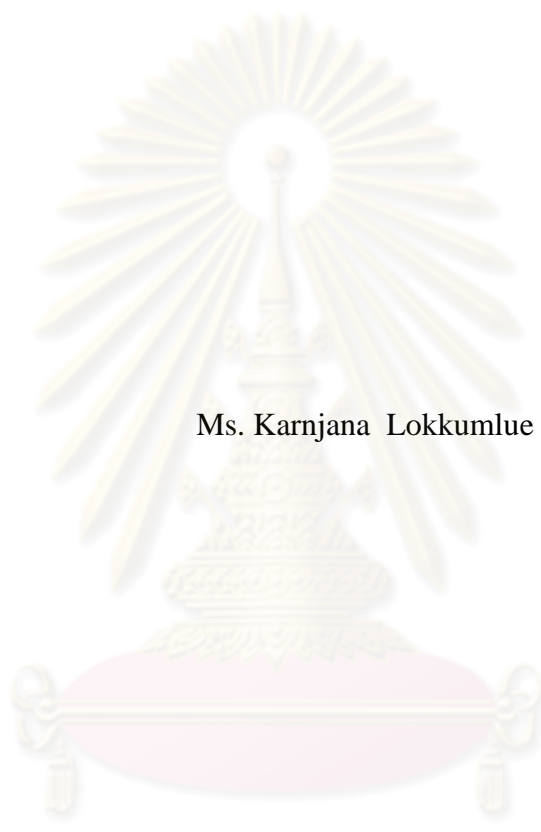
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REMEDICATION OF LEAD FROM CONTAMINATED SEDIMENT USING
ELECTROCOAGULATION PROCESSES



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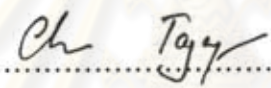
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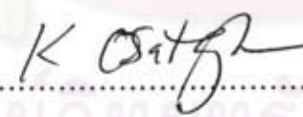
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กาญจนา โลกคำลือ: การฟื้นฟูตะกั่วในตะกอนดินที่มีการปนเปื้อน โดยกระบวนการอิเล็กโทรโคแอกกูเลชัน (REMEDIATION OF LEAD FROM CONTAMINATED SEDIMENT USING ELECTROCOAGULATION PROCESSES) อ. ที่ปรึกษา
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ตะกั่วที่ปนเปื้อนดินตะกอนและน้ำก่อให้เกิดปัญหาสุขภาพที่ร้ายแรง และความมั่นคงทางอาหาร วัตถุประสงค์หลักของการศึกษานี้ คือ ประยุกต์ใช้กระบวนการอิเล็กโทรโคแอกกูเลชัน เพื่อกำจัดตะกั่วจากทั้งตะกอน และน้ำ สภาวะที่เหมาะสม และค่าคงที่อัตราจลนศาสตร์ถูกคำนวณเพื่อระบุชุดพารามิเตอร์ที่ใช้ออกแบบในการเพิ่มประสิทธิภาพกระบวนการอิเล็กโทรโคแอกกูเลชัน และประเมินความเสถียรของตะกั่วในสลัดจ์ที่ผ่านการบำบัด สารละลายตะกอนดิน (ซเลอรี) ที่ใช้ถูกเก็บตัวอย่างจากห้วยคลิตี้ กาญจนบุรี ประเทศไทย ตะกอนมีตะกั่วเป็นองค์ประกอบและมีความเข้มข้นสูงถึง 21,833 มก./กก. บีกเกอร์บอโรซิลิเกตขนาดความจุ 1.0 ล. ถูกใช้เป็นปฏิกรณ์สำหรับกระบวนการอิเล็กโทรโคแอกกูเลชัน แผ่นโลหะจำนวน 5 แผ่นถูกนำมาจัดเรียงเป็นอิเล็กโทรดในรูปแบบไบโพลาร์ โดยติดตั้งตรงกลางปฏิกรณ์ อิเล็กโทรดสองชนิด: อลูมิเนียม และเหล็กกล้า ขนาด 140×50×3 มม. ถูกนำมาใช้ทดสอบในการศึกษานี้ ปัจจัยสำคัญที่ควบคุมประสิทธิภาพการกำจัดตะกั่วด้วยกระบวนการอิเล็กโทรโคแอกกูเลชัน ประกอบด้วย การถ่ายเทมวล รูปแบบของโคแอกกูแลนต์ และปฏิกิริยาระหว่างตะกั่วและโคแอกกูแลนต์ สมดุลของปฏิกิริยาไฮโดรไลซิสเกิดขึ้นภายในเวลา 50 นาที กระบวนการอิเล็กโทรโคแอกกูเลชันที่ใช้อลูมิเนียมเป็นอิเล็กโทรดนั้นสามารถเพิ่มประสิทธิภาพ หากโมโนเมอร์ริกของ $Al(OH)_4^-$ ถูกจ่ายเข้าระบบที่พีเอชเท่ากับ 6.1 เมื่อระบบถูกจ่ายไฟฟ้ากระแสตรงที่ 10, 20 และ 30 มิลลิแอมแปร์ ค่าอัตราจลนศาสตร์เท่ากับ 0.37, 0.99 และ 1.26 ล./มก.-นาที ตามลำดับ ตะกั่วส่วนใหญ่จะตกค้างในสลัดจ์ สำหรับอิเล็กโทรดเหล็ก หากโมโนเมอร์ริกของ $Fe(OH)_2$ ถูกจ่ายในระบบที่พีเอชเท่ากับ 8 สภาวะที่เหมาะสมจะปรากฏขึ้น ไอออนของโคแอกกูแลนต์ Fe^{2+} ที่ได้รับในระบบจะถูกแปรสภาพอย่างรวดเร็วเป็น Fe_2O_3 ซึ่งมีความเสถียรสูงมาก ปฏิกิริยาระหว่างโคแอกกูแลนต์ Fe และตะกั่วถูกสันนิษฐานว่าเป็นการตกตะกอนแบบกวางค เนื่องจากฟล็อกของสนิมที่แน่นสามารถปิดทับตะกั่วไว้ได้ ดังนั้นตะกั่วที่ไม่ว่องไวต่อปฏิกิริยาจึงตรวจพบได้ เกณฑ์ด้านเศรษฐศาสตร์แสดงให้เห็นว่า กระบวนการอิเล็กโทรโคแอกกูเลชันที่มีอิเล็กโทรดเหล็ก และอลูมิเนียมสามารถดำเนินการลงทุนได้ก็ต่อเมื่อราคาน้ำดื่ม น้ำสูงถึง 0.5 หรือ 3.1 บาท/ล. ตามลำดับ

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KARNJANA LOKKUMLUE: REMEDIATION OF LEAD FROM CONTAMINATED SEDIMENT USING ELECTROCOAGULATION PROCESSES. ADVISOR: THIDARAT BUNSRI, Ph.D., 71 pp.

Lead (Pb) contamination in sediments and water could pose a serious problem to human health and sustainability of food. The main purpose of this study was to apply the electrocoagulation (EC) process to remediate Pb from both of sediment and water. The optimum conditions and the kinetic rate constant were determined to define a set of design criteria for enhancing EC process and to evaluate the stability of lead in treated sludge. The sediment slurry used in this study was collected from Klity creek, Kanchanaburi, Thailand. The sediments contained a high concentration of Pb that was 21,833 mg/kg. The borosilicate beaker with a working capacity of 1.0 L was used as the EC batch reactor. The five metal sheet electrodes were arranged in bipolar mode at the centre of reactor. Two types of electrode: aluminium and mild steel with a dimension of 140×50×3 mm were employed in this study. The key parameters in Pb removing efficiency using electrocoagulation were including of mass transfer, form of coagulants and the reaction between Pb and coagulants. The equilibrium of Pb hydrolysis was achieved within 50 minutes. The electrocoagulation with Al electrode could be enhanced if the mono meric of $Al(OH)_4^-$ was generated at pH of 6.1. When the system was supplied with 10, 20 and 30mA of DC power, the rate constants were 0.37, 0.99 and 1.26 L/mg-min, respectively. Most of Pb was remained in sludge as inert Pb. With Fe electrode, if the favoured monomeric of $Fe(OH)_2$ was generated at pH of 8, the optimum condition could be earned. The Fe^{2+} coagulants yielded in this study was quickly transformed to Fe_2O_3 that was highly stable. The reaction between Fe coagulant and Pb was assumed to be sweep coagulation as the rust dense floc could cover the Pb. Therefore the inert Pb was obtained. In economic aspect, the electrocoagulation with Fe and Al electrodes could be invested when the price of drinking water was higher than 0.5 and 3.1 THB/L., respectively.

Field of Study: Environmental Management

Student's Signature: Thida

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CHAPTER I

INTRODUCTION

1.1 Overview

Lead (Pb) was the most widely used metal in many heavy industries. Lead could resist the corrosion and rarely react with sulfuric acid and sulfur compounds. Lead could be used for fabrication of many appliances that require highly durable and sulfur resistant. More than 40 years ago, lead was applied as a major component in many appliances such as lead-acid batteries, corrosion resistance coating material, painting pigment, pesticide and leaded petrol. Production and consumption of lead was increased in every year during industrialisation. Approximately 8 million ton/year of lead was supplied to industries and half of the utilised Pb was obtained from recycling of scrap. Metallic lead always formed a combination with metals such as zinc, silver and copper and it was naturally bounded with inorganic constituents such as sulfur, sulphate and carbonate. The major forms of lead compounds were galena (PbS), Cerussite (PbCO₃) and anglesite (PbSO₄).

According to the life cycle of these Pb contained products, lead contamination may be widely observed as a result of washing out, depositing of lead gasoline or leaking from slag. The human activity, such as mining, waste disposal and agriculture could discharge the residual slag, sludge and waste that were contaminated with lead into environment. The level of lead exposure seemed to be relied upon the human activities. Therefore, the level of lead contamination was different in area by area. Lead was accounted as a poisonous metal, which can potentially harm to nervous connection and cause blood and brain disorders. Lead could enter to the body via the ingestion system, when lead contaminated water and food were consumed. The health impact dealing with lead poisoning might be present in different levels depending on the exposure levels. The people who lived in the lead enrichment land such as mining area or industrial estates tended to either perceive or accumulate lead at high level into the body. The primary symptoms of acute toxicity of lead were fatigue, colic anaemia, neuritis, seizures and other neurologic disorders as well as carcinogenic effects. In adults, approximately 10% of ingested lead could be absorbed into the body whereas children could absorb 40-53% of lead intake (Lawrence et al., 2009). Approximately 80–95% of lead was found in skeleton of adults and 73% of lead was in skeleton of children. The biological half-life of lead was approximately 16–40 days in blood and about 17–27 years in bones (Rabinowitz et al., 1976).

Recently, Blacksmith Institute published “World’s Worst Pollution Problems Report 2010”. The report had provided the ranking of “The Top Six Toxic Threats”. It had shown that six major pollutants that jeopardise the health of tens of millions of people. The high numbers of people were faced with lead poison. Kanchanaburi province, Thailand was recognised as the locations where the land and water sources were seriously contaminated with lead (Jitrapun et al., 2007). In particular, the newspapers were reported that the people lived near the Klity creek that was the cataract of water, had been suffered with lead poison since 1998. As the water from Klity creek was used for drinking and farming purposes, the villagers had lead content in their blood over the maximum allowable limit ($40\mu\text{g/dL}$ for adult and $10\mu\text{g/dL}$ for children) (Sroisiri et al., 2005). The lead contamination in Klity village was still critical until the present, as people could not yield safe water from other sources, except Kilty creek.

Sediments were the largest storage and they were both mobile and immobile sources of heavy metals that could play a very important role in metal migration. The sediment, which often acted as a carrier could be a potential source of heavy metal in aquatic environment (Theofanis et al., 2001). In some circumstances, more than 99% of heavy metals in the river could be founded in the bottom sediments in various forms (Salomons and Stigliani, 1995). However, heavy metals could be bounded in sediment for some certain periods. The variation of the physical and chemical characteristics of water could stimulate the releasing of heavy metals. To reduce the impact of heavy metal on health, the remediation of water and sediment had to be concerned.

Various methods could be applied to remediate heavy metals from sediment. The in-situ remediation of sediment aimed to increase the stabilisation of some metals such as the mobile and the exchangeable fractions, while the ex-situ remediation mainly focused on the removal of the potential mobile metals by bounding with other constituents such as Mn-oxides and organic matter (OM) (Peng et al., 2009). The electrocoagulation (EC) was introduced in this research as this technology could serve the removal of lead in sediment and water by generating an effective coagulant via electrolytic oxidation process of an appropriate anode material. Generally, either aluminium or steel was widely investigated to be anode electrodes, the electrolytic reaction could induce the dissolution of active ionic form of ferrous and aluminium. The ionic elements of coagulants could form a complex compound with lead,

generating the bounded lead in flocculants. In practical aspect, the electrocoagulation required a simple equipment and it was not costly (Mollah et al., 2001). The electrochemical reaction occurred at electrode could precipitate heavy metals and generate the highly stable oxide sludge (Franco, 1974; Duffey, 1983; Renk, 1989). Electrocoagulation was a powerful tool that could be perhaps applied to remove, stabilise and recovery of lead in the contaminated sediments and water.

The main purpose of this study was to apply the electrocoagulation process to remediate lead form sediments and water. The optimal conditions and the kinetic rate constant were determined to define a set of design criteria for enhancing electrocoagulation process and the stability of heavy metals in treated sediments were evaluated.

1.2 Objectives

This study mentioned on the remediation of lead from contaminated sediment and water by electrocoagulation process. The objectives of this study were:

- 1) To describe the electrocoagulation process including coagulant discharging and lead-monomeric coagulant bounding and to estimate the stability and recovery of heavy metal sludge.
- 2) To determine the optimum condition and define a set of design criteria for enhancing electrocoagulation process.
- 3) To estimate the cost of electrocoagulation for assessing the possible cost of small scale electrocoagulation unit applied to remediation Pb.

1.3 Scope of Study

To achieve the established objectives, results were obtained from a laboratory scale electrocoagulation, which was fed with constant concentration of sediments. The sediment slurry was completely stirred during operating to give the maximum mass transfer process. The variables influenced the performance of lead removal and stability of treated sediments including of types of metal electrodes and electrical current density were investigated. The scopes of study were included:

- 1) The kinetic rate constant of reaction between heavy metals and monomeric coagulant was determined to describe the mechanism of electrocoagulation process.
- 2) The removal efficiency of lead and stability of treated sediments were examined to define the optimum condition of the electrocoagulation process

employed in this research as well as to access the possible way to enhance the electrocoagulation system.

1.4 Chapter Organisation

The concept of development of this research is given in Figure 1-1.

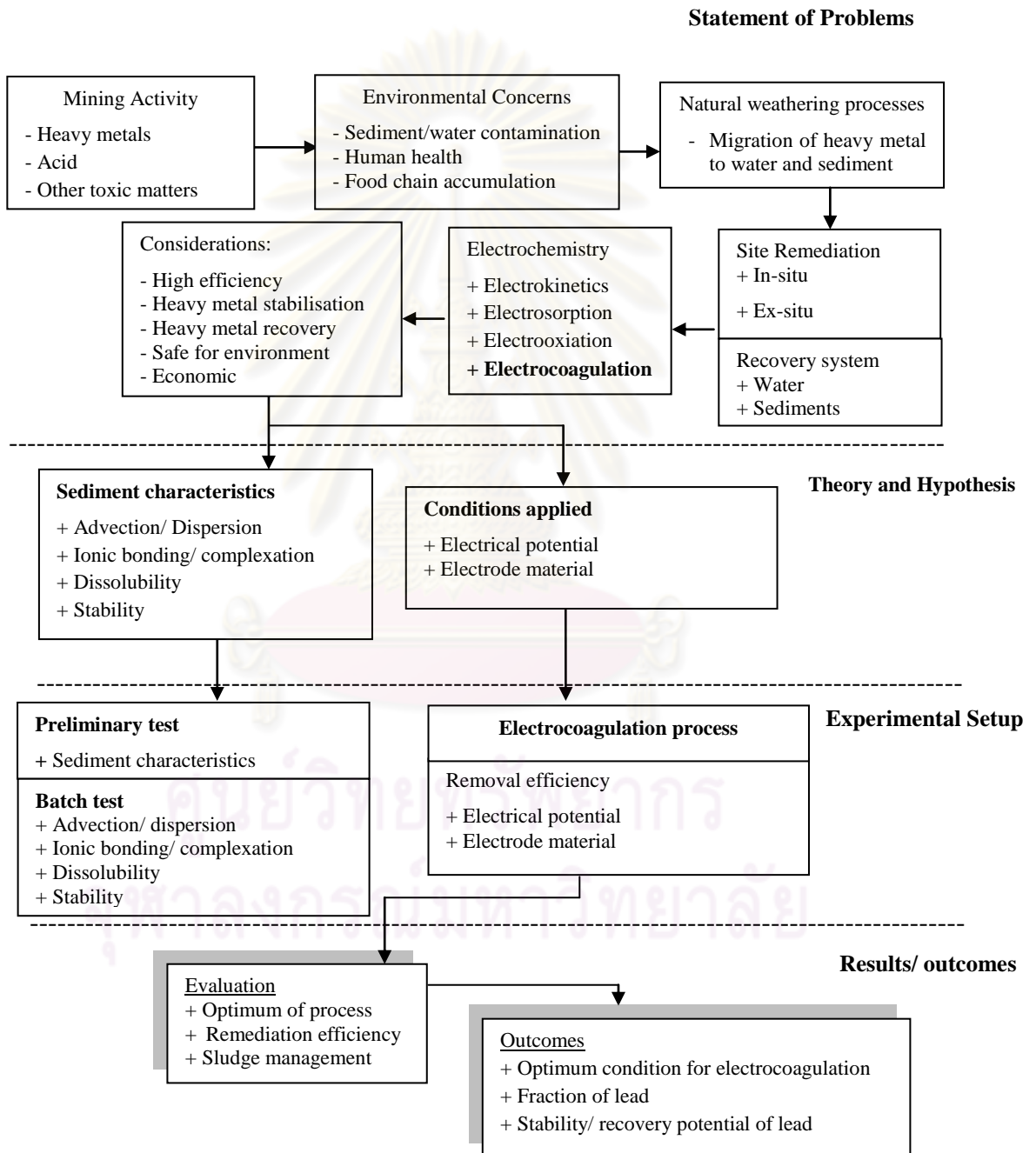


Figure 1-1 Schematic of research development

The thesis was overviewed and presented in Chapter 1 Introduction. The background and historical researches/studies were provided in Chapter 2 Literature Review and the experimental setup and analytical methods used in this research was presented in Chapter 3 Methodology. The obtained results were presented and critically discussed in Chapter 4 Results and Discussions. The findings in this research were summarised and the recommendation for the future study was provided in Chapter 5 Conclusions and Recommendations.



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CHAPTER II

LITERATURE REVIEW

2.1 Lead

Lead (Pb) could be found in multiple isotopes, only Pb-208 was stable isotope. Atomic weight of lead was 207.17 and specific gravity was 11.37. The physical properties of lead were a metallic lustre, opaque and flexibility. Boiling point and melting point of lead ore was 1,740 and 327.4 °C, respectively. Generally, the natural bonded lead was found in 3 different types as Galena (PbS), Cerussite (PbCO₃) and Anglesite (PbSO₄). The solubility of lead in each compounds was in an order of Galena < Cerussite < Anglesite. The degree of hardness was in an inverse order of solubility as Galena > Cerussite > Anglesite.

Lead was a naturally occurring element found in the earth's crust in trace quantities of approximately 8 to 13 ppm (Rudnick and Fountain, 1995; Taylor and McLennan, 1995). Lead exists in the crust in a number of ores, predominantly as lead sulfide (galena). In the absence of human activity, small amounts of lead would reach the surface environment by natural weathering processes. To create a baseline exposure in localised areas or in mineral zones could be very good practice in controlling the Pb related problems. The abundant and widespread presence of lead in our current environment was largely a result of anthropogenic activity. The amount of lead in surface water depended on the pH and the dissolved salt content. In the environment, the divalent form (Pb²⁺) was the stable ionic form of lead. The forms of lead most often found in soil were PbSO₄ and PbCO₃ (NSF, 1977).

A majority of the particulate metals especially Pb, their specific gravity was very high. They could settle down quickly and they could be deposited near the confluent channels (Yousef et al., 1986). The dissolved metals may be removed by biological and chemical processes which may eventually accumulate on the bottom sediment. Accumulation of boom sediment and associated heavy metals may become detrimental to the water quality and living organisms. The environmental occurrence of heavy metals is shown in Figure 2-1.

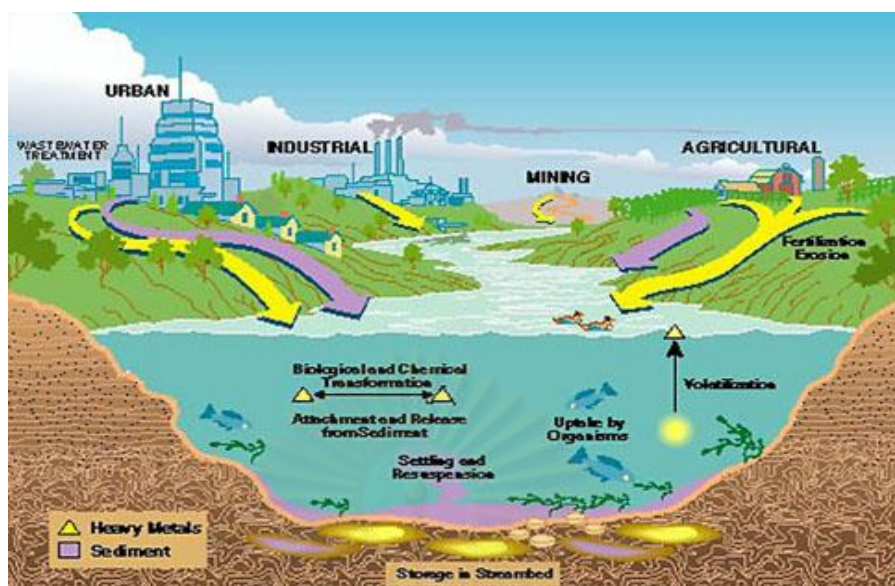


Figure 2-1 Environmental occurrence of heavy metals

Lead was accounted as poisonous metal as it could bring an adversely affect to human health. The care had to be input since handling until disposal of lead. Dealing with lead cycle, the exposure to lead and its compounds could be observed in air, water and soil. This could cause a 'lead burden'. The normal lead burden was the amount of lead derived from the environment mainly through food. Working conditions may increase the total lead burden. The Threshold Limit Value (TLV) for lead compounds, such as lead acetate, lead arsenate, lead carbonate and lead phosphate, was 0.15 mg/m^3 . The TLV was 0.05 mg/m^3 for lead chromate and tetraethyl lead. For total dust, lead metal and most of its inorganic compounds, the TLV was 0.1 mg/m^3 in some countries (Ahamed and Siddiqui, 2007).

The standards were established to classify the risk of health effect, when lead was occasionally uptaken. The standards of maximum allowable concentration of lead in contaminated sediments and drinking water were enforced in Klity area. The standard of drinking water established and enforced in Thailand and other standards of safe drinking water were summarised in Table 2-1. The heavy metals founded in the natural water were usually lower than the specified values in the standard, except iron. However, iron was the minor element that was consumed by living organism as well as it was relatively stable. The iron was easily removed by the natural process, especially aeration. Iron was not harm to human health as it was the composition of haemoglobin in blood (Benito et al., 1997). The major concern heavy metal in this study was lead, there was no report that gave a specific value of lead contamination in

water. This might associate with the fact that lead was rarely observed in metallic form and it was active metals that could be transformed into insoluble forms. The presence of lead in environment was predominantly resulted from industries and human activities. The maximum allowable lead in drinking water that enforced in Thailand was higher than the other standards.

Table 2-1 Drinking water standards

Heavy metals	Natural water	WHO standards (since 1993)	EU standards (since 1998)	Thailand (since 1991)
Aluminium (Al)		0.2 mg/L	0.2 mg/L	0.2 mg/L
Antimony (Sb)	< 4 µg/L	0.005 mg/L	0.005 mg/L	
Arsenic (As)		0.01 mg/L	0.01 mg/L	0.05 mg/L
Barium (Ba)		0.3 mg/L	Not mentioned	1.0 mg/L
Boron (B)	< 1 mg/L	0.3 mg/L	1.00 mg/L	
Bromide (Br)		Not mentioned	0.01 mg/L	
Cadmium (Cd)	< 1 µg/L	0.003 mg/L	0.005 mg/L	0.005 mg/L
Chromium (Cr)	< 2 µg/L	0.05 mg/L	0.05 mg/L	0.05 mg/L
Copper (Cu)		2 mg/L	2.0 mg/L	1.0 mg/L
Iron (Fe)	0.5 - 50 mg/L	No guideline	0.2 mg/L	0.3 mg/L
Lead (Pb)		0.01 mg/L	0.01 mg/L	0.05 mg/L
Manganese (Mn)	< 0,5 µg/L	0.5 mg/L	0.05 mg/L	0.05 mg/L
Mercury (Hg)		0.001 mg/L	0.001 mg/L	0.001 mg/L
Nickel (Ni)	< 0.02 mg/L	0.02 mg/L	0.02 mg/L	
Selenium (Se)	<< 0.01 mg/L	0.01 mg/L	0.01 mg/L	0.01 mg/L
Zinc (Zn)		3 mg/L	Not mentioned	5.0 mg/L

The standard of heavy metal contamination in soil or sediment in Thailand was not established, only Department of Agriculture had recently prepared the guideline of acceptable levels of heavy metals in agricultural areas in Thailand. The guideline for agricultural soil is shown in Table 2-2 (DOA, 1999).

Table 2-2 Guideline for agriculture soil in Thailand (DOA, 1999)

Heavy metals	Minimum (mg/kg)	Maximum (mg/kg)	Basis Level (mg/kg)
Arsenic (As)	0.08	124	30
Cadmium (Cd)	0.01	0.29	0.15
Cobalt (Co)	0.1	113	20
Chromium (Cr)	0.14	295	80
Copper (Cu)	0.16	350	45
Mercury (Hg)	0.01	0.27	0.1
Nickel (Ni)	0.1	270	45
Lead (Pb)	0.1	550	55
Zinc (Zn)	0.1	140	70

Canada and Australia standards for agricultural soil are given in Tables 2-3 and 2-4, respectively.

Table 2-3 Canadian guidelines for sediment and soil (CCME, 1999)

	Sediment Quality Guidelines for the Protection of Aquatic Life				Soil Quality Guidelines for the Protection of Environmental and Human Health			
	Freshwater		Marine		(mg/kg dry weight)			
	ISQG*	PEL**	ISQG*	PEL**				
Heavy metals	ISQG*	PEL**	ISQG*	PEL**	Agricultural	Residential/ parkland	Commercial	Industrial
Arsenic	5.9	17	7.24	41.6	12	12	12	12
Cadmium	0.6	3.5	0.7	4.2	1.4	10	22	22
Chromium	37.3	90	52.3	160	64	64	87	87
Cobalt	No data	No data	No data	No data	40	50	300	300
Copper	35.7	197	18.7	108	63	63	91	91
Lead	35	91.3	30.2	112	70	140	260	600
Zinc	123	315	124	271	200	200	360	360

Note: *Interim marine sediment quality guidelines (ISQGs) and ** Probable effects levels (PELs).

Table 2-4 Australian guidelines for sediment and soil (NEPC, 1999)

Heavy metals	Assessment levels for sediment		Assessment levels for soil			
	ISQG-Low	ISQG-High	A	B	C	D
	(mg/kg dry weight)		(mg/kg dry weight)			
Antimony (Sb)	2	25	30	-	-	820
Arsenic (As)	20	70	100	400	200	500
Cadmium (Cd)	1.5	10	20	80	40	100
Chromium (Cr)	80	370	210	-	-	-
Copper (Cu)	65	270	1,000	4,000	200	500
Lead (Pb)	50	220	300	1,200	600	1,500
Mercury (Hg)	0.15	1	15	60	30	75
Nickel (Ni)	21	52	600	2,400	600	3,000
Zinc (Zn)	200	410	7,000	28,000	14,000	35,000

Note: A. Standard residential with garden/accessible soil (home grown produce contributing less than 10% of vegetable and fruit intake; no poultry); this category includes children's daycares centres, kindergartens, pre-schools and primary schools. B. Residential with minimal opportunities for soil access: includes dwellings with fully or permanently paved yard space such as high-rise apartments and flats. C. Parks, recreational open space and playing fields, includes secondary schools. D. Commercial/Industrial includes premises such as shops and offices as well as factories and industrial sites.

The different standards gave the different maximum allowable lead content in agricultural soil. This associated with the fact that the standards were established based on both of technology and risk.

2.2 Lead Contamination in Klity Creek

The reports of Pollution Control Department (PCD) and other researches had shown the monitoring data of contamination of lead in Klity creek. The possible evidences had been assumed such as a leakage of water from the tailings pond sediment storage in mining plant and the natural weathering process. The PCD mentioned on the impact on health of local people when lead contaminated in the water, sediment and aquatic animals to and the alternatives way to cleanup the contaminated sites were also investigated. The sampling stations had been installed and Pb concentration was monitored. The locations of sampling stations and the averaged Pb content at each location are illustrated in Figures 2-2 and 2-3, respectively.

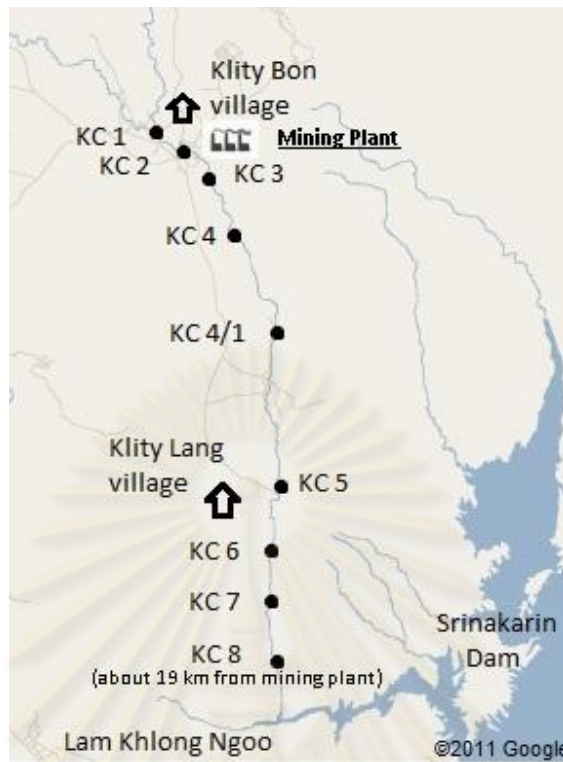


Figure 2-2 Map of sampling stations along Klity Creek (MNRE, 2010)

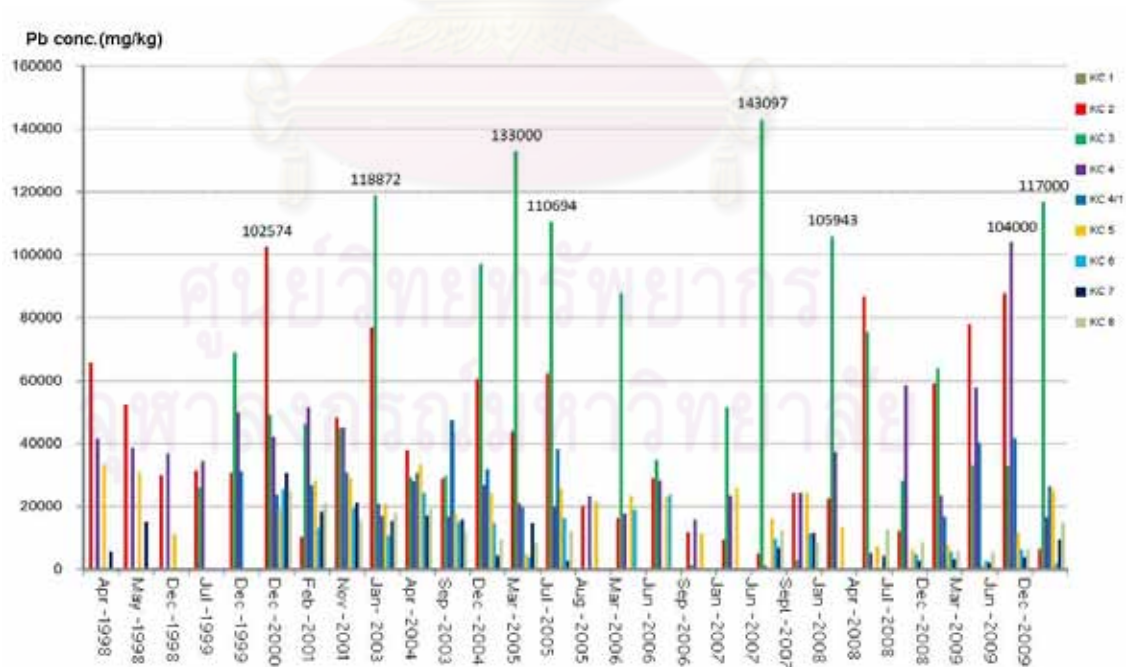


Figure 2-3 Pb concentration in the sediment (MNRE, 2010)

The guidelines of soil and sediment were compiled to these monitoring data, it could be concluded that the lead content in sediment was much higher than the acceptable values in these guidelines. Sediment samples that were collected at the station K3 was the highest contaminated with lead. According to the map, this sampling station was closed to the smelter. The possible source of lead in sediment was from the lead releasing from mining activities. As sediments could migrate along the Klity creek, the villagers at Klity Lang were under a highly risk on lead poison. The station KC5, which closed to the location of village, the lead content in sediments was still higher than the acceptable values stated in these guidelines. Hence, it was necessary to access the way to eliminate lead in sediments and water. The possible technologies could be applied to remediate both of sediments and water for the sake of relieving the impact of lead on human health.

2.3 Possible Technologies for Lead Remediation

Heavy metals contamination had become a major concern worldwide. Most of heavy metals entered into river and they were stored in sediment or accumulated in the living beings. The remediation of sediment was necessary. There were many existing technologies that had been developed to remediate the contaminated water, for example, physicochemical remediation, phytoremediation process and microbial bioremediation. The common physicochemical treatment processes for metal remediation in water were included precipitation, ion exchange and reverse osmosis. The removal of metal contaminants from water through phytoremediation was conducted based on the three major mechanisms, there were phytoextraction, rhizofiltration and phytostabilisation (Lasat, 2000; UNEP, 2010). Microbial bioremediation was defined as the process by which microorganisms could actively degrade hazardous organic contaminants and turn into the environmentally safe levels.

Similarly soil remediation, a two-tiered remediation strategy had also been adopted for remediating the sediment contamination by heavy metals. The first strategy focused on improving metal stabilisation, in which mainly by enhancing metal sorption, precipitation, complexation capacity on sediment and bioavailability of the toxic metals or by reducing the potential mobility. These techniques were usually being carried out “in-situ” since their remediation costs were reasonable (Lombi et al., 2002; Raicevic et al., 2006). The other strategy was extraction, in which

heavy metals contaminated sediment could be degraded through series of chemical, physical and biological methods. These remediation techniques were usually carried out “ex-situ” and they could almost remove even the mobile metals (Mora et al., 2005; Clemente et al., 2006). Some remediation techniques could be applied both in-situ and ex-situ. However, in-situ remediation technologies always gave more benefits than ex-situ remediation technologies. Dealing with the easiness on operation, low costs and fast rate of in-situ remediation, the in-situ techniques seemed to be applied widely. However, the immobilised metals still remained in sediment and they may possible release into water again under some specific conditions. Therefore, the releasing of possible pollution from the natural and remediated sediment should be concerned. The ex-situ remediation techniques were required to be further developed until they could be fitted with all expectations (Peng et al., 2009). Even though, some technologies could be investigated for remediating both of water and sediments, none of these existing technologies had assured the long term impacts. Therefore, there were worthy to access the impacts such as stability of remediation, economical approach in the long term, if any tools of remediation had been employed (Akpor and Muchie, 2010).

Electrocoagulation was one of effective technology, which could provide a benefit on the operating cost as there was no chemical adding and chemical sludge generating. By comparison, the conventional coagulation or chemical precipitation could consume an enormous cost of sludge transportation and disposal at least 1/10 of chemical consumption cost. Regarding the maintenance aspect, the electrodes, electricity and mixing devices were required to be placed into the reactor. If the applied load was at a normal level, the electrodes could be used for at least one year to treat the domestic wastewater. In addition, the electrocoagulation system could generate a simple and small amount of sludge (Vik et al., 1984). Moreover, the electrochemical reaction could precipitate heavy metals and generate the highly stable oxide sludge. Specific example was the sludge of NiFe_2O_4 , which could be produced in the electrochemical reaction and the sludge was highly stable even in an acid solution. Most of sludge was composted of the detoxified metals (Franco, 1974; Duffey, 1983; Renk, 1989).

It could not be denied that the electrochemical process, especially electrocoagulation might be an economical choice for removal of lead from sediments

and clarified water. Therefore the detail of this process was discussed and presented in the following topic.

2.4 Electrocoagulation

Coagulation was a phenomenon in which the charged particles in colloidal suspension were neutralised by mutual collision with ions and agglomerated. Coagulant was added in the form of suitable chemical substances. In the electrocoagulation process (EC), the coagulant was generated in-situ by electrolytic oxidation of an appropriate anode material. The simple EC reactor was made up of an electrolytic cell with one anode and one cathode. The ionic coagulant released from electrode as a result of oxidation that was commonly known as 'sacrificial electrodes' (Mollah et al., 2001).

Electrocoagulation was a simple and efficient method for treatment of many water and wastewaters. During the late nineteenth century, it was a competitive technology in treating of several water pollutants. The electrocoagulation was firstly installed in the wastewater treatment plants in London and it could successfully remove many pollutants (Vik et al., 1984; Matteson et al., 1995). The electrocoagulation was built in Salford treatment plant, England. The iron electrodes were employed to charge the seawater in order to obtain the chlorine disinfectant. The electrolytic sludge treatment plants were investigated in early 1911 at many parts of the United States of America (Vik et al., 1984). In the following decades, the electrocoagulation was constructed to treat municipal wastewater. The electrocoagulation was costly comparing to the conventional wastewater treatment plant, therefore it was applied to eliminate the high strength and non-biodegradable pollutants from wastewater (Vik et al., 1984).

In recent years, smaller scale electrocoagulation processes had been developed to treat some specific non-biodegradable pollutants, especially heavy metals. The portable electrocoagulation was improved to be more reliable and economically cost. The applications of electrocoagulation on removal of heavy metals are summarised in Table 2-5. This could confirm that electrocoagulation was highly effective process.

Table 2-5 Summary of heavy metals remediation by electrocoagulation

Reference	Pollutants	Current	voltage (V)	Electrode materials, Connections	Flow rates Treatment	Efficiency (%)	Reactor
Gnusin et al. (1985)	Cd ²⁺	10–30 A m ⁻²	–	Steel- monopolar	–	65–91	CSTR
Pozhidaeva et al. (1989)	Ni, Cr	2000 A m ⁻²	–	Steel	–	60–85	CSTR
Poon (1997)	Ni, Zn, Pb, Cu	110–220 A m ⁻²	3–5	Stainless steel screen cathode	19 L min ⁻¹	75–96	SBR and CSTR
Balasubramanian and Madhavan (2001)	As	50–125 A m ⁻²	–	Two Fe/ stainless steel	–	75–95	SBR
Park et al. (2002)	Cd	420 mA	24	Al/Al- monopolar	–	80–90	SBR
Ninova (2003)	Cu, Zn	100 –500 A m ⁻²	–	Two Fe electrodes	–	65–88	SBR
Kumar et al. (2004)	As	15–22 A m ⁻²	5–15	Two Fe, or Al or Ti	–	Max 99	SBR
Hansen et al. (2005)	As	8–12 A m ⁻²	–	Two Fe electrodes	50 mL min ⁻¹	80–98	CSTR
Gao et al. (2005)	Cr(VI)	0.1 A, 2.5 Fm ⁻³	–	Fe/Fe monopolar	50 mL min ⁻¹	80–97	CSTR
Parga et al. (2005)	As	4–5 A	20–40	Seven parallel plates of Fe and Carbon steel	600 mL min ⁻¹	60–99	CSTR

The study of Balasubramanian and Madhavan (2001) on application of electrocoagulation in treating of arsenic contaminated water suggested that the rate of heavy metal removal depend on some key parameters including initial concentration of arsenic, current density, pH and electrolysis time. The results also revealed that the hydrous metal oxides such as ferric or aluminium hydroxides could strongly adsorb arsenic. Some researches recommended that the electrocoagulation with sufficient activation energy could provide the stabilised sludge. For example, nickel could be formed as an acid resistant oxide sludge of NiFe₂O₄. Based on the Toxic Classification Leaching Procedure (TCLP), NiFe₂O₄ sludge could tolerate the acid leaching, which allows the sludge to be reclassified as non hazardous waste (Franco, 1974; Duffey, 1983; Renk, 1989). Therefore, electrocoagulation might be adapted for either eliminate heavy metal or sludge stabilisation.

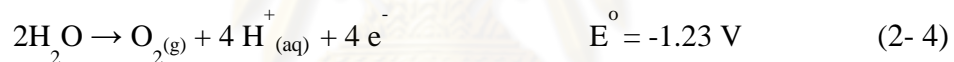
2.5 Possible Reactions in Electrocoagulation

Reactions occurred in electrocoagulation process was depended on types of electrode materials. The aluminium and steel electrodes were traditionally applied to electrocoagulation. The generation of coagulant ions were occurred at anode, the equations are given as follows (Mollah et al., 2001).

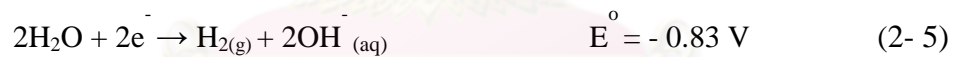


Upon electric field application, decomposition of water (electrolysis reactions) was occurred at the electrodes. The electrolysis reactions generate oxygen gas and hydrogen ions (H^{+}) due to oxidation at the anode. Hydrogen gas and hydroxyl ions (OH^{-}) were yielded due to reduction at cathode. The equations are expressed as follows (Mollah et al., 2001).

Anode (oxidation):



Cathode (reduction):



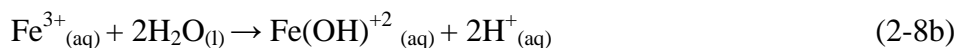
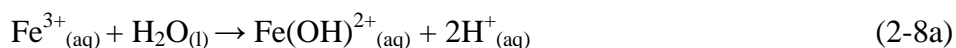
Under acidic conditions, hydrogen could escape the system via reduction as:



Aluminium was the most frequently used as sacrificial anode in an electrocoagulation reactor. The aluminium cation had a variety of available pathways depending on the pH of the aqueous medium. The aluminium could directly interact with the pollutant and it could be hydrolysed and form a hydro-aluminium complex, as well as it could precipitate. The reactions could be described as (Mouedhen et al., 2008):



Similar to Al ions, Fe ions may undergo hydration and depending on pH of the solution hydroxo Fe species may be present under acidic conditions. The reactions involved in this process are (Moreno et al., 2009):



Under alkaline condition, $\text{Fe}(\text{OH})_6^-$ and $\text{Fe}(\text{OH})_4^-$ ions may present. The adsorption and absorption of heavy metals by polymeric Fe and Al hydroxo complexes has been extensively reported, nevertheless they were beyond the scope of the current review.

According to the electromotive force, Pb ion might be removed by reduction at the electrodes. This reaction could be defined as a current or polarisation potential-induced adsorption phenomena on the surface of the charged electrodes. In particular, when an external electrostatic field was exposed to the surface of the electrodes immersed in an aqueous electrolyte solution. The charged ions were forced to move towards the oppositely charged electrodes, allowing the occurrence of charge separation across the interface, resulting in the formation of strong electrical double layers near the high conductivity and high surface area surfaces (Oren, 2008). After achieving neutralisation, the charge on the electrode was compensated to ionic countercharges in the electrolyte at the interface, that could be accomplished with the contact adsorption of ions (Ban et al., 1998) or the accumulation of counter ions in the outer Helmholtz plane and the diffuse layer. These processes can be written as shown in Figure 2-4.

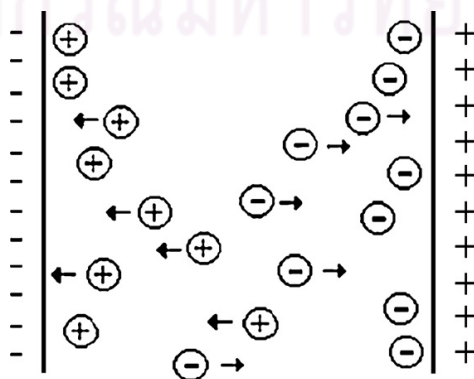


Figure 2-4 Electrosorption deionisation operating principle (Zou et al., 2008)

2.6 Possible Reactions in Coagulation

Coagulation process was commonly used for reducing colloidal particles. The colloidal particles could suspend and make turbidity in water. As colloid particle was too small, the weight of colloid was not enough for self settling under gravity. To increase the settling velocities, the colloid particles had to be bounded or combined with each others. The coagulants such as alum, ferrous sulphate or ferric chloride were used as the binders to glue the colloidal particles together. Since the colloids were bounded, the cluster of particles was called 'floc'. The mixing had to be controlled to a proper speed as floc was easily broken. This step was named 'flocculation'. The colloidal particles had high surface/volume ratio, these surfaces were negatively charged, resisting collisions with other negatively charged particles. The surface properties of colloid could be disturbed during adding the coagulant. The amount of coagulant in the system could make the different mechanisms in bounding particles. The mechanisms for coagulation were recognised as (Ravina, 1993):

1) Ionic Layer compression: high concentration of ionic species may reduce the thickness of the charged layer around the particle, making the particles less resisting to agglomeration.

2) Adsorption and charge neutralisation: the neutral or positively charged ions may attach to the surface and the particles were neutralised.

3) Sweep coagulation: the excessive amounts of coagulant were added to build a high concentration of colloidal, this heavy floc could be settled at reasonable rates as well as they could carry the smaller particles and settled down together.

4) Interparticle bridging: the filamentous coagulant was added to attack the particles as bridge.

The relationship between alum and ferrous and form of complexes together with the mechanism of floc forming are provided in Figure 2-5.

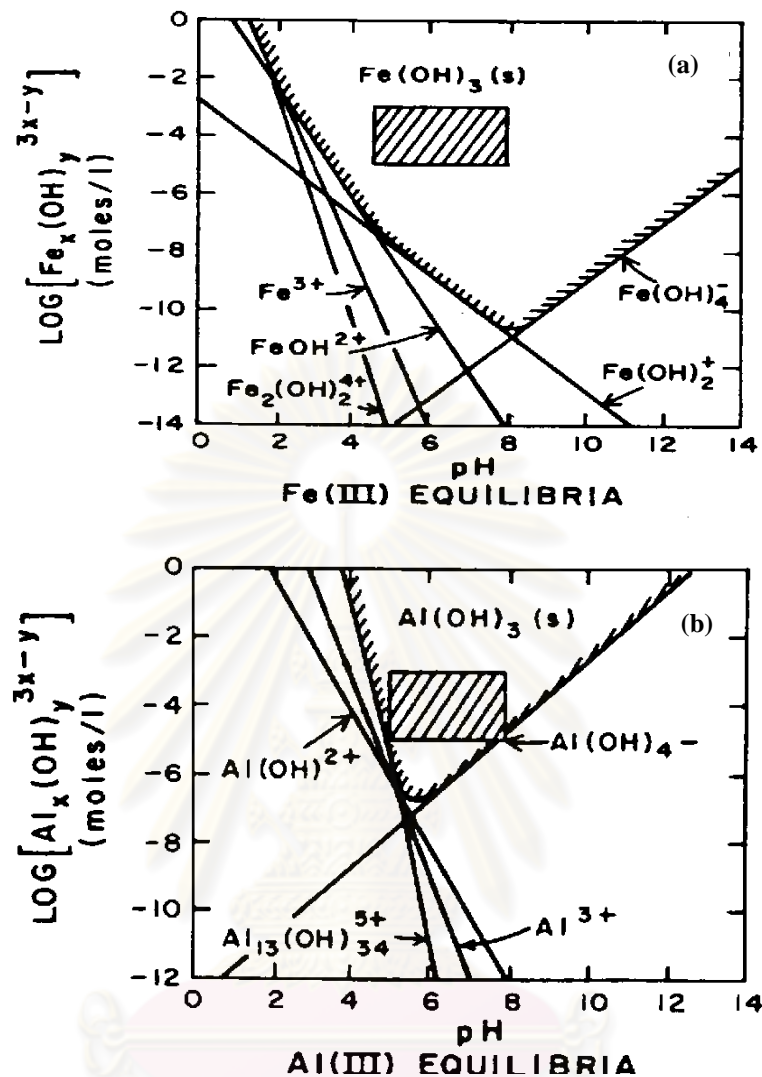
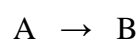


Figure 2-5 Diagramme of pattern of floc forming in a coagulation system with (a) Fe(III) and (b) Al(III) coagulants (Stumm and O'Melia, 1968)

2.7 Kinetic Reaction Rate

Chemical kinetics, also known as reaction kinetics, was the study of rates of chemical processes. Kinetics reaction rate could represent the influences of key parameters on the speed of a chemical reaction. The kinetics rate of reaction was useful to describe the characteristics and the limitation as well as the inhibition of a chemical reaction occurred in the considered system. The differential equations were applied to derive the rate of reaction. The rate of reaction was proportional to the change in concentrations of either reactants or products. The simplified equation can be described as (Salzman, 2000):



(2-9)

The rate of reaction (r), is given by (Salzman, 2000):

$$r = -\frac{d[A]}{dt} \quad (2-10)$$

The kinetic reaction rate constant k was defined to quantify the speed of a chemical reaction (Salzman, 2000). The reaction obeyed a first-order rate law can be explained as (Salzman, 2000):

$$r = k[A] \quad (2-11)$$

By substituting Equation 2.11 into 2.10, yielded:

$$r = -\frac{d[A]}{dt} = k[A] \quad (2-12)$$

At $t = 0$, the concentration of A was defined as $[A]_0$. The integrated form of the kinetic rate equation can be obtained as (Salzman, 2000):

$$[A] = [A]_0 e^{-kt} \quad (2-13)$$

For the zero, first, second order reaction, the kinetic rate were formulated as given in Table 2-6 (Salzman, 2000). The symbols A and B were represented species A and B, which were the reactants in any chemical reactions, respectively.

Table 2-6 Summary of equations for determining the kinetics rate of reactions

Reaction Order	Differential Rate Law	Integrated Rate Law	Characteristic Kinetic Plot	Slope of Kinetic Plot	Units of Rate Constant
Zero	$\frac{d[A]}{dt} = -k[A]^0$	$[A] = [A]_0 - k t$	$[A]$ vs t	$-k$	mole L ⁻¹ sec ⁻¹
First	$\frac{d[A]}{dt} = -k[A]^1$	$[A] = [A]_0 e^{-kt}$	$\ln [A]$ vs t	$-k$	sec ⁻¹
Second	$\frac{d[A]}{dt} = -k[A]^2$	$[A] = \frac{[A]_0}{1 + kt[A]_0}$	$1/[A]$ vs t	k	L mole ⁻¹ sec ⁻¹
	$\frac{d[A]}{dt} = -k[A][B]$	$\ln \frac{[A][B]_0}{[B][A]_0} = kt([A]_0 - [B]_0)$	$\ln \frac{[A][B]_0}{[B][A]_0}$ vs t	$k([A]_0 - [B]_0)$	

2.8 Stability of Sludge in Electrocoagulation

The toxicity characteristic leaching procedure was the most commonly used regularly to estimate the stability of heavy metals in waste as it was presented in a protocol. However, it may underestimate the leachability of some redox sensitive elements, typically Arsenic (As). Since redox reactions could be occurred during the extraction (Meng et al., 2001), the sequential extraction would be recommended. The sequential extraction could be applied to determined the forms of heavy metal accumulated in waste, which could either escape or stay in waste after leaching (Jing et al., 2004).

The possible forms of heavy metals were classified in accordance with the leaching of series extraction reagents. The forms and extraction reagents used in sequential extraction were described as follows (Tessier et al., 1979).

1) Exchangeable: The sediments or constituents (clays, hydrated oxides of iron and manganese) could attract the trace metals. The exchangeable could be changed based on the water ionic compositions (e.g., in estuarine waters), which could either destroy or stabilised this free ion, similarly the sorption-desorption processes.

2) Bound to Carbonates: The significant amount of trace metal could be glued with carbonates. This fraction would be susceptible to changes of pH.

3) Bound to Iron and Manganese Oxides: Iron and manganese oxides could be existed as nodules, concretions, cemented particles, or simply as a coating on particles. These metal oxides were excellent scavengers for trace metals and were thermodynamically unstable under anoxic conditions.

4) Bound to Organic Matter: Trace metals may be bound to various forms of organic matter involving living organisms, detritus, coatings on mineral particles and others. The complexation and peptisation properties of natural organic matter (notably humic and fulvic acids) were well recognised since these were the phenomenon of bioaccumulation in certain living organisms. Under oxidising conditions occurred in natural water resources, organic matter could be degraded, leading to a release of soluble trace metals.

5) Residual (Inert): Once the first four fractions had been removed, the residual solid would contain mainly primary and secondary minerals, which could be able to store trace metals within their crystal structures. These metal compounds were not expected to be released in solution over a long period under the normal condition encountered in nature.

2.9 Economical Tools

An economic analysis was the important tool for decision making, the cost of remediation of lead using the electrocoagulation was evaluated. There were many competitive techniques could eliminate lead from sediment and water, nevertheless the cost had to be reasonable. Only the technical aspect was not enough to justify the investment of electrocoagulation for remediating lead in this specified local scale.

The Benefit-Cost analysis was commonly used to evaluate public projects. The procedure involved the economic evaluation of improvement alternatives to develop effective improvement projects from the candidate alternatives. It was one of the most widely-used methods of screening programs and projects that were being considered for investment. The Benefit-Cost analysis could identify that the worth of project. If the B/C ratio was greater than 1.0, the profit of project could be earned. In this project, the investment of EC in eliminating Pb may return the low B/C ratio. The environmental economic was also added to evaluate the benefit in saving environment, as the values of clean water and soil could not be estimated.

2.10 Summary

Mining was a major cause of lead contaminated in soil, water and sediment. Almost of lead in water was stored in the sediments and they were carried by runoff, soil erosion and other natural processes. Lead could post the serious health impact to aquatic livings and human and destroy the ecological system. The remediation techniques, typically electrocoagulation was adapted to stabilise lead in both clarified water and sediments. The optimum of electrocoagulation and the stability of lead in sludge were investigated in this study. The experiments were carried out to find out the optimum condition of electrocoagulation and set of key factors that influenced the performance of electrocoagulation in remediation and stablisation of lead. The details of experimental design had been explicably given in Chapter 3.

CHAPTER III

METHODOLOGY

The feasibility of electrocoagulation and the optimum condition of operation as well as the suitable design for a portable electrocoagulation were introduced to eliminate lead for sediments and water. These issues were undertaken in a laboratory tests. The experimental setup and analytical methods employed were presented in this chapter. The experiment presented in this study could be demonstrated the mechanism presented in electrocoagulation and the kinetic constants of key parameters, which might be basic information in designing and operating the electrocoagulation process.

3.1 Sample Preparation

Lead contaminated soil were collected from agricultural area around the mine, the sampling location was at downstream of Klity creek, sediments and soil slurry were collected before entering the irrigation channel and they were kept air-dried and sieved via the standard sieve #10 to eliminate rock, gravel and other impurities. Sediment slurry was prepared by mixing 3% (w/w) of sediments into deionised water (30 g dried soil in 1 L of deionised water) and it was stirred by magnetic stirrer until achieving the equilibrium of Pb hydrolysis.

3.2 Analytical Methods

The metal concentrations including of lead, aluminium and iron were analysed according to ICP-OES (Method 200.7) and US EPA guidelines. The plastic containers and glasswares used in the experiment were carefully washed and soaked into 10% (v/v) of HNO₃ solution. For aqueous samples, they were immediately filtered through a 0.45 µm pore diameter of membrane filter and these filtered samples were acidified with nitric acid to maintain the pH below 2. For particulate samples, they were digested by followed the method of microwave acid digestion in accordance with the method for extraction of the metals from soil (EPA method 3052).

3.3 Experimental Setup

The experiment of this study was separated into two parts including of preliminary test- properties of sediment slurry, laboratory scale electrocoagulation experiment and stability of treated sediment. The schematic diagram of experimental setup is provided in Figure 3-1.

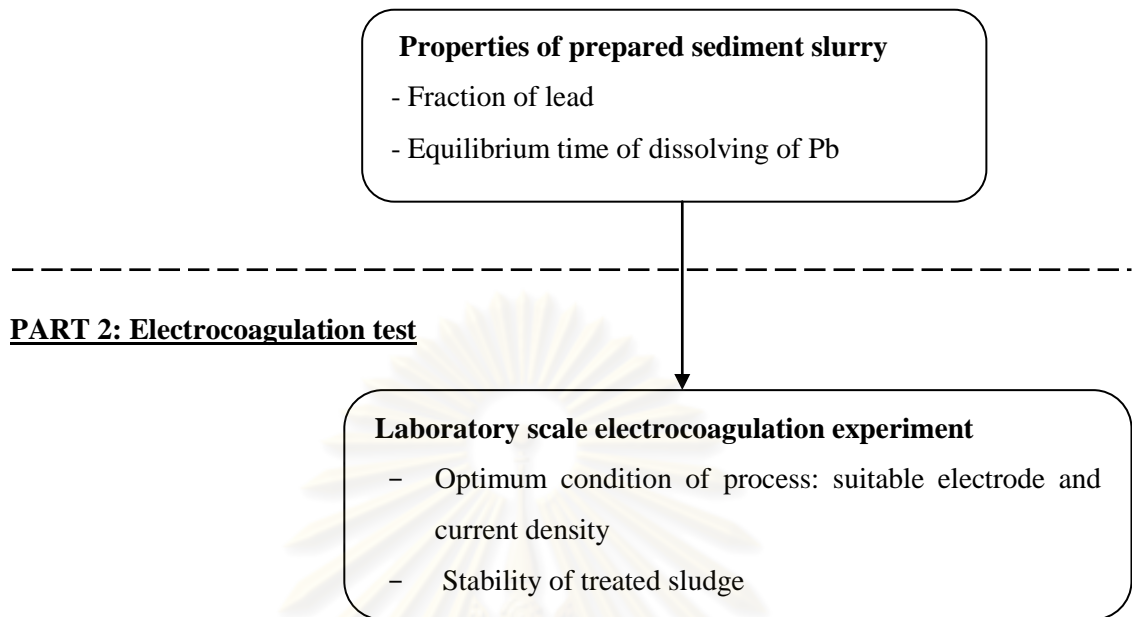
PART 1: Preliminary test

Figure 3-1 Schematic diagramme for experimental design

Part 1: Preliminary test

Soil samples were collected according to the random sampling techniques for contaminated site. The composite sample was obtained by mixing the samples grabbed in the specified locations. The sample was kept air dried and sieved before testing. The preliminary test was undertaken to determine the properties of soil sample utilised in this study. The soil sample was soaked with deionised water to prepare the sediment slurry, which had the constant properties, especially initial concentration of lead and pH for every test. The considered parameters are given in Table 3-1. The soil physical and chemical properties were tested at least five times for each parameter because of heterogeneity. The quartering technique was applied the randomly sample the utilised soil.

Table 3-1 Soil and sediment properties determination

Parameter	Analytical method	Reference
<i>Physical properties</i>		
Particle size distribution	Sieving in combination with hydrometer method	ASTM (1997)
Soil classification	The textural triangle nomenclature	ASTM (1997)
Hydraulic conductivity	Standard test method for permeability	ASTM (1997)
Bulk density	Core Method	Birkeland (1984)
water content	Oven drying method	ASTM (1997)
Specific gravity	Soil particle density	ASTM (1997)
<i>Chemical properties</i>		
pH	Electrode pH meter method	ASA.-SSSA (1982)
Electrical conductivity, EC	Conductivity meter method	ASA.-SSSA (1982)
Cation exchange capacity, CEC	Ammonium saturation	Rhoades (1982)

Part 2: Electrocoagulation experiment

Electrocoagulation experiment was conducted to clarify the optimum condition of electrocoagulation process. The key factors influenced the performance of the system were electrodes material and electrical potential. The electrocoagulation reactor consisted of a reactor and five electrodes. The borosilicate beaker with a working capacity of 1.0 L was used as the electrocoagulation reactor. Aluminium and steel plates which were cut from a commercial grade metal sheet (99% purity) of 3 mm thickness were used as electrode materials with a dimension of 140×50×3 mm. The electrodes sets (anode and cathode) consisted of five parallel pieces of metal sheets with the same material. The spacing between each electrode was kept at 6 mm to prevent the short circuit. The five electrodes were connected in bipolar mode in the middle of reactor, and kept spacing between each electrode at 6 mm to prevent the short circuit as shown in Figure 3-2. The DC power supply was connected to the end of electrodes located on the far left and right hand sides. During operating time, the magnetic stirrer was turned on to mix the sediments with water, to increase the mass transfer. The experimental apparatus is setup as illustrated in Figure 3-3.

Electrocoagulation experiment was conducted to clarify the optimum condition of electrocoagulation process. The key factors influenced the performance of the system were type of electrodes and electrical consumption. Aluminium and steel were used to be electrodes with providing electrical current densities of 10mA, 20mA and 30mA.

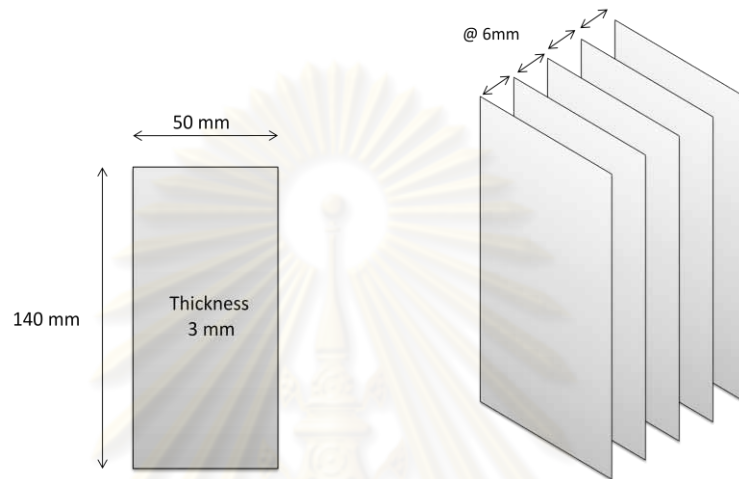


Figure 3-2 Dimension of electrode

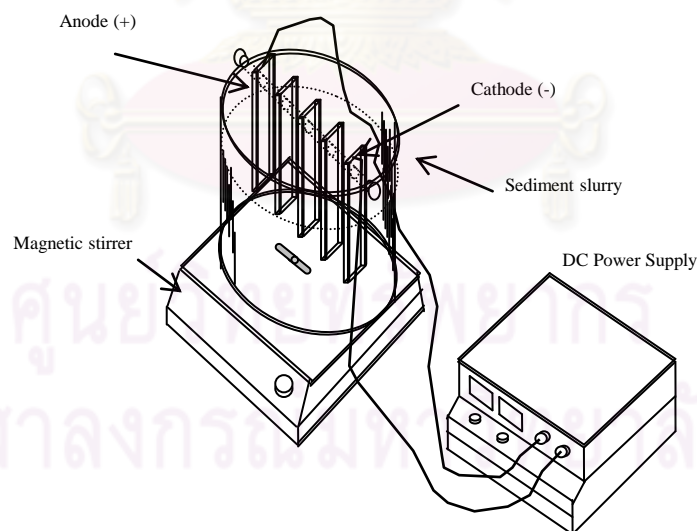


Figure 3-3 Electrocoagulation unit

After the electrocoagulation process was completely undertaken, the stability of sludge was quantified by sequential extraction according to Tessier's method (1979). This method could determine the fraction of lead by extraction with different reagents as shown in Table 3-2.

Table 3-2 Regents applied for leaching lead

Fraction	Reagents
1. Exchangeable	1 M $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
2. Bound to Carbonates	1 M NaOAc
3. Bound to Iron and Manganese Oxides	0.04 M $\text{NH}_2\text{OH} \cdot \text{HCl}$
4. Bound to Organic Matter	0.02 M HNO_3 , 30% (v/v) H_2O_2 and 3.2 M NH_4OAc
5. Residual (Inert)	Residue from (4) was digested by microwave.

Sludge was sampled and weight for 1 g (dry weight of the original sample used for the initial extraction). The sample was placed into 50 mL of polypropylene centrifuge tube and soaked with a 15 mL of deionised water for 2 hours. The sample was continuously agitated on the wrist action shaker. Then, sludge was leached with a series of reagent to classify the forms of lead.

1) Exchangeable: The sediment was extracted at room temperature for 1 hour with 8 mL of either magnesium chloride solution (1 M MgCl , pH 7.0) or sodium acetate solution (1 M NaOAc, pH 8.2). The sample was completely mixed over a period of extraction.

2) Bound to Carbonates: The residual sludge from (1) was leached at room temperature with 8 mL of 1 M NaOAc adjusted to pH 5.0 with acetic acid (HOAc). Continuous agitation was maintained and the time necessary for complete extraction was evaluated.

3) Bound to Fe-Mn Oxides: The residue from (2) was extracted with 20 mL of 0.04 M $\text{NH}_2\text{OH} \cdot \text{HCl}$ dissolving in 25% (v/v) of HOAc. The temperature was maintained at 96 ± 3 °C, with occasional agitation and the time needed for complete dissolution of the free iron oxides was evaluated.

4) Bound to Organic Matter: The residue from (3) were added into 3 mL of 0.02 M HNO_3 and 5 mL of 30% (v/v) H_2O_2 with adjusting the pH to 2 with HNO_3 . During the mixing period, the sample was heated to 85 ± 2 °C for 2 hours with occasional agitation. A 3-mL aliquot of 30% H_2O_2 (pH 2 with HSO_3) was added and the sample was reheated to a temperature of 65 ± 2 °C for 3 hours with intermittent

agitation. After cooling, 5 mL of 3.2 M NH_4OAc dissolving in 20% (v/v) HNO_3 was added and the sample was diluted to 20 mL and it was agitated continuously for 30 minutes. The NH_4OAc was added to prevent adsorption of extracted metals onto the oxidised sediment.

5) Residual (Inert): The residue from (4) was digested by microwave and the aliquot was analysed to determine the lead content.

Along the transferring of leaching steps, the residual sediment was separated by centrifuging, at the speed of 10,000 rpm for 30 minutes. The supernatant was decanted and filtered through a 0.2 μm nylon syringe filter. Five drops of 1:10 HNO_3 were added into the sample to maintain the pH below 2. The residue was washed with 8 mL of deionised water by vigorous hand shaking and centrifuged for 30 minutes with speed at 10,000 rpm to separate and discard the supernatant.

3.4 Summary

The experiment of this study was set up to determine the results of suitable design of electrocoagulation and stability of Pb in sludge. The first part of experiment was a preliminary test. The properties of sediment, the fraction of lead and equilibrium time of dissolving of Pb were examined. The second part of experiment was undertaken in a laboratory scale electrocoagulation. This part was conducted to clarify the optimum condition of electrocoagulation process with the key factors influenced the performance of the system including type of electrodes and electrical consumption. All of results were discussed to define the optimum condition and the data were further applied to access the B/C ratio. The results were critically discussed and presented in the following chapter.

CHAPTER IV

RESULTS AND DISCUSSIONS

Results obtained in this study were presented and discussed in this section. In accordance with the designed experiments, the results were cover the preliminary test and electrocoagulation test. The fundamentals were applied to critically discuss the finding and the evaluated kinetic reaction rate constants were used for justification of the optimum condition and the suited design of electrocoagulation that could be the basic information for the field application. The results had shown that the electrocoagulation could perhaps be applied to remediate the lead from contaminated sediments and water. The cost analysis was performed to access the possibility of applications in economic aspect. The results were discussed deeply as follows.

4.1 Sediment Properties

The properties of sediments are given in Table 4-1. The sediment was mainly composted of sand, so specific gravity and hydraulic conductivity value were almost the same as sand. Lead concentrations in sediment were on average 21,833 mg/kg which was closed to the data obtained from the report of Pollution Control Department (PCD) in December 2009. The concentration of Pb was higher than the level of contamination in natural soil, generally in the range of 0.10 to 550 mg/kg (DOA, 1999). In addition, the level of Pb contamination significantly exceeded the level stated in guidelines for maximum concentration of lead in agricultural soil (Jitrapun et al., 2007). The other metals composted in the utilised sample are shown in Table 4-2. In order to understand the fraction of Pb presented in sediments, the sediment was analysed by sequential extraction, as shown in Table 4-3. The results found that Pb in the sediment was almost associated with sediment carbonates (70%). It implied that the sediment would be susceptible to changes of pH.

Table 4-1 Physical and chemical properties of sediment

Properties	Value
Bulk density (g/cm ³)	1.21
Hydraulic conductivity (cm/s)	3.15x10 ⁻⁴
Specific gravity	2.61
pH (1:5)	7.31
EC (1:5) (μS/cm)	33.6
CEC (meq/100 g soil)	12.3
Soil classification	sand
Pb (mg/kg dry weight)	21,833

Table 4-2 Other metals concentration in sediment

Metals	mg/kg	Metals	mg/kg
Iron (Fe)	20,853	Cadmium (Cd)	61
Nickel (Ni)	208	Chromium (Cr)	74
Strontium (Sr)	229	Copper (Cu)	42
Zinc (Zn)	1,412	Magnesium (Mg)	5,461
Aluminium (Al)	32,785	Manganese (Mn)	962
Calcium (Ca)	27,084	Lithium (Li)	39

Table 4-3 Fraction of Pb in sediment

Fraction	Pb concentration	
	(mg/kg)	(%)
Exchangeable	135.2	0.62
Bound-to-carbonates	15,280	69.99
Bound-to-Fe & Mn oxides	3,900	17.86
Bound-to-organic matter	723.6	3.31
Residual	1,793.45	8.22

4.2 Equilibrium Time of Pb Hydrolysis

As Pb could partially release from sediments due to hydrolysis, the equilibrium time of Pb dissolving was evaluated. The sediment slurry with 3% SS had the total Pb of 655 mg-Pb/L. The sediments were soaked into deionised water, the equilibrium time for hydrolysis was 50 minutes. The Pb concentration in effluent was 0.06 mg/L. It was only 0.01% of total Pb released from sediment. This referred that the Pb was strongly bounded with soil minerals and organic constituent. The result is presented in Figure 4-1. The SS contained in sediment slurry was enough for the mechanism of adsorption-destabilisation and Pb concentration may enough for both of adsorption-destabilisation and sweep coagulation.

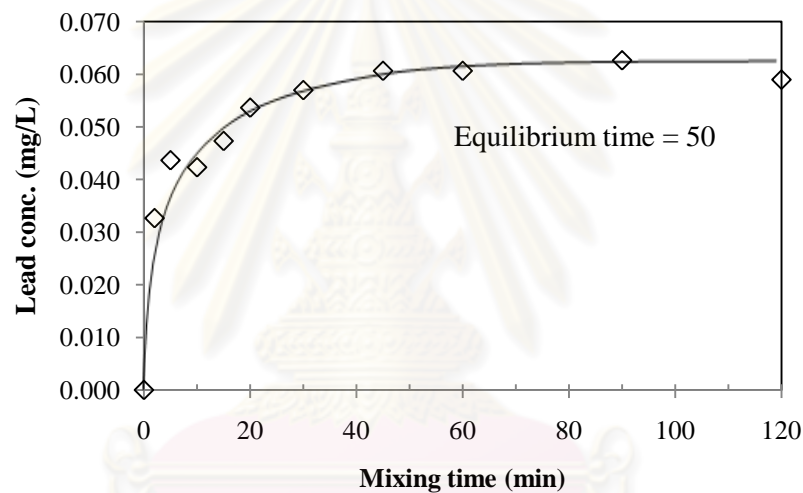


Figure 4-1 Equilibrium time of Pb hydrolysis

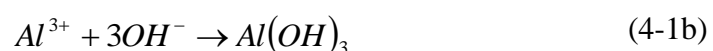
4.3 Electrocoagulation Experiment

According to the study of Chen (2004) and Adhoum et al. (2007), the possible mechanisms of electrocoagulant discharging, which took place at the anode are given as follows.

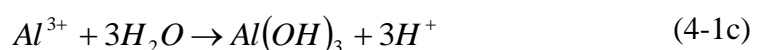
Al anode:



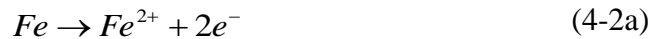
under alkaline condition



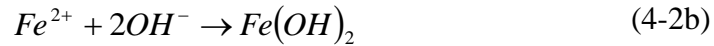
under acidic condition



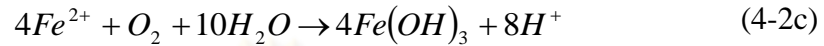
Fe anode:



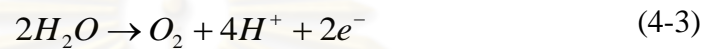
under alkaline condition



under acidic condition



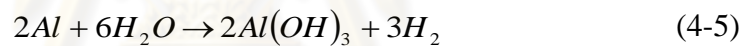
In addition, the oxygen evolution reaction could be occurred during electrocoagulation process. The reaction could be expressed as:



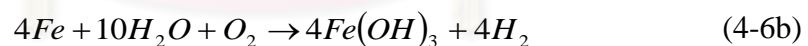
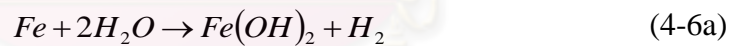
The reaction at cathode was:



Based on these equations, the redox reaction of the electrocoagulation process with Al electrodes could be possibly described as:



As the oxidation state of Fe could be either 2 or 3, the redox reaction of the electrocoagulation process with Fe anode could be suggested as:



The coagulant hydroxide flocs of $Al(OH)_3$, $Fe(OH)_2$ and $Fe(OH)_3$ could act either adsorbent or trap the ions of Pb. By these mechanisms the soluble Pb could be eliminated. However, the electrocoagulation process was complicate and several operating parameters such as sediment properties, current density and type of electrodes could affect the performance of electrocoagulation. In order to enhance the electrocoagulation process to eliminate the Pb in the sediments, the effects of these key parameters were explored.

4.3.1 Electrocoagulation with Al electrodes

The Al electrodes were introduced to electrocoagulation process and the various DC voltages was applied. Since the DC power was applied to the electrocoagulation system the minerals bounded into sediments were ionised. The major mineral contained in the sediments, particularly Fe could escape and act as electrocoagulants. The concentrations of Al, Fe and Pb ions remained in effluent samples were analysed. The result is presented in Figure 4-2. The Al electrodes could generate aluminium ions and electrons. The electrons could enhance Fe and Pb ionisation in a very short period. The higher electrical current could much encourage the ionisation of Al coagulant. On the other hand, Fe could quickly release from sediments within 10 minutes. The concentration of Fe coagulants reduced sharply, it was associated with the oxidisation of Fe^{+2} to be Fe^{+3} , which was more stable. Pb ions were ionised and they could release from sediments. The higher DC power was supplied, the higher releasing rate of Pb was obtained. These released Pb ions might be attracted with Al coagulants due to electrostatic force. The ionic aluminium and Pb could immediately form the white-floc that could be able to sink down. The soluble Fe remained in the effluent was ranged between 0.02-0.08 mg/L, which was less than the maximum allowable concentration of drinking water (0.3 mg/L). The effluent contained Pb with a concentration of 0.001-0.003 mg/L, which was lower than the maximum allowable concentration of Pb in drinking water (0.01 mg/L). However, the aluminium ion was remained in the solution with concentrations of 4.8, 3.6 and 3.1 mg/L, in systems with applying 10, 20 and 30 mA of electrical current, respectively. The aluminium concentration in effluent was higher than 0.2 mg/L (WHO and EU standards), which could induce the risk on Alzheimer's disease (Flaten, 2001). In the electrocoagulation systems with direct electrical currents of 20 and 30 mA could achieve the maximum Pb removing at the same time that was 30 minutes and 60 minutes for the system with 10 mA, respectively.

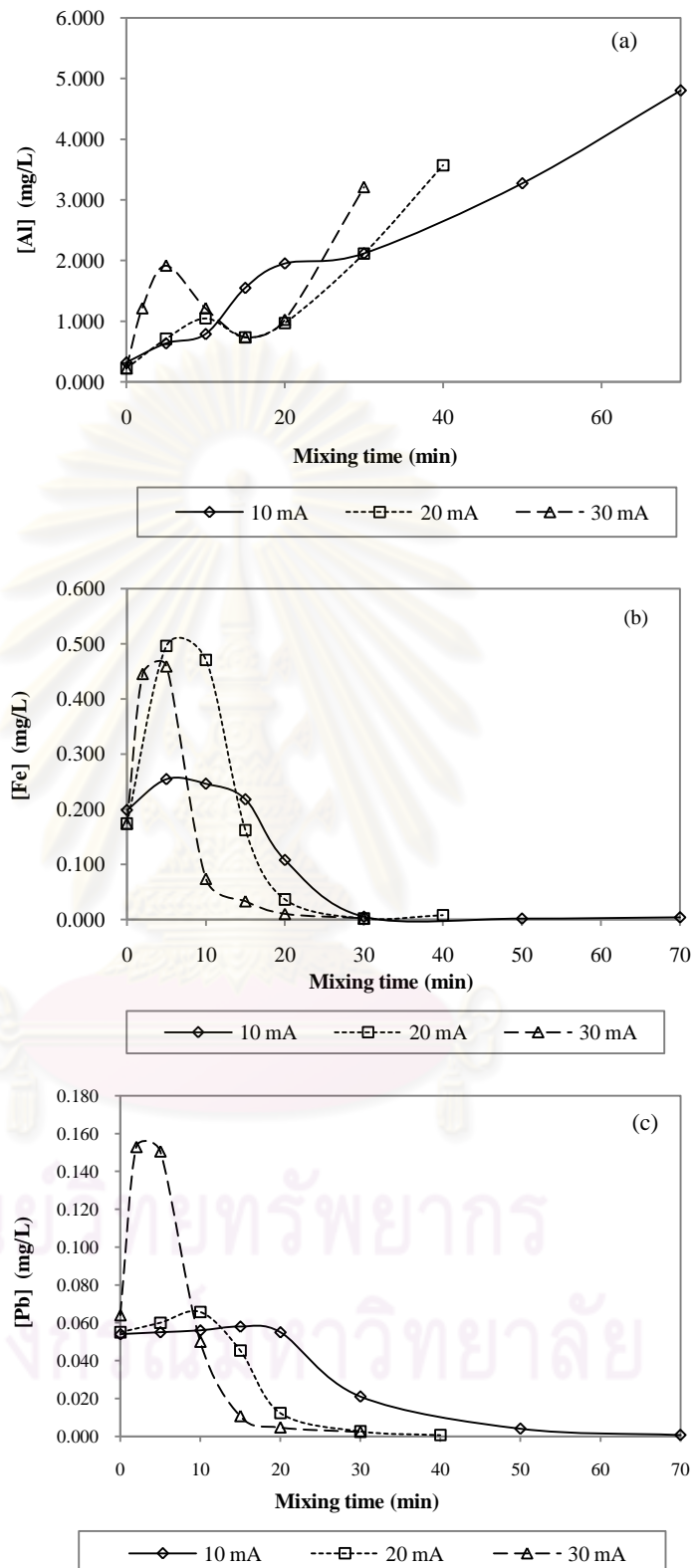


Figure 4-2 (a) Al (b) Fe and (c) Pb concentration in effluent grabbed from electrocoagulation with Al electrode

In order to identify the reaction occurred in electrocoagulation process, the pH of the system with various voltage of DC power supply was measured. The results of Al and Fe ionisation of the electrocoagulation system with Al electrodes are illustrated in Figure 4-3.

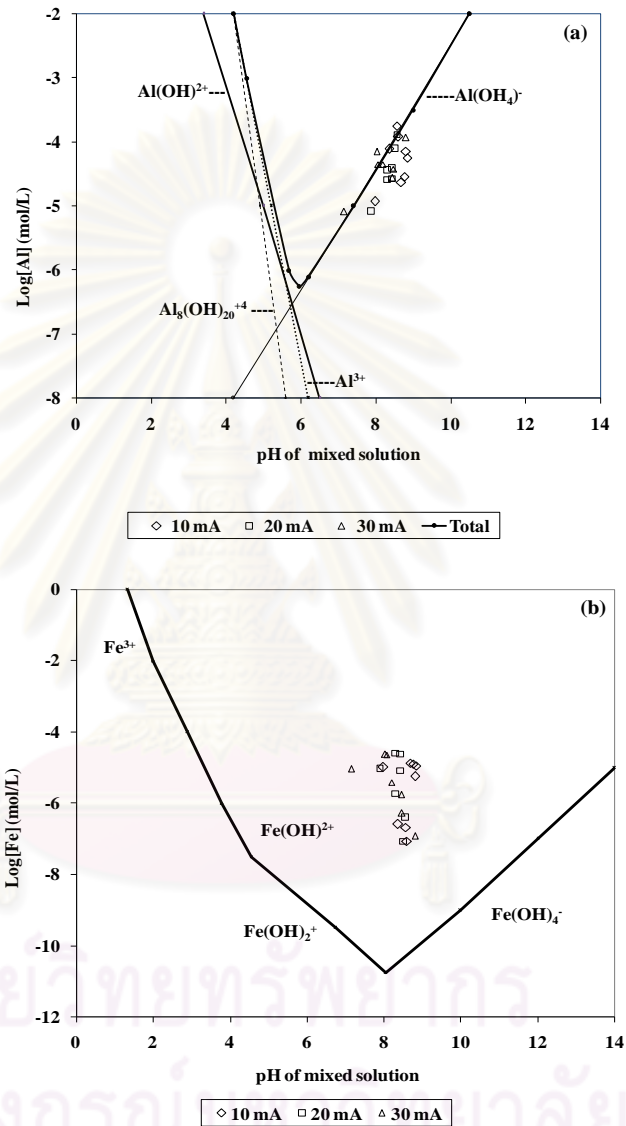


Figure 4-3 Coagulation domain diagram for electrocoagulation process with Al electrode (a) Al ionisation and (b) Fe ionisation

Typically, $Al_{13}O_4(OH_{24})^{7+}$ could be easily to precipitate in a form of $Al(OH)_3$ (Kobyta et al., 2003; Holt et al., 2005). The Fe ions were observed in various forms, there were $Fe(OH)_2^+$, $Fe(OH)^{2+}$ and $Fe(OH)_4^-$. However, the concentrations of the Fe complexes were too low to perform the sweep coagulation. Therefore, the polymeric iron ions may not be able to further remove Pb. The species of coagulants was depended upon the pH of the system. The Al ions generated from Al electrodes

were enough to provide both of sweep coagulation and adsorption. As the pH of mixed solution was alkaline, most of Al ions could react with hydroxide and they were monomeric anions $Al(OH_4)^-$. Whenever the pH of the system was maintained between 4-8, all Al ions could form the polymeric species, typically $Al_{13}O_4(OH_{24})^{7+}$, which could be easily to precipitate in a form of $Al(OH)_3$ (Kobya et al., 2003; Holt et al., 2005).

The effect of current density and charge loading on coagulant dosage rate was examined. The coagulation system with 10, 20 and 30 mA DC power supplied, the current intensities of these systems were 0.014, 0.029 and 0.043 A/dm². Figure 4-4 describes the normalised concentrations profiles of Al coagulant, where the initial pH was 7-8. It was observed that the higher current intensity could generate more Al coagulants. The reaction occurred at anodes could not only increase the concentration coagulant species, but also add the rate of bubbles generations. These bubbles could stimulate the electrofloatation (Adhoum and Monser, 2004; Holt et al., 2005). The size of bubble was decreased when the current intensity was increased, this was beneficial to the separation process (Khosla and Venkatachalam, 1991).

Faraday's law may be used to relate the mass (m) of electrolytically generated aluminium going into solution to the operating current (I) and the run time (t). In this relationship, M is the atomic weight of aluminium, z is the number of electrons transferred in the anodic dissolution (here z was 3), while F is Faraday's constant (96,486 C/mole). Therefore, the amount of coagulant delivered to the solution may be calculated by the equation (Holt et al., 2005) as follow.

$$m = \frac{ItM}{zF} \quad (4-7)$$

The simulation could fit the ionisation rate of Al in the system with 10 mA DC power supply. The observation results were overestimated. For the systems with 20 mA DC power supply, the simulation could be effectively fitted to the observation but the system with 30 DC power supply could not be well fitted. The reason of this finding was made that the Al ions were discharged into system very fast and they could immediately form the monomeric anion with hydroxide. The oscillations on measuring of Al coagulant concentration were yielded. The generating rate of Al ions in the system was determined using the simulation data. The half saturation concentration of Al ions (K_s) of each systems were occurred at different time, the

electrocoagulation systems with 10, 20 and 30 mA had achieved the K_s within 35, 27 and 22 minutes, respectively. The calculated K_s values suggested that the 30 mA could generate Al ions very fast, achieving the saturation level within a very short period.

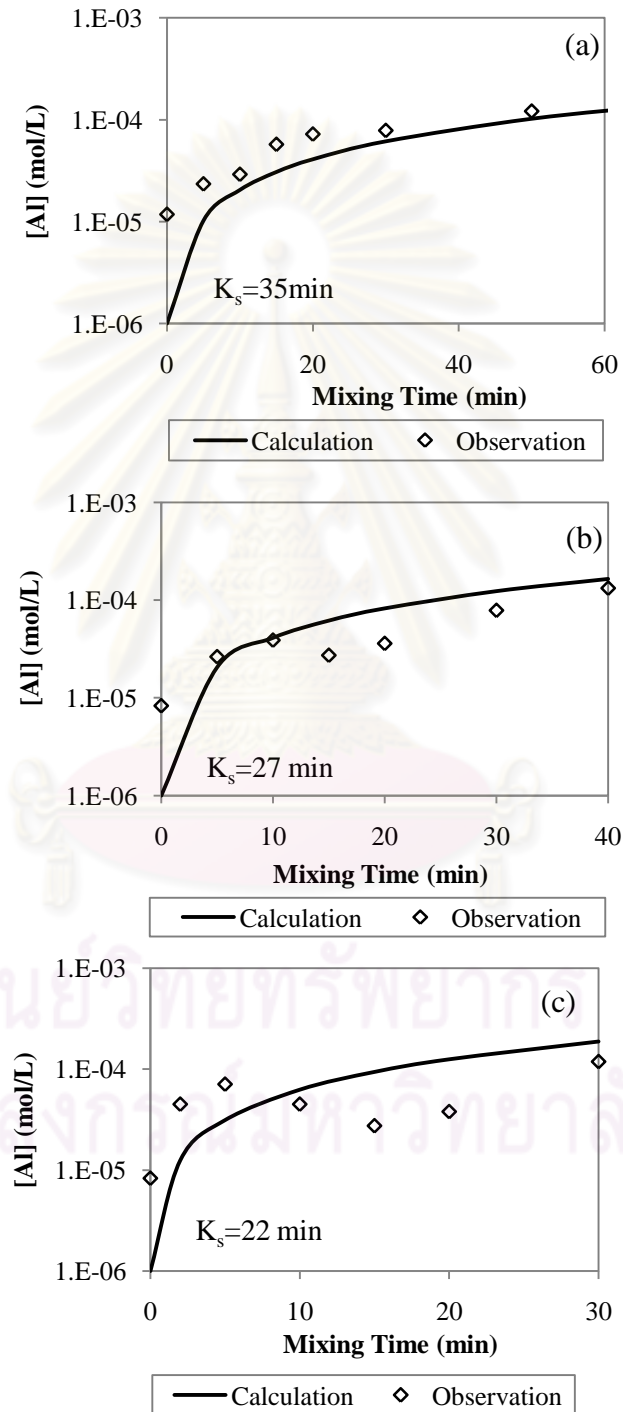


Figure 4-4 Effect of current intensity on Al dosing in electrocoagulation process with Al electrode under (a) 10, (b) 20 and (c) 30 mA DC power supply

Figure 4-5 shows the relationship between charge loading and mixing time. It was found that the EC values of systems were gradually increased over considered period. The little change of EC in the electrocoagulation system was a result of electroflocculation as soon as the ionic Al coagulants were emitted from the anode, they could immediately form a white floc of Al hydroxide. Hence, they could be less soluble, resulting in constant EC value in the system.

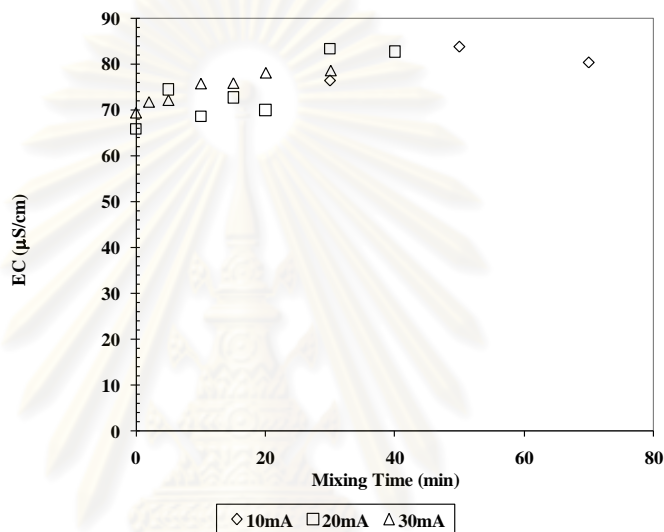


Figure 4-5 Relationship between EC and mixing time in electrocoagulation process with Al electrode

The kinetic reaction rate constants were calculated to describe the influence of electrical current on coagulant generating, electrocoagulation and electrosorption. The rates of electrocoagulation between Al and Pb, and Fe and Pb were analysed. It was observed that the rate of electrocoagulation reaction between Al and Pb could be fitted with the second order kinetic reaction by equation 4-8. The fitted curves are presented in Figure 4-6.

$$\frac{1}{[Al]_0 - [Pb]_0} \ln \left\{ \frac{[Pb][Al]_0}{[Al][Pb]_0} \right\} = kt \quad (4-8)$$

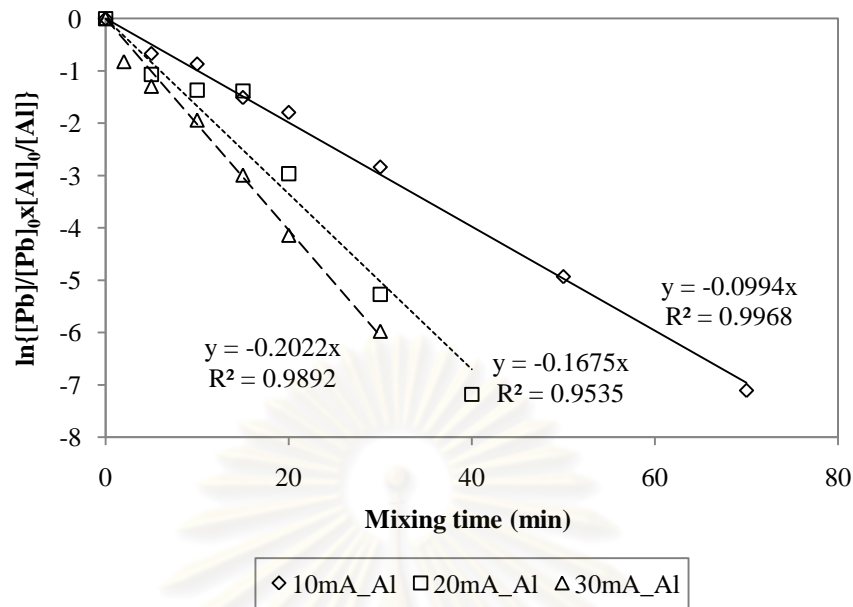


Figure 4-6 Kinetic reaction rates for electrocoagulation with Al electrode

The kinetic rate constants for systems with 10, 20 and 30 mA applying were 0.37, 0.99 and 1.26 L/mg-min, respectively. The system with 30 mA was suited for eliminating Pb from sediment slurry. The high current density could stimulate the cationic hydrolysis products of aluminium to further react with OH^- ions to transform finally in the bulk solution into amorphous $\text{Al}(\text{OH})_3$ (Kobyas et al., 2003; Bayramoglu et al., 2004). Besides, the negatively charged colloids could be neutralised by cationic hydrolysis products and incorporation of impurities in the amorphous hydroxide precipitate (sweep flocculation) (Duan and Gregory, 2003). However, the rate of kinetic reactions between Fe and Pb could not be fitted with the equation of the second order kinetic reaction rate. This was according to the fact the polymeric complex of Fe was little produced, by this low amount of these compounds could not neither adsorb nor trap Pb ions.

4.3.2 Electrocoagulation with Fe electrodes

The observations of Al, Fe and Pb concentrations remained in effluent are presented in Figure 4-7.

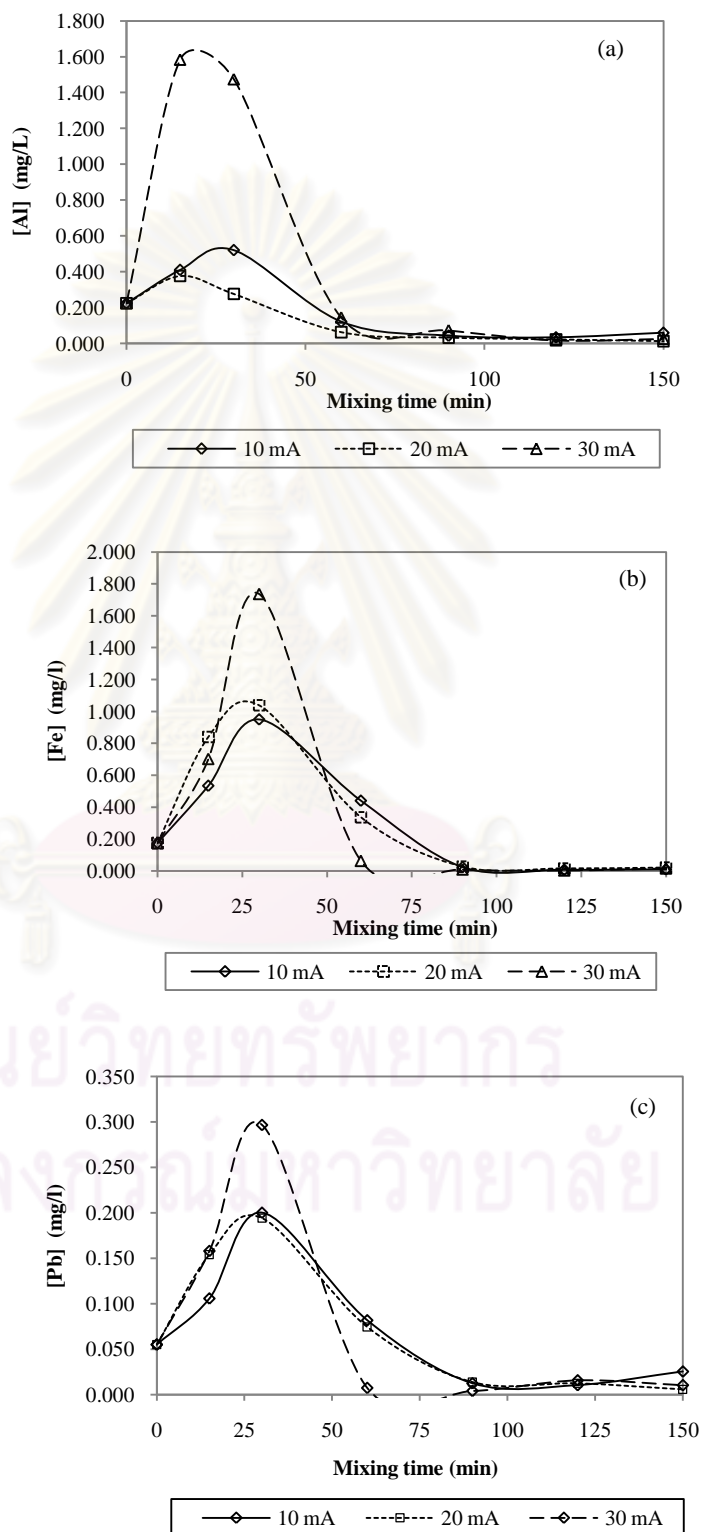


Figure 4-7 (a) Al, (b) Fe and (c) Pb concentration in effluent grabbed from electrocoagulation with Fe electrode

As the sediments contained high content of Al, the electrocoagulation may not discharge only Fe coagulants, the Al coagulant could be further released from sediment. Similar to previous reactor test, the electrical current could activate the Al, Fe and Pb ions to escape from sediments and electrode, respectively. The effluent contained Pb with concentration of 0.01-0.06 mg/L that was lower than the maximum allowable concentration of Pb in drinking water (0.01 mg/L). The ionic Fe remained in effluent was very low concentration at 0.02 mg/L, which was less than the maximum allowable concentration for drinking water (0.3 mg/L). Although the Fe concentration in effluent was low, the color of treated water was brownish yellow. In the aesthetic aspect, the color might not be accepted. The rust coloured effluent was governed due to the oxidation of ferrous ion to be ferric ion. The Al concentration in effluent was 0.012-0.025 mg/L that was higher than 0.2 mg/L. The formations of coagulants are illustrated in Figure 4-8.

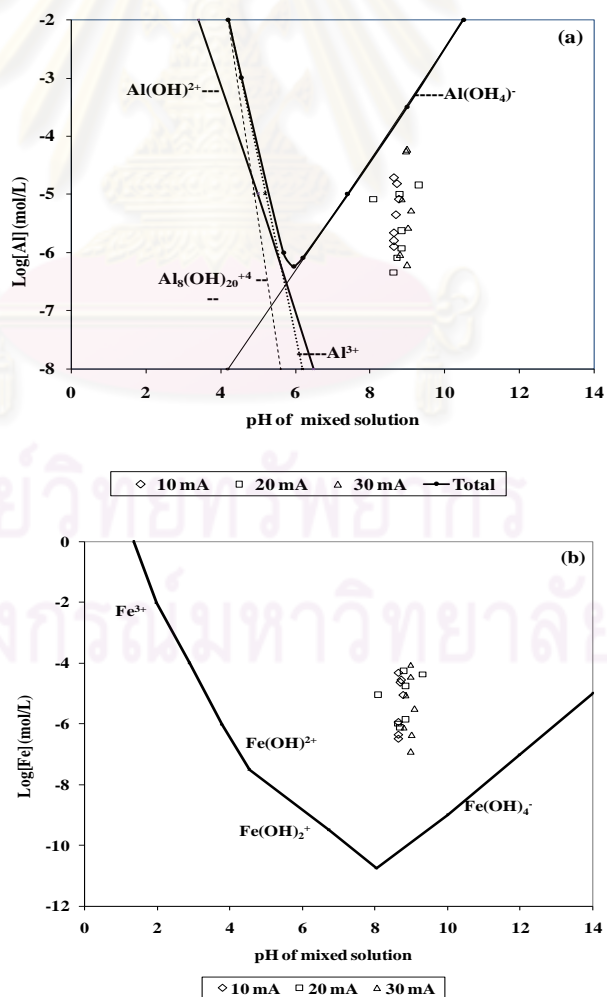
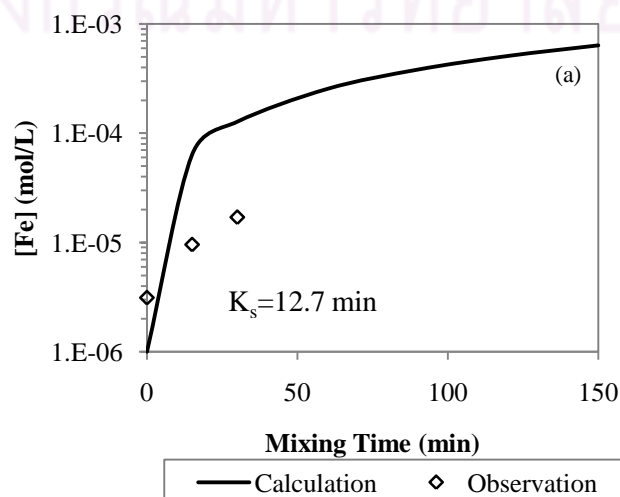


Figure 4-8 Coagulation domain diagram for electrocoagulation process with Fe electrode (a) Al ionisation and (b) Fe ionisation

The ionic Al presented in this system was too low concentration. The Al may act neither adsorb nor sweep coagulation. On the other hand, the Fe ions were enough to encourage the sweep coagulation. According to the pH of system, most of Fe was in a form of polymeric complex $Fe(OH)^{2+}$, $Fe(OH)_2^+$ and $Fe(OH)_4^-$.

As small portions of Pb ions were suspended in the solution, the mass transfer may affect the flocculation process. The estimated dosing of Fe over time is presented in Figure 4-9. The simulations could fit to the observation at initial stage. As the mixing time increased, the Fe ions were possibly oxidised to be Fe^{3+} , which was easily settled down as rust coloured sludge. The estimated half dosing concentrations (K_s) of Fe in the systems with 10, 20 and 30 mA DC power supply were achieved at 27.6, 17.8 and 17.5 minutes, respectively. The system with the highest voltage applied could fill the Fe polymeric in the shortest periods. Nevertheless the obtained Fe coagulants were high in concentration, they were stable compounds and less active. The reason was associated with the oxidising of Fe. At initial the ion Fe^{2+} was generated from the electrode with a plenty of dissolved oxygen, the Fe^{2+} could be oxidised to be Fe^{3+} , which was quickly form the oxide of Fe. Coincidentally, the rust was quickly observed in the electrocoagulation with Fe electrode. The concentration of Fe ion in clarified effluent at the equilibrium was relatively low. Even though the electricity current was still supplied, the oxide of Fe could not be further released. This could benefit to the system as the residual Fe was naturally oxidised and form the highly stable rust. In case of no natural aeration, the concentration of Fe discharge in the water might be highly yielded. The electrocoagulation with Fe electrode might be enhanced by limiting the dissolved oxygen in the system.



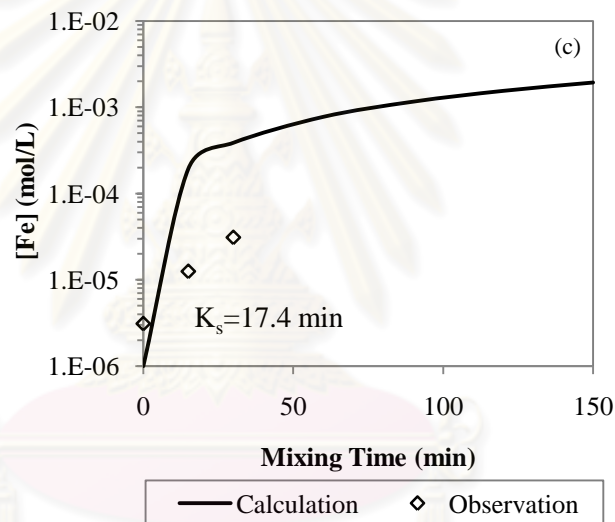
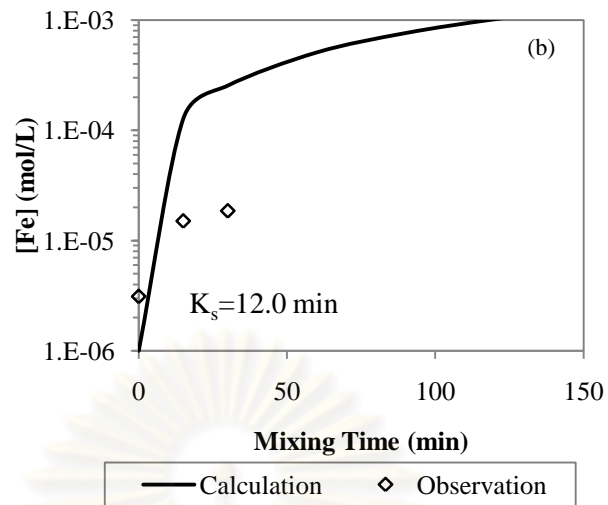


Figure 4-9 Effect of current intensity on Fe dosing in electrocoagulation process with Fe electrode under (a) 10, (b) 20 and (c) 30 mA DC power supply

The relationship between EC and mixing time is described in Figure 4-10. The EC values in the systems were oscillated all the considered period. This finding could reflect the reversible reaction in the system, the ionic species could escape from the floc.

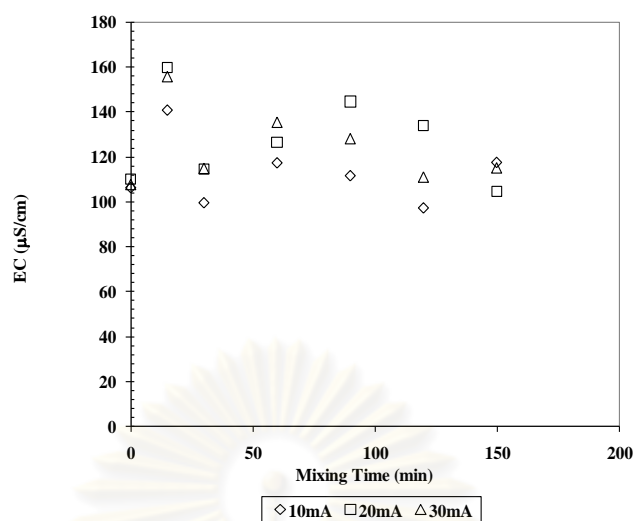


Figure 4-10 Relationship between EC and mixing time in electrocoagulation process with Fe electrode

The kinetic reaction rate were determined, the equation of second order reaction rate could not be able to fit with the observation as show in Figure 4-11. As noticed earlier, the Fe and Pb ionisation took approximately 30 minutes and these ions were transformed to sludge very quickly. Besides, Pb could release from the sludge, after 90 minutes of reaction. Therefore the Pb might be slightly adhered or attract on floc due to van de Walls force, the reversible reaction could be happened. The first kinetic reaction equation was applied to fit the dissociation of Al, Fe and Pb. In accordance with the expectation, Al ions could slightly emit from sediments. The first order kinetic reaction rate could not match with the observation. Only Fe and Pb ionisation could be fitted with the first order kinetic rate. Figure 4-12 presents the kinetic reaction rates of Fe and Pb dissolubility. The kinetic rates of Pb ionisation were 0.04, 0.05 and 0.06 min^{-1} for systems with 10, 20 and 30 mA current applied, respectively. The kinetic rates of Fe ionisation were 0.06 and 0.07 and 0.08 min^{-1} for systems with 10, 20 and 30 mA current applied, respectively. This revealed that the ionisation of Fe and Pb were in competitive condition. The electrocoagulation was inhibited as lack of Fe and Pb ions.

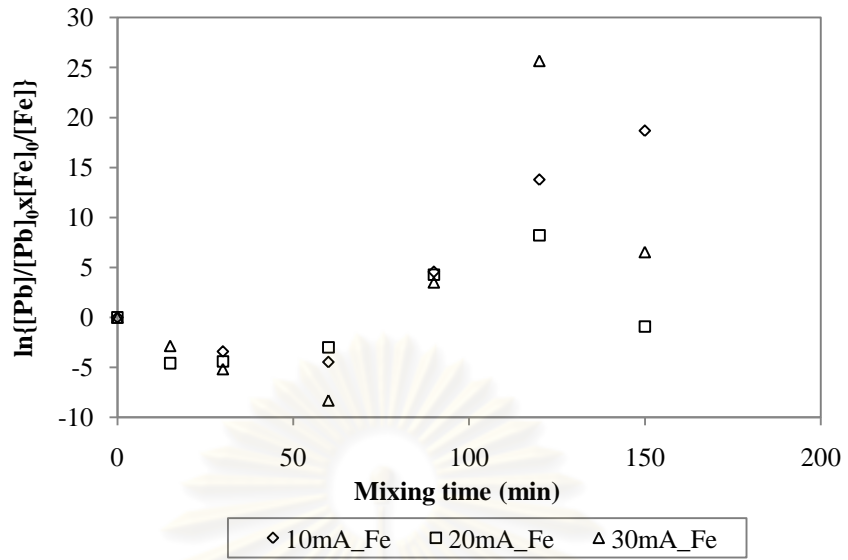


Figure 4-11 Second order kinetic reaction rates for electrocoagulation with Fe electrode

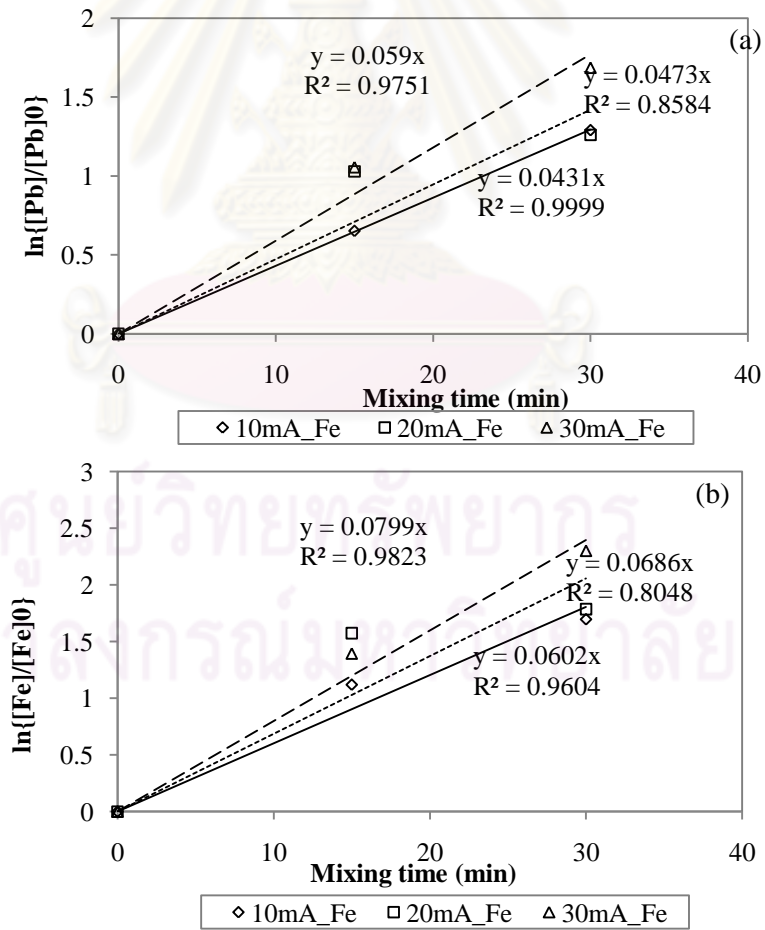


Figure 4-12 Kinetic reaction rates for electrocoagulation with Fe electrode
(a) Fe and (b) Pb dissociation

4.4 Lead Recovery

Pb was found in treated sediment, aqueous effluent and deposited on electrode. The results were calculated by mass balance, as shown in Table 4-4.

Table 4-4 Fraction of Pb accumulation

Experiment (Current_electrode)	Treated Sediment		Clarified effluent		Electrodes	
	mg	%	mg	%	mg	%
30mA_Al	359	54.8	0.002	0.0003	296	45.2
20mA_Al	366	55.9	0.001	0.0002	289	44.1
10mA_Al	431	65.8	0.001	0.0002	224	34.2
30mA_Fe	414	63.1	0.010	0.0015	241	36.9
20mA_Fe	447	68.3	0.006	0.0009	208	31.7
10mA_Fe	498	76.0	0.025	0.0038	157	24.0

The effluent water remains very low Pb concentration, the mass of Pb in water could be ignored. Lead could be partially removed by depositing on electrodes and almost of lead was still in the sediments. The percent removal of Pb by depositing on electrode was increased when the higher DC power was supplied. The electrocoagulation systems with Al electrodes could better eliminate lead than Fe electrodes. Lead adhered on electrodes could be recovered, if the cost was reasonable.

4.5 Stability of Pb in Sludge

After electrocoagulation process, the most fraction of lead was still kept in the sediment. The bottom sludge had to analyse by sequential extraction to classify the forms of Pb. The results are provided in Table 4-5.

Table 4-5 Chemical forms of Pb in treated and untreated samples

Chemical form (%)	Experiment (Current_electrode)						
	Untreated	30mA_Al	20mA_Al	10mA_Al	30mA_Fe	20mA_Fe	10mA_Fe
Exchangeable	0.62	0.66	0.71	0.65	0.14	0.31	0.18
Bound-to-carbonates	69.99	48.14	44.59	52.37	31.34	39.18	48.20
Bound-to-Fe & Mn oxides	17.86	15.71	19.02	16.58	19.15	15.70	11.33
Bound-to-organic matter	3.31	3.55	4.25	3.44	3.45	3.50	2.86
Residual (Inert)	8.21	31.93	31.43	26.96	45.93	41.31	37.43

Lead in natural condition was predominantly bounded on carbonate species. The electrocoagulation could activate the ionic Pb to be bounded with ionic coagulant as residue. Under the electrocoagulation system with Al electrodes, some amounts of Pb were in residual, which were accumulated in the $Al(OH)_4^-$ floc. Even though the electrocoagulation process could enhance the dissociation of Fe, the fraction of Pb bound with Fe & Mn was not much different from untreated sediments. This could confirm that Fe ions discharged in the system was inactive as they were transformed to be ferric ions. The electrocoagulation system with Fe electrodes, Pb bound-to-Fe & Mn oxides was increased in the system with higher DC power supply. The indicated that the sediments became stable form of oxide sludge (Franco, 1974; Duffey, 1983; Renk, 1989). The stability of Al-Pb floc was as same as Fe-Pb floc, as Pb was still bound with active hydroxide floc.

4.6 Economical Consideration

An economic analysis was another issued that was useful for making decision. The benefit-cost analysis was applied to estimate the B/C ratio. The benefit earned from electrocoagulation process was made on the Pb recovery. The standard price of 30% and 55% of Pb ore was 15,000 and 25,000 THB/ton or 15 and 25 THB/kg (Ministry of Commerce, 2011). The costs of electrocoagulation process were included the electrode and electricity. The cost of Fe sheet with 3 mm thickness was 22 THB/kg and Al sheet with 3 mm thickness was 154 THB/kg (Ministry of Commerce 2011). The weight of electrodes were 0.8 for Fe and 0.6 kg for Al. Once the electrodes were used, the mass of electrodes were lost in anode and the mass of cathode was increased due to Pb deposition. Based on the observation, the weight of Fe and Al anodes were reduced less than 1% of the total weight of Al and Fe electrodes. However, the surface of electrodes had been scratched using the coarse sandpaper. The life span of each electrode was assumed that a half weight of Fe and Al electrodes could be used. Hence, Fe electrodes could be used for 40 times and Al electrodes could be served for 30 times. The cost of electricity was averaged at 3 THB/kw-hour (Metropolitan Electricity Authority 2011). The time for remediation were estimated as twice of time for reaction achieving the half saturation (K_s). The labour cost was excluded as the portable electrocoagulation had no cost in installation

and maintenance. The calculation of B/C ratio is provided in Table 4-6. The B/C ratio of electrocoagulation with Fe and Al electrodes were 0.03 and 0.005, respectively.

Table 4-6 Benefit and cost analysis

Experiment (Current_electrode)	Pb _{Sediment} (mg)	Pb _{electrode} (mg)	Total Benefit (THB)	Electrode (THB)	Ks (min)	Electricity consumption (Kw-hour)	Electricity (THB)	Total Cost (THB)
30 mA_Al	359	296	0.016	3.08	22	0.0005	0.0014	3.0813
20 mA_Al	366	289	0.016	3.08	27	0.0004	0.0011	3.0811
10 mA_Al	431	224	0.016	3.08	35	0.0002	0.0007	3.0807
30 mA_Fe	414	241	0.016	0.44	17.4	0.0004	0.0011	0.4411
20 mA_Fe	447	208	0.016	0.44	12.0	0.0002	0.0005	0.4405
10 mA_Fe	498	157	0.016	0.44	12.7	0.0001	0.0003	0.4402

Another benefit of electrocoagulation was reducing the cost of sludge disposal. The cost of stabilisation and disposal of sludge was 20,000 THB/ton (Tiew 2001) and 1,500 THB/ton (excluded transportation) (IWMB, 2009), respectively. Besides, the volume of sludge after solidification and stabilisation could be increased at least 12.85% (Tiew, 2001). If the conventional coagulation was applied, the cost of stabilisation and disposal of sludge would be 2.76 THB/kg of coagulant adding. The benefit on this issue could not be calculated as the weight of sludge generating from electrocoagulation could not be measured. As the coagulant and sediments was mixed together, they cannot be separated.

The B/C ratio for the electrocoagulation unit in treating Pb from sediments and water was less than 1.0. It could not be refused that the benefit of Pb remediation in real situation was not only Pb recovery and the safe water was also obtained. If the benefit of safe water was obtained at the same price as raw water for water supply plant that was 0.65 THB/m³ (Metropolitan Waterworks Authority 2011), the clarified water could be sold at 0.0007 THB for every test. The B/C ratio of electrocoagulation with Fe and Al electrodes were 0.04 and 0.006, respectively. If there were some serious issues especially the lack of safe drinking water, the price of water had increased up to 0.5 THB/L, the electrocoagulation with Fe electrode could be reasonably invested. If the price of drinking water was 3.1 THB/L, the electrocoagulation with Al electrode could give B/C ratio greater than 1.0.

4.7 Summary

The electrocoagulation process with Al electrodes could provide the high efficiency on Pb removal. Most of Al ions were highly active and they were in a form of monomeric anions $Al(OH)_4^-$. The electrocoagulation could stimulate Pb and Fe dissociation, only Pb could quickly react with $Al(OH)_4^-$ and form a white dense floc. The accumulated Pb was in the hydroxide aluminium floc, which was highly stable. The system with 30 mA DC power supply could provide the highest performance on treating soluble Pb and return the stabilised Pb in sludge. The electrocoagulation with Fe electrode could generate a limit amount of Fe polymeric complex and Pb ions. Due to the limit amount of these ionic species, the Fe-Pb floc could be little yielded. Most of Fe^{2+} was transformed to be insoluble Fe^{3+} , which were inactive species. Almost a half of total Pb could be deposited on cathodes. The inert Pb was highly obtained. The rust colour floc that was very dense might cover the Pb in bottom sludge and the Pb releasing could slow down in some certain periods. In economic aspect, the Benefit-Cost analysis suggested that the electrocoagulation could provide the little benefit on Pb recovery but the high costs on electrodes and electricity were yielded. The B/C ratio from both systems was much lower than 1.0 they were 0.03 for EC with Fe electrodes and 0.005 for EC with Al electrodes, respectively. The electrocoagulation could be useful when the serious water issues were happened and the lack of safe drink water was in an extreme situation. If the price of safe drinking water was increased to 0.5 THB/L, the EC with Fe electrode could be worth to be invested. In case of EC with Al electrode, it could be competitive when the price of drinking water became 3.1 THB/L.

จุฬาลงกรณ์มหาวิทยาลัย

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 General Aspect

The sediment in Klity watershed had contaminated with lead, the Pb content was 21,833 mg/kg. This could pose the serious health impact, if these sediments could enter to the water bodies. The electrocoagulation was technically applied to eliminate and stabilised the Pb contaminated sediments and clarified effluent. The electrocoagulation unit was supplied with various electrical current at 10, 20 and 30 mA, respectively. The electrocoagulation with Al electrodes could proceed faster reaction rate than Fe electrodes. The reaction between Al and Pb ions could be fitted with 2nd order kinetic reaction equation. The clarified effluent had contained the whit dense floc. The most of Al ion discharged were in form of monomeric $Al(OH)_4^-$. This monomeric alum complex could quickly react with sediments. The settled sediment had contained a higher fraction of inert Pb, when the higher electrical current was applied. At least half of Pb was deposited on Al cathodes dealing with electrooxidation. On the other hand, the ionisation of Fe and Pb observed in the electrocoagulation with Fe electrode was fitted to the 1st order kinetic reaction. The Fe^{2+} coagulants could quickly be oxidised and transformed to Fe^{3+} , which could be further from the Fe oxide with oxygen. The rust colour floc was observed. The half of Pb was accumulated on the Fe cathodes. Most of Pb was settled down with sweep coagulation of Fe rust floc. The higher fraction of inert Pb was obtained when the higher electrical current was applied.

5.2 Specific Aspect

The electrocoagulation process could highly remediate Pb, if it was operated under the optimum condition. The key parameters played a significant role in Pb removing efficiency were including of mass transfer rate, form of coagulants and the reaction between Pb and coagulants. The completely mix of sediment slurry could be recommend to achieved the equilibrium of Pb hydrolysis, the equilibrium took time for 50 minutes. The electrocoagulation with Al electrode could be enhanced if the monomeric of Al ion was generated at pH of 6.1. The preferable monomeric Al was $Al(OH)_4^-$, this species could react with Pb quickly. The 10, 20 and 30mA of DC

power were supplied to the system, the rate constants were 0.37, 0.99 and 1.26 L/mg-min, respectively. Most of Pb was remained in sludge as inert Pb.

In the system with Fe electrode, the monomeric of $Fe(OH)_2^+$ ion was generated at pH of 8, conducting the optimum condition. The preferable monomeric Fe was $Fe(OH)_2^+$ not earned in this study. The Fe^{2+} could be easily to be oxidised to Fe^{+3} and react with oxygen and finally this oxide Fe could be highly stable. In order to enhance the reactive Fe, the alkaline solution had to be added and the natural aeration could be prohibited. The reaction between Fe coagulant and Pb was clearly seen, it was assumed to be sweep coagulation as the rust dense floc could cover the Pb. Therefore the inert Pb was obtained.

In economic aspect, the electrocoagulation unit could not provide the benefit at this moment. The B/C ratio was applied to evaluate the worth of electrocoagulation process in treating Pb. Both systems could not provide the profit as B/C ratio was less than 1.0. The electrocoagulation with Fe and Al electrodes could be invested when the price of drinking water was higher than 0.5 and 3.1 THB/L, respectively.

5.3 Recommendations

This thesis had demonstrated the small electrocoagulation unit in remediating of Pb from sediments and water. The recommendations were made for the future research as:

- 1) The pre conditioning of pH may be required to increase the ionisation of Al, Fe coagulants and Pb.
- 2) The high surface electrodes Al and Fe might be applied at cathodes in order to increase the Pb depositing process.
- 3) The environmental economic should be applied to estimated the hidden benefits such as cost of safe environment and ecology.

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APPENDICES

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

Appendix A

Table A-1 Bulk density of soils

Replicate	Weight (g)	Volume (cm ³)	Bulk density (g/cm ³)	Average
1	404.6	330	1.226	1.214
2	399.8	330	1.212	
3	397.9	330	1.206	

Table A-2 Hydraulic conductivity of soils

Replicate	High (cm)	Time (min)	Q (cm ³)	A (cm ²)	Lc (cm)	k (cm/s) = QLc/ΔHAt
1	123.5	60	7.0	28.51	12.51	3.15×10 ⁻⁴
2		60	7.0			
3		60	7.0			
4		60	7.0			

Table A-3 Specific gravity of soils

Replicate	Dry Soil + Container (g)	Flask + Water + Soil (g)	Correction factor	Specific gravity	Average
1	496.6	728.7	0.9957	2.67	2.61
2	512.7	726.7	0.9957	2.64	
3	506.9	784.1	0.9957	2.52	

Table A-4 pH of soils

Replicate	pH (1:5)	Average
1	7.38	7.31
2	7.48	
3	7.21	
4	7.17	

Table A-5 Electrical conductivity of soils

Replicate	pH (1:5)	Average
1	45.3	41.2
2	40.2	
3	38.0	

Table A-6 Cation exchange capacity of soils

Replicate	Weight (g)	Volume of HCl (ml)	Blank (mL)	CEC (meq/100g soil)	Avg	Stdev.
1	5.0412	26.00	0.1	12.3799	12.3168	0.2899
2	5.0600	25.30	0.1	12.0010		
3	5.0800	26.60	0.1	12.5700		

Table A-7 Sieve Analysis

sieve No.	sieve opening (mm)	Wt. sieve (g)	Wt. sieve+soil (g)	Wt. soil retained (g)	% Retained	cumulative %retained	% Finer
#10	2	421	442	21	2.27	2.27	97.73
#16	1.18	412	480	68	7.36	9.63	90.37
#40	0.425	573	797	224	24.24	33.87	66.13
#50	0.3	556	635	79	8.55	42.42	57.58
#100	0.15	537	720	183	19.81	62.23	37.77
#200	0.075	513	744	231	25.00	87.23	12.77
pan	-	496	614	118	12.77	100.00	0.00

Table A-8 Hydrometer Analysis

elapse time (t)	R	temp	Rc	%finer actual	% finer adjust	L	L/t	K	D (mm)
0	0	0	0	0	0	0	0	0	0
0.25	40	24	42	0.85	10.88	9.70	38.80	0.01317	0.0820
0.5	32	24	34	0.69	8.80	11.10	22.20	0.01317	0.0620
1	24	24	26	0.53	6.73	12.40	12.40	0.01317	0.0464
2	16.5	24	18.5	0.38	4.79	13.60	6.80	0.01317	0.0343
5	9	25	11.3	0.23	2.93	14.80	2.96	0.01302	0.0224
10	5	24.5	7.15	0.14	1.85	15.50	1.55	0.01310	0.0163
20	3	24	5	0.10	1.29	15.80	0.79	0.01317	0.0117
40	1.5	25	3.8	0.08	0.98	16.05	0.40	0.01302	0.0082
80	0.5	24	2.5	0.05	0.65	16.20	0.20	0.01317	0.0059
120	0	24.5	2.15	0.04	0.56	16.30	0.14	0.01310	0.0048
1096	-1	25	1.3	0.03	0.34	16.50	0.02	0.01302	0.0016

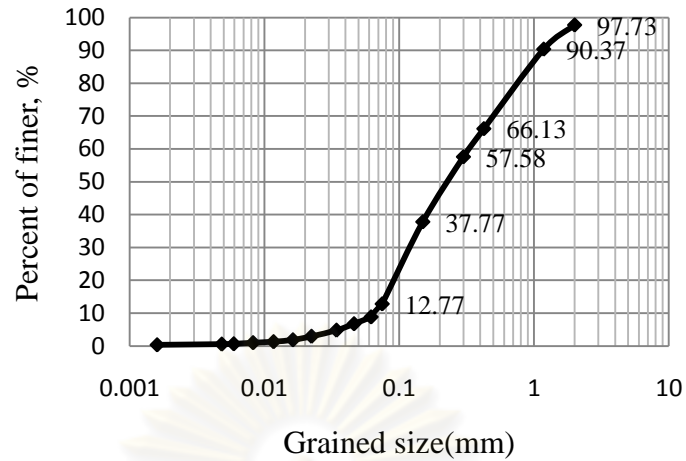


Figure A- 1 Particle size of sediment

Table A-9 Percent of soil texture

Soil Texture (%)			Soil classification
Clay	Sand	Silt	
6.73	89.12	4.15	Sand

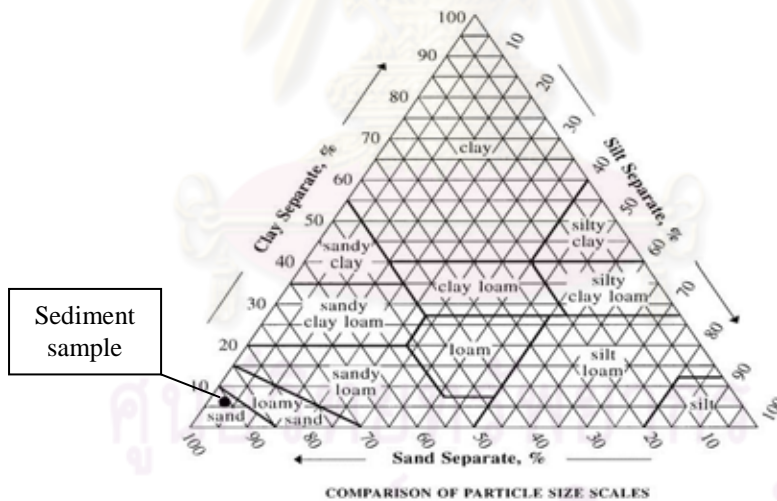


Figure A-2 Classification of sediment

Table A- 10 Concentration of lead in sediment sample

replicate	ICP (mg/l)	Volume of extract (ml)	Dilution factor	Wt. of sediment (g)	Concentration of lead in sediment (mg/kg)	Avg
1	0.216	100	100	0.1	21,600	21,833
2	0.210	100	100	0.1	21,000	
3	0.211	100	100	0.1	21,100	
4	0.224	100	100	0.1	22,400	
5	0.229	100	100	0.1	22,900	
6	0.220	100	100	0.1	22,000	

Table A-11 The other metals concentration in sediment

replicate	ICP (mg/l)	Volume of extract (ml)	Dilution factor	Wt. of sediment (g)	Pb concentration in sediment (mg/kg)	Avg
Fe	0.21013	100	100	0.1	21,013	20,853
	0.20099	100	100	0.1	20,099	
	0.21446	100	100	0.1	21,446	
Ni	0.00450	100	100	0.1	450	208
	0.00076	100	100	0.1	76	
	0.00098	100	100	0.1	98	
Sr	0.00357	100	100	0.1	357	229
	0.00166	100	100	0.1	166	
	0.00162	100	100	0.1	162	
Zn	0.00739	100	100	0.1	739	1,412
	0.01969	100	100	0.1	1,969	
	0.01527	100	100	0.1	1,527	
Al	0.32536	100	100	0.1	32,536	32,785
	0.29011	100	100	0.1	29,011	
	0.36808	100	100	0.1	36,808	
Ca	0.30962	100	100	0.1	30,962	27,084
	0.26457	100	100	0.1	26,457	
	0.23834	100	100	0.1	23,834	
Cd	0.00076	100	100	0.1	76	61
	0.00058	100	100	0.1	58	
	0.00049	100	100	0.1	49	
Cr	0.00110	100	100	0.1	110	74
	0.00070	100	100	0.1	70	
	0.00042	100	100	0.1	42	
Cu	0.00028	100	100	0.1	28	42
	0.00066	100	100	0.1	66	
	0.00033	100	100	0.1	33	
Mg	0.05887	100	100	0.1	5,887	5,461
	0.04970	100	100	0.1	4,970	
	0.05525	100	100	0.1	5,525	
Mn	0.00988	100	100	0.1	988	962
	0.00965	100	100	0.1	965	
	0.00934	100	100	0.1	934	
Li	0.00072	100	100	0.1	72	39
	0.00027	100	100	0.1	27	
	0.00018	100	100	0.1	18	

Appendix B

Table B-1 Released Pb from sediments due to hydrolysis

mix time (min)	Lead concentration (mg/l)			Avg.
	1	2	3	
0	0	0	0	0.000
2	0.028	0.032	0.038	0.033
5	0.043	0.043	0.045	0.044
10	0.043	0.042	0.042	0.042
15	0.044	0.045	0.053	0.047
20	0.050	0.054	0.057	0.054
30	0.057	0.058	0.056	0.057
45	0.058	0.057	0.067	0.061
60	0.059	0.060	0.063	0.061
90	0.061	0.065	0.062	0.063
120	0.058	0.060	0.059	0.059

Table B-2 Pb and Al concentration in the water from electrocoagulation process with Al electrodes and 10 mA

Mixing time (min)	0	5	10	15	20	30	50	70	
Lead (mg/l)	1	0.061	0.046	0.058	0.064	0.066	0.021	0.007	0.006
	2	0.066	0.034	0.048	0.067	0.044	0.026	0.012	0.002
	3	0.035	0.035	0.035	0.043	0.055	0.016	0.000	0.000
	Avg.	0.054	0.055	0.056	0.058	0.055	0.021	0.004	0.001
Aluminum (mg/l)	1	0.327	0.631	0.800	1.595	2.010	2.179	3.347	4.828
	2	0.314	0.646	0.780	1.534	1.922	2.088	3.186	4.789
	3	0.317	0.626	0.782	1.515	1.921	2.084	3.285	4.819
	Avg.	0.319	0.634	0.787	1.548	1.951	2.117	3.273	4.804
Iron (mg/l)	1	0.232	0.261	0.235	0.218	0.106	0.004	0.002	0.004
	2	0.181	0.262	0.254	0.215	0.109	0.006	0.002	0.004
	3	0.183	0.241	0.250	0.221	0.109	0.005	0.001	0.004
	Avg.	0.199	0.255	0.246	0.218	0.108	0.005	0.002	0.004

Table B-3 Pb and Al concentration in the water from electrocoagulation process with Al electrodes and 20 mA

mix time (min)		0	5	10	15	20	30	40
Lead (mg/l)	1	0.059	0.073	0.075	0.049	0.018	0.005	0.003
	2	0.050	0.053	0.054	0.047	0.010	0.003	0.000
	3	0.056	0.054	0.068	0.040	0.009	0.000	0.002
	Avg.	0.055	0.060	0.066	0.045	0.012	0.003	0.001
Aluminum (mg/l)	1	0.235	0.726	1.109	0.755	0.980	2.124	3.667
	2	0.215	0.716	1.023	0.727	0.966	2.110	3.544
	3	0.221	0.687	1.011	0.722	0.966	2.110	3.503
	Avg.	0.224	0.710	1.048	0.735	0.971	2.115	3.571
Iron (mg/l)	1	0.201	0.492	0.468	0.160	0.037	0.001	0.010
	2	0.165	0.504	0.487	0.165	0.036	0.002	0.007
	3	0.156	0.492	0.457	0.161	0.036	0.002	0.006
	Avg.	0.174	0.496	0.471	0.162	0.036	0.002	0.008

Table B-4 Pb and Al concentration in the water from electrocoagulation process with Al electrodes and 30 mA

mix time (min)		0	2	5	10	15	20	30
Lead (mg/l)	1	0.061	0.152	0.148	0.047	0.008	0.005	0.000
	2	0.059	0.154	0.152	0.051	0.011	0.004	0.002
	3	0.072	0.153	0.152	0.052	0.013	0.005	0.007
	Avg.	0.064	0.153	0.151	0.050	0.011	0.005	0.002
Aluminum (mg/l)	1	0.235	1.166	1.932	1.227	0.730	1.019	3.216
	2	0.215	1.249	1.893	1.216	0.733	1.026	3.209
	3	0.221	1.227	1.926	1.199	0.762	1.030	3.208
	Avg.	0.224	1.214	1.917	1.214	0.742	1.025	3.211
Iron (mg/l)	1	0.201	0.504	0.471	0.074	0.043	0.010	0.003
	2	0.165	0.412	0.451	0.075	0.023	0.012	0.003
	3	0.156	0.420	0.455	0.073	0.034	0.009	0.001
	Avg.	0.174	0.445	0.459	0.074	0.033	0.010	0.002

Table B-5 Pb and Fe concentration in the water from electrocoagulation process with Al electrodes and 10 mA

Mixing time (min)	0	15	30	60	90	120	150	
Lead (mg/l)	1	0.059	0.110	0.209	0.087	0.023	0.020	0.031
	2	0.050	0.112	0.201	0.083	0.003	0.004	0.031
	3	0.056	0.095	0.190	0.075	0.011	0.007	0.014
	Avg.	0.055	0.106	0.200	0.082	0.012	0.010	0.025
Aluminum (mg/l)	1	0.235	0.404	0.523	0.120	0.043	0.034	0.059
	2	0.215	0.410	0.516	0.121	0.043	0.034	0.060
	3	0.221	0.417	0.523	0.122	0.042	0.033	0.059
	Avg.	0.224	0.410	0.521	0.121	0.043	0.034	0.059
Iron (mg/l)	1	0.201	0.535	0.958	0.440	0.023	0.007	0.008
	2	0.165	0.538	0.951	0.441	0.023	0.006	0.009
	3	0.156	0.527	0.940	0.438	0.022	0.006	0.009
	Avg.	0.174	0.533	0.950	0.440	0.023	0.006	0.009

Table B-6 Pb and Fe concentration in the water from electrocoagulation process with Al electrodes and 20 mA

mix time (min)	0	15	30	60	90	120	150	
Lead (mg/l)	1	0.059	0.156	0.204	0.078	0.020	0.019	0.009
	2	0.050	0.153	0.189	0.064	0.010	0.012	0.002
	3	0.056	0.153	0.189	0.081	0.011	0.006	0.006
	Avg.	0.055	0.154	0.194	0.074	0.014	0.012	0.006
Aluminum (mg/l)	1	0.235	0.373	0.273	0.063	0.032	0.022	0.012
	2	0.215	0.375	0.280	0.062	0.032	0.023	0.012
	3	0.221	0.380	0.275	0.062	0.032	0.021	0.013
	Avg.	0.224	0.376	0.276	0.062	0.032	0.022	0.012
Iron (mg/l)	1	0.201	0.841	1.038	0.336	0.026	0.016	0.020
	2	0.165	0.847	1.038	0.336	0.026	0.017	0.020
	3	0.156	0.833	1.038	0.335	0.026	0.011	0.020
	Avg.	0.174	0.840	1.038	0.336	0.026	0.015	0.020

Table B-7 Pb and Fe concentration in the water from electrocoagulation process with Al electrodes and 30 mA

mix time (min)		0	15	30	60	90	120	150
Lead (mg/l)	1	0.059	0.156	0.293	0.013	0.017	0.024	0.015
	2	0.050	0.158	0.291	0.003	-0.008	0.017	0.014
	3	0.056	0.160	0.306	0.006	0.003	0.006	0.002
	Avg.	0.055	0.158	0.297	0.007	0.004	0.016	0.010
Aluminum (mg/l)	1	0.235	1.652	1.479	0.144	0.073	0.017	0.025
	2	0.215	1.535	1.493	0.142	0.071	0.017	0.025
	3	0.221	1.562	1.449	0.146	0.073	0.015	0.025
	Avg.	0.224	1.583	1.474	0.144	0.072	0.016	0.025
Iron (mg/l)	1	0.201	0.705	1.847	0.072	0.008	0.002	0.018
	2	0.165	0.697	1.677	0.057	0.009	0.003	0.014
	3	0.156	0.702	1.684	0.058	0.008	0.002	0.013
	Avg.	0.174	0.701	1.736	0.062	0.008	0.002	0.015

Table B-8 pH and EC in the water from electrocoagulation process with Al electrodes and 10 mA

Time (min)	0	5	10	15	20	30	50	70
pH	7.98	8.68	8.77	8.84	8.81	8.37	8.6	8.57
EC	68.7	105.3	115	108.6	99.5	76.5	83.8	80.4

Table B-9 pH and EC in the water from electrocoagulation process with Al electrodes and 20 mA

Time (min)	0	5	10	15	20	30	40
pH	7.89	8.32	8.44	8.44	8.32	8.52	8.56
EC	65.8	74.4	68.6	72.7	69.9	83.3	82.7

Table B-10 pH and EC in the water from electrocoagulation process with Al electrodes and 30 mA

Time (min)	0	2	5	10	15	20	30
pH	7.15	8.07	8.03	8.2	8.45	8.47	8.81
EC	69.3	71.7	72.1	75.8	75.9	78.2	78.7

Table B-11 pH and EC in the water from electrocoagulation process with Fe electrodes and 10 mA

Time (min)	0	15	30	60	90	120	150
pH	8.77	8.72	8.64	8.7	8.64	8.64	8.64
EC	106.6	141	99.9	117.6	111.9	97.6	117.8

Table B-12 pH and EC in the water from electrocoagulation process with Fe electrodes and 20 mA

Time (min)	0	15	30	60	90	120	150
pH	8.1	9.33	8.81	8.87	8.86	8.71	8.65
EC	110	160	114.5	126.5	144.8	134.2	104.6

Table B-13 pH and EC in the water from electrocoagulation process with Fe electrodes and 30 mA

Time (min)	0	15	30	60	90	120	150
pH	8.85	9	8.98	9.1	9.02	9	8.8
EC	108	156	115.2	135.7	128.4	111.3	115.4

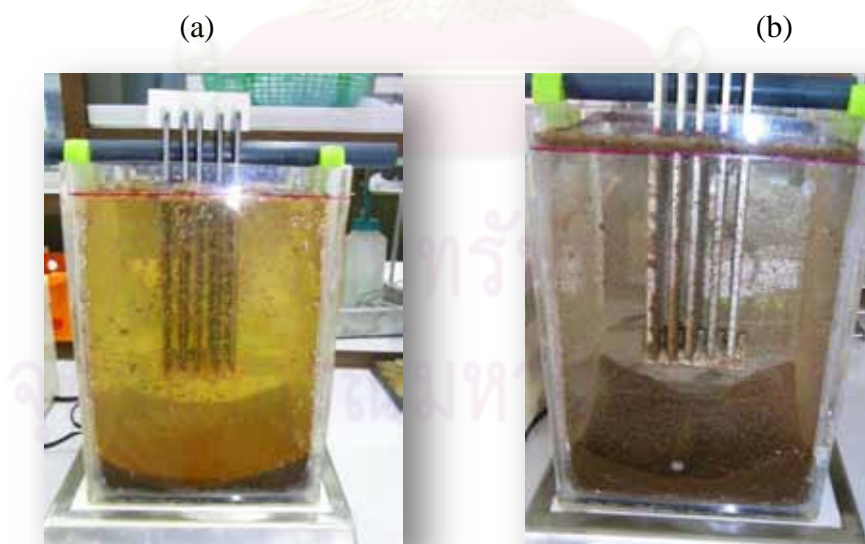


Figure B-1 Treated water with (a) Fe and (b) Al electrodes

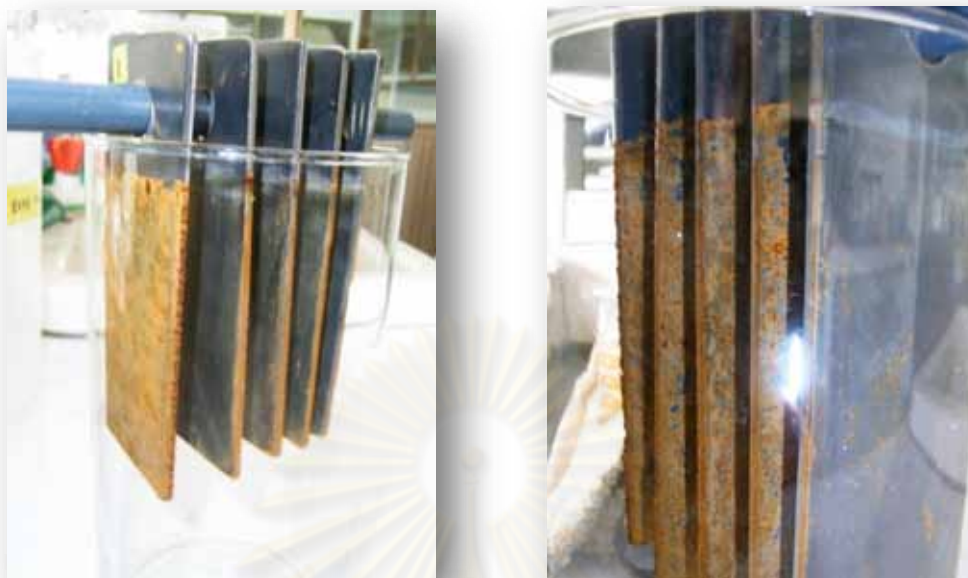


Figure B-2 Fe electrodes after process



Figure B-3 Al electrodes after process

Table B-14 Concentration of lead in treated sediment

Treated sediment	ICP (mg/l)	Volume of extract (ml)	Dilution factor	Wt. of sediment (g)	Concentration of lead in sediment (mg/kg)
30mA_Al	1.1964	100	10	0.1	11,964
20mA_Al	1.2200	100	10	0.1	12,200
10mA_Al	1.4358	100	10	0.1	14,358
30mA_Fe	1.3786	100	10	0.1	13,786
20mA_Fe	1.4907	100	10	0.1	14,907
10mA_Fe	1.6598	100	10	0.1	16,598



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Appendix C

Table C-1 Chemical forms of Pb in untreated sediment

Natural	ICP	Volume of extraction	Mass of Pb	soil	Concentration of Pb	
	mg/l	ml	mg	g	mg/kg	%
Exchangeable	16.9	8	0.1352	1.0	135	0.62
Bound-to-carbonates	1,910	8	15.28	1.0	15,280	69.99
Bound-to-Fe & Mn oxides	195	20	3.9	1.0	3,900	17.86
Bound-to-organic matter	20.1	36	0.7236	1.0	724	3.31
Residual					1,793	8.21

Table C-2 Chemical forms of Pb in treated sediment with 10mA and Al electrode

10mA_Al	ICP	Volume of extraction	Mass of Pb	soil	Concentration of Pb	
	mg/l	ml	mg	g	mg/kg	%
Exchangeable	11.7	8	0.0936	1.0	94	0.65
Bound-to-carbonates	940	8	7.52	1.0	7,520	52.37
Bound-to-Fe & Mn oxides	119	20	2.38	1.0	2,380	16.58
Bound-to-organic matter	13.7	36	0.4932	1.0	493	3.44
Residual					3,870	26.96

Table C-3 Chemical forms of Pb in treated sediment with 20mA and Al electrode

20mA_Al	ICP	Volume of extraction	Mass of Pb	soil	Concentration of Pb	
	mg/l	ml	mg	g	mg/kg	%
Exchangeable	10.9	8	0.0872	1.0	87	0.71
Bound-to-carbonates	680	8	5.44	1.0	5,440	44.59
Bound-to-Fe & Mn oxides	116	20	2.32	1.0	2,320	19.02
Bound-to-organic matter	14.4	36	0.5184	1.0	518	4.25
Residual					3,834	31.43

Table C-4 Chemical forms of Pb in treated sediment with 30mA and Al electrode

30mA_Al	ICP	Volume of extraction	Mass of Pb	soil	Concentration of Pb	
	mg/l	ml	mg	g	mg/kg	%
Exchangeable	9.8	8	0.0784	1.0	78	0.66
Bound-to-carbonates	720	8	5.76	1.0	5,760	48.14
Bound-to-Fe & Mn oxides	94	20	1.88	1.0	1,880	15.71
Bound-to-organic matter	11.8	36	0.4248	1.0	425	3.55
Residual					3,821	31.93

Table C-5 Chemical forms of Pb in treated sediment with 10mA and Fe electrode

10mA_Fe	ICP	Volume of extraction	Mass of Pb	soil	Concentration of Pb	
	mg/l	ml	mg	g	mg/kg	%
Exchangeable	3.7	8	0.0296	1.0	30	0.18
Bound-to-carbonates	1,000	8	8	1.0	8,000	48.20
Bound-to-Fe & Mn oxides	94	20	1.88	1.0	1,880	11.33
Bound-to-organic matter	13.2	36	0.4752	1.0	475	2.86
Residual					6,213	37.43

Table C-6 Chemical forms of Pb in treated sediment with 20mA and Fe electrode

20mA_Fe	ICP	Volume of extraction	Mass of Pb	soil	Concentration of Pb	
	mg/l	ml	mg	g	mg/kg	%
Exchangeable	5.8	8	0.0464	1.0	46	0.31
Bound-to-carbonates	730	8	5.84	1.0	5,840	39.18
Bound-to-Fe & Mn oxides	117	20	2.34	1.0	2,340	15.70
Bound-to-organic matter	14.5	36	0.522	1.0	522	3.50
Residual					6,158	41.31

Table C-7 Chemical forms of Pb in treated sediment with 30mA and Fe electrode

30mA_Fe	ICP	Volume of extraction	Mass of Pb	soil	Concentration of Pb	
	mg/l	ml	mg	g	mg/kg	%
Exchangeable	2.4	8	0.0192	1.0	19	0.14
Bound-to-carbonates	540	8	4.32	1.0	4,320	31.34
Bound-to-Fe & Mn oxides	132	20	2.64	1.0	2,640	19.15
Bound-to-organic matter	13.2	36	0.4752	1.0	475	3.45
Residual					6,331	45.93



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

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