# การบำบัดน้ำเสียปิโตรเคมีโดยกระบวนการรวมตะกอนด้วยไฟฟ้า

นางสาว เชาวรัตน์ รัตนกรเกศ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2552

# TREATMENT OF PETROCHEMICAL WASTEWATER BY ELECTROCOAGULATION PROCESS

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program Environmental Management
(Interdisciplinary Program)
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| Thesis Title | TREATMENT OF PETROCHEMICAL WASTEWATER BY ELECTROCOAGULATION PROCESS |
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| Field of Study | Environmental Management |
| Thesis Advisor | Associate Professor Orathai Chavalparit, Ph.D. |
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เชาวรัตน์ รัตนกรเกศ: การบำบัดน้ำเสียปิโตรเคมีโดยกระบวนการรวมตะกอนด้วยไฟฟ้า (TREATMENT OF PETROCHEMICAL WASTEWATER BY ELECTROCOAGULATION PROCESS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. อรทัย ชวาลภาฤทธิ์, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ. ดร. มณีรัตน์ องค์วรรณดี, 86 หน้า

งานวิจัยนี้เป็นการศึกษาสภาวะที่เหมาะสมในการบำบัดน้ำเสียไบโอดีเซลโดยกระบวนการรวมตะกอนด้วยไฟฟ้า ซึ่งในงานวิจัยนี้ได้แบ่งการทดลองออกเป็น 2 ขั้นตอน คือ

ขั้นตอนที่ 1 เป็นการออกแบบการทดลองแบบใช้ตัวแปรเดี่ยวในการทดลองแต่ละครั้ง โดยทำการปรับเปลี่ยนตัวแปรในการทดลองทั้งหมด 4 ตัวแปร คือ ค่าพีเอชเริ่มต้นของน้ำเสียตั้งแต่ 4 ถึง 9 ค่าความความหนาแน่นของกระแสไฟฟ้าตั้งแต่ 5.11 ถึง 12.13 โวลต์ ระยะเวลาทำปฏิกิริยา ตั้งแต่ 10 ถึง 40 นาที สภาวะที่เหมาะสมในบำบัดน้ำเสียไบโอดีเซล คือ ใช้ขั้วไฟฟ้าแบบอลูมิเนียม-แกรไฟต์ พีเอชเริ่มต้นของน้ำเสียเท่ากับ 6 ใช้ความหนาแน่นของกระแสไฟฟ้าเท่ากับ 8.32 มิลลิแอมแปร์/ตร.ซ.ม. ระยะเวลาในการทำปฏิกิริยานาน 25 นาที พบว่า ประสิทธิภาพในการกำจัดซีโอดี ของแข็งแขวนลอย และน้ำมันและไขมันเท่ากับร้อยละ 97.49 76.92 และ 79.09 ตามลำดับ น้ำหนักขั้วที่สลายไปเท่ากับ 330.4 กรัม สามารถผลิตก๊าซจากปฏิกิริยาที่เกิดขึ้นได้เท่ากับ 390 มิลลิลิตร ใช้ค่าพลังงานเท่ากับ 5.19 กิโลวัตต์ต่อลูกบาศก์เมตร เสียค่าไฟฟ้าในการบำบัดเท่ากับ 10.02 บาทต่อลูกบาศก์เมตร

ขั้นตอนที่ 2 เป็นการออกแบบการทดลองแบบบ็อกซ์-เบห์นเคน โดยทำการปรับเปลี่ยนตัวแปรในการทดลองทั้งหมด 3 ตัวแปร คือ ค่าพีเอชเริ่มต้นของน้ำเสีย ค่าความต่างศักย์ไฟฟ้า ระยะเวลาทำปฏิกิริยา โดยใช้ขั้วไฟฟ้าแบบอลูมิเนียม-แกรไฟต์ จากการทดลองพบว่า สภาวะที่เหมาะสมในการบำบัดน้ำเสียปิโตรเคมี มีค่าใกล้เคียงกับผลการทดลองในขั้นตอนที่ 1 และมีประสิทธิภาพการกำจัดรวมทั้งค่าใช้จ่ายใกล้เคียงกันด้วย ซึ่งเป็นการยืนยันว่าผลการทดลองของทั้ง 2 วิธี สามารถเชื่อถือได้ ซึ่งในการนำไปใช้งาน ต้องเลือกสภาวะที่มีความเหมาะสมกับเครื่องมือและเทคโนโลยีที่ใช้ สามารถควบคุมง่าย เกิดความคุ้มทุนสูงสุด

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต เชาวรัตน์ รัตนกรเกศ
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ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม

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CHAOWARAT RATTANAKORNKET: TREATMENT OF PETROCHEMICAL WASTEWATER BY ELECTROCOAGULATION PROCESS. THESIS ADVISOR: ASSOC. PROF. ORATHAI CHAVALPARIT, Ph.D., THESIS CO-ADVISOR: ASSIST. PROF. MANEERAT ONGWANDEE, Ph.D., 86 pp.

The research aimed to study the optimal condition for petrochemical wastewater treatment by electrocoagulation. The experiment was divided into two steps.

The first part: Different operational conditions were examined using one variable at a time method. The electrode material for anode and cathode were used aluminum and graphite. The initial pH from 4-9, current density from 5.11 to 12.10 $mA/cm^2$ and retention time from 10 to 40 minutes were tested. The result showed that the optimal condition for treatment of petrochemical wastewater was using initial pH of 6, current density 8.32 $mA/cm^2$ and retention time of 25 minutes. The removal efficiency was found to be 97.49% for COD, 76.92% for SS and 79.09% for grease & oil (G&O). Furthermore, 330.4 grams of electrode lost after the experiment 390 ml of gases occurred from the reaction.

The second part: Box-Behnken. The parameters are initial pH of wastewater, voltage and retention time by using Al-C electrode. The experiment showed that the suitable condition is similar to the 1st part experiment including the removal efficiency and the electric cost. It does can confirm that the result of both experiment are reliable. However, the treating condition for the treatment plant should proper to the equipment and technology for the easier operation and the most benefit.

Field of Study: Environmental Management Student's Signature......Chaowarat Rattanakorhket
Academic Year: 2009 Advisor's Signature........................
Co-Advisor's Signature......................

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# CONTENTS

# LIST OF TABLES

**Page**

# LIST OF FIGURES

# CHAPTER I

# INTRODUCTION

## 1.1 Motivations

Nowadays, the demand in energy and fuel are increasing that make petrochemical industry is the main business in Thailand but it consumes more natural resource and has output in form of wastewater, hazardous waste and air pollution that make more pollution to environment. Petrochemical industry also has the problem in wastewater treatment process because petrochemical wastewater contains high content of COD and oil.

Petrochemical is usually confined to products that are derived from petroleum and natural gas and are made on a large scale. The petrochemical industry is a part of the chemical industry, and quite distinct from refining, except in so far as it uses some products of refining as raw materials. The petrochemical industry's main business is chemicals. Petrochemical wastewater is characterized with high content of COD and oil wastewater from petrochemical product ion process contains COD and oil of 6,032 mg/L and 132.5 mg/L, respectively. Generally, petrochemical industry employs Dissolved Air Floatation (DAF) followed by activated sludge process to treat their wastewater. However, oil removal efficiency of DAF is in range of 9.69- 57.71 % wastewater after treated by Dissolved Air Floatation still contained high COD & oil content. However, most of previous works on petrochemical were mainly focused on technical processes of the production, while its environmental management aspect has been usually neglected (Chavalparit *et al.*, 2007).

Electrocoagolation process is the alternative option that can apply in petrochemical wastewater treatment process. This technique is a process consisting of creating a floc of metallic hydroxides within the effluent to be treated by electrodissolution of soluble anode. The coagulant are mentioned by dissolution of sacrificial anode, electrolytic reaction at electrode surface, formation of coagulants by electrolytic oxidation in aqueous phase and adsorption of colloidal particles on coagulant and removal by sedimentation or flotation to removal COD and oil from wastewater. In addition this technique provides some advantages: simple equipment and easy operation (Ivonne *et al.,* 2008).

## 1.2 Objectives

In the present study, the objectives are:

- To determine optimal operating conditions for removal of oil and chemical oxygen demand (COD) from petrochemical wastewater using electrocoagulation (EC) process.
- To study the effects of pH, current density and retention time on removal efficiencies of G&O and COD from petrochemical wastewater.

## 1.3 Hypothesis

- Electrocoagulation process can be used as a primary treatment system to remove oil and COD from petrochemical wastewater.
- The operating condition such as pH, current density and retention time can be effect on removal efficiencies of G&O and COD from petrochemical wastewater.

## 1.4 Scopes of the research

This study was conducted at Department of Environment Engineering, Faculty of Engineering, Chulalongkorn University.

- Test wastewater was collected from the petrochemical industry located in Mabtaput industrial estate.
- Electrocoagulation experiments were conducted using a 1-L monopolar batch reactor.
- The materials of electrodes in this experiment are aluminum and graphite.

- The levels of current density, retention time period and initial pH levels were varied as follows:
    - Current density: 5.11, 8.42, 9.12, 10.93 and 12.13 mA/cm$^2$
    - Retention time: 10, 15, 20, 25, 30 and 40 min.
    - Initial pH of wastewater: 4, 6 and 9.

# CHAPTER II

# THEORY AND LITERATURE REVIEWS

## 2.1 Electrocoagulation Process

### 2.1.1 Principle of electrocoagulation process

Electrocoagulation process is a process consisting of creating a floc of metallic hydroxides within the effluent to be treated by electrodissolution of soluble anode.

The coagulant are mentioned by dissolution of sacrificial anode, electrolytic reaction at electrode surface, formation of coagulants by electrolytic oxidation in aqueous phase and adsorption of colloidal particles on coagulant and removal by sedimentation or flotation to removal COD and oil from wastewater.

The electrochemical reactions with electrode metals can be summarized as follows:

**Reduction Reaction** that occurs at a cathode

$$aOx_1 + ne^- \longrightarrow cRed_1 \qquad (2\text{-}1)$$

**Oxidation Reaction** that occurs at an anode

$$bRed_2 \longrightarrow dOx_2 + ne^- \qquad (2\text{-}2)$$

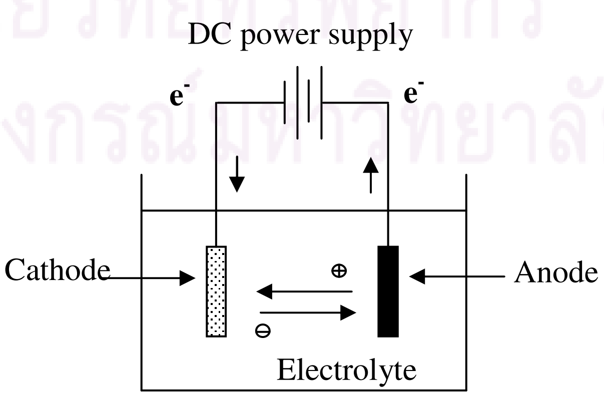


Figure 2.1 The electrochemical reactions (Larue and Vorobiev, 2003)

### 2.1.2 Principle of electrochemical reaction

Principle of electrochemical contain with DC power supply and 2 electrodes in electrolyte show in Figure 2.2

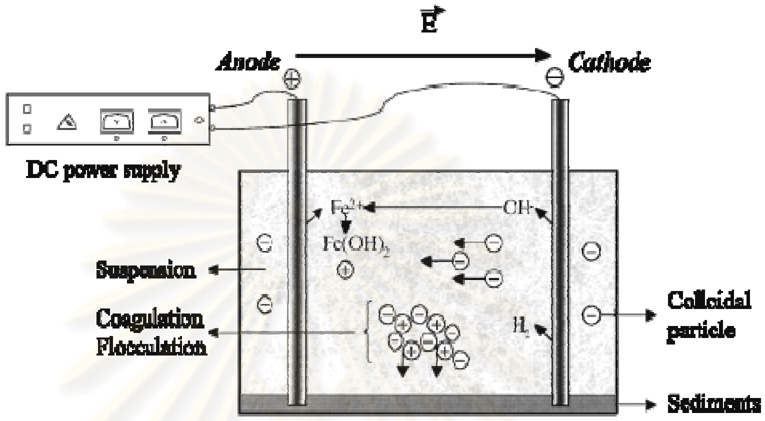


Figure 2.2 Electrochemical reaction (Larue and Vorobiev, 2003)

When electric was produce into the process the electrochemical reaction with electrode metals (M) can be summarized as follows:

At an anode (Oxidation): $M_{(s)} \longrightarrow M_{(ag)}^{3+} + 3e^-$ (2-3)

At a cathode (Reduction): $3H_2O + 3e- \longrightarrow 3/2H_{2\,(g)} + 3OH^-$ (2-4)

In the solution: $M_{(aq)}^{3+} + 3H_2O \longrightarrow M(OH)_3 + 3H^+$ (2-5)

$M_{(aq)}^{3+}$ and $OH^-$ ions, which are produced via the reactions (2-3) and (2-4), respectively, can react to form various monomeric species, depending on a pH range, and then they are finally transformed into $M(OH)_3$ according to complex precipitation kinetics. Freshly formed amorphous $M(OH)_3$ (sweep flocs) has large surface areas that are beneficial for rapid adsorption of soluble organic compounds and trapping of colloidal particles. Consequently, these flocs can be removed by sedimentation or by floatation using $H_2$ bubbles, which is produced at the cathode.

### 2.1.3 Control of electrochemical

1) Controlled-Potential Method or Potentiostatic Mode is the control potential of electrode and standard electrode to be steady that makes the electricity change with time. At the optimum potential cation in electrolyte oxidize with cathode at surface and after that ion concentration at surface decrease, so the control potential of electrode and standard electrode were increase that the electricity decrease to reduce the potential steady as shown in Figure 2.3

$E_1$ is an initial voltage before the reaction and $E_2$ is a voltage at diffusion limited rate or mass transfer limited the reduction reaction occurs with oxidizing agent that can reduce the cation at surface to zero, so the reducing of ion concentration in electrolyte can effect on decrease electricity in process as shown in (b) because electricity is directly proportional to the concentration (I=kC)

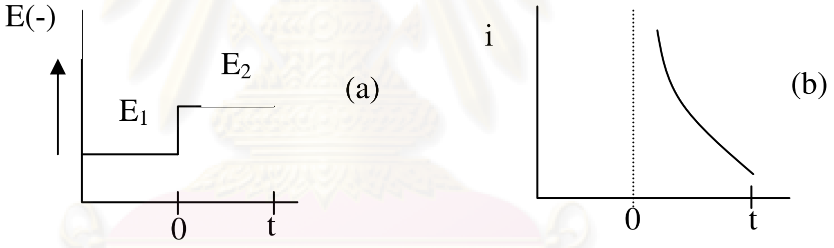


Figure 2.3 (a) The relationship between potential and time with controlled-potential method.
(b) The relationship between electricity and time with controlled-potential method (Friedrich, 1962)

2) Controlled-Current Method or Galvanostatic Mode or Chronopotentiome - tric technique is control the concentration of electricity though electrode to be steady that makes the electricity change with time. When control electricity though both of electrode to be steady that make the reduction reaction occur oxidizing agent ($M^{n+}$) transform to reducing agent (M) with steady rate.

$$M^{n+} + ne^- \longrightarrow M$$

So, the potential vary with the concentration of reducing agent from the transform of $M^{n+}/M$ at surface electrode and time. After that the concentration of $M^{n+}$ at surface electrode decreases same with the potential at surface electrode as follow the Nernst Equation. The Transition time ($\tau$) is the period which has the change of potential with steady electricity this value has the relationship with concentration and diffusion coefficient as shown in Figure 2.4

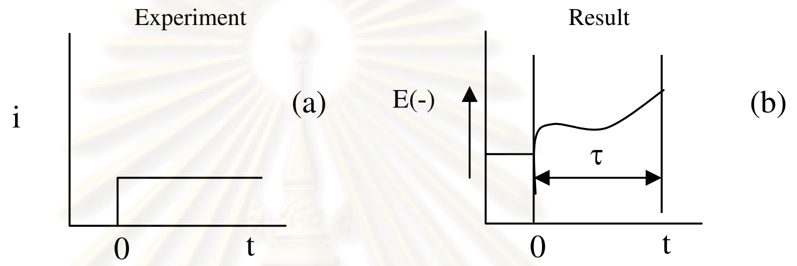


Figure 2.4 (a) The relationship between potential and time with controlled-current method.
(b) The relationship between electricity and time with controlled-current method. (Friedrich, 1962)

The change of potential with the oxidizing agent concentration as shown with Nerns's equation

$$E = E^0 + \frac{RT}{nF} \ln \frac{[Ox]}{[red]} \qquad (2\text{-}6)$$

When:

E = the potential between anode and cathode at any condition (Volt)
$E^0$= the standard potential between anode and cathode (Volt)
R = gas constant = 8.314 (J/mole/K)
T = temperature (K)
n = the number of electron in reaction (ion/mole)
F = Faraday's constant = 96,500 (amp.sec/ion)
[Ox],[red] = the concentration of oxidizing and reducing agent (mole/L)

To get highest elimination rate the ion reduction should be mass transport control, so the equation of this rate is

$$-V\frac{dc}{dt} = \frac{-I_L}{nF} = k_m A_e \qquad (2\text{-}7)$$

When:

V = the volume of solution ($cm^3$)

C = the concentration of metal ion (mole/L)

t = time (sec)

$I_L$= limiting current (amp)

$k_m$= mass transfer coefficient

$A_e$ = surface area of electrode ($m^2$)

When integral eq. xx with time as this equation

$$\frac{C_{(t)}}{C_{(0)}} = \exp\frac{(-k_m A_e t)}{V} \qquad (2\text{-}8)$$

When:

C (0) = the metal ion concentration in initial solution (mole/L)

C (t) = the metal ion concentration in electrolyte at time (mole/L)

So, from the equation the change rate of metal ion concentration vary with

1. mass transportation from electrolyte to surface electrode up to characteristic of electrolyte and electrode (stirring increase mass transportation)
2. Surface electrode

### 2.1.4 Electromotive force

In electric cell has flow of electricity because the electron movement through electric conductivity one electric cell wants energy for 1 Joule that make ion 1 coulomb (C) movement and the distance has potential 1 volt, so 1 volt equal to 1 J/C and in electrochemical call electromotive force (emf).

$$\text{Work of electricity } (W_{elec}) = \text{Coulomb} \times \text{Volt} \qquad (2\text{-}9)$$

But work from electric cell has electron transfer, so the number of ion in coulomb unit up to the number of electron in reaction that every 1 mole of electron has 96,487 coulombs assumes in the reaction has electron transfer n mole this equation change to

$$W_{elec.} = (nF)(E) = nE \times 96{,}487 \qquad (2\text{-}10)$$

This reaction is reversible so free energy ($-\Delta G$) equal to work

$$\Delta G = -nFE \qquad (2\text{-}11)$$

The symbol of $\Delta G$ has the meaning if $\Delta G$ is minus this reaction is spontaneous but $\Delta G$ is plus this reaction non-spontaneous for steady state $\Delta G$ is zero and the relationship as follow eq. 2-11

Table 2.1 The symbol meaning of $\Delta G$ and $\Delta E$

| **Type of reaction** | **$\Delta G$** | **$\Delta E$** |
|---|---|---|
| Spontaneous | - | + |
| Non-spontaneous | + | - |
| Steady state | 0 | 0 |

### 2.1.5 Electric conductivity

Electric conductivity is directly effect on electricity for wastewater treatment and effect on ion quality from reaction as follow with 1st Faraday's law that if high ion quality can make enough aluminum to be metal hydroxide and has more floatation. From Ohm's law that the potential is equal to electricity multiply by electric resistance as follow eq. 2-16

$$V = I \times R \tag{2-16}$$

So;

$V$ = electric potential (Volt)
$I$ = electricity (Amp)
$R$ = resistance (Ohm)

and has the relationship with work of electricity as eq. 2-17

$$W_{elec} = C \times V = nE \text{ x } 96{,}487 \tag{2-17}$$

The electric resistance in electrochemical process is the electric resistance in electrolyte solution and has the relationship with electric conductivity in electrolyte solution as eq. 2-18

$$R = I \,/\, (C \text{ x } A) \tag{2-18}$$

When;

$R$ = electric resistance in electrolyte solution (Ohm)
$I$ = distance between electrode (cm)
$C$ = electric conductivity of electrolyte solution (Ohm)
$A$ = surface area of electrode that connect with electrolyte ($cm^2$)

### 2.1.6 Ion exchange and ion movement

The moment of ion from place to place can make the electricity measure in ampere unit (Amp) the number of electricity though surface area cans measure in current intensity (I) by conductivity as

$$I = \sigma.E_f \tag{2-19}$$

$$E_f = I/\sigma = V/R\sigma \tag{2-20}$$

So;

σ = electric conductivity (M/cm)

V = the potential between two place (Volt)

R = the resistance between two place (Ohm)

I = electricity (Amp)

### 2.1.7 Faraday's law in electrochemical

The electricity 1 Faraday is the electricity pass though electrolyte solution for oxidation-reduction reaction or the multiply of electric ion with 1 mole of electron

$$\begin{aligned} 1 \text{ Faraday} &= eN = (1.602 \times 10^{-19} \text{ Coulomb})(6.02 \times 10^{23} \text{ mol}^{-1}) \\ &= 96{,}487 \text{ Coulomb/mol} \\ \text{get } X \text{ Coulomb} &= I \text{ (Amp)} \times t\text{(sec)} \end{aligned}$$

For example;

Add electricity 1 Faraday in $Al^{+3}$: $Al_{(s)}$ 1 mol = mole of Al/ion

= 26.98/3 = 9 g.

The relationship between electricity and dissolved electrode in electrolyte solution can explain with Faraday's law follow this equation

$$W = I.t.M/Z.F \tag{2-21}$$

So;

W = amount of dissolve electrode (g)

I = the electricity in experimental

M = weight of anode electrode

t = time (min)

Z = number of electron in redox reaction

F = Faraday's constant = 96,487

The mass from Faraday's law is the mass from theory that means all electricity were used to reduction reaction but in experiment all electricity weren't used in all reaction because some electricity lost, such as the hydrolysis at cathode.

$$\text{The efficiency} = \frac{\text{Mass from experiment}}{\text{Mass from theory}} \qquad (2\text{-}22)$$

### 2.1.8 Effect on electrocoagulation efficiency

1) pH: The effect of pH on the removal efficiency of oil and COD, it was varied between 4 and 9, the pH increase to hydrogen evolution at cathodes. However this increase in pH by release of $CO_2$ from wastewater owing bubbles. In addition, the chemical dissolution of aluminum will consume $H^+$ and gives rise to the pH increase also the removal efficiency of oil and COD as a function of initial pH.

2).Voltage: is a critical parameter, as it is the only operational parameter that can be directly controlled, it was suggested that voltage determines both coagulant dosages and bubble generation rate.

3).Time: the removal efficiency of oil and COD increase according to time.

### 2.1.9 Control factor in electrochemical

1) The capability of ion movement up to size of ion.

2) Temperature of electric movement is directly proportional to temperature of solution.

3) Electricity is directly proportional to surface area of electrode.

4) Electricity is up to the distance that ion move from electrode, such as near distance can increase electricity.

5) High number of ion can increase electric movement.

6) The conductivity of solution is directly proportional to concentration of solution.

### 2.1.10 Advantages of EC

1) EC is requires simple equipment and easy to operate with sufficient operational latitude to handle most problems encountered or running.

2) Wastewater treated by EC gives palatable, clear, colorless and odorless water.

3) Sludge formed by EC tends to be readily settable and easy to de-water, because it is composed of mainly metallic oxides/hydroxides. Above all, it is a low sludge producing technique.

4) Flocs formed by EC are similar to chemical floc, except that EC floc tends to be much larger, contains less bound water, is acid-resistant and more stable and can be separated faster by filtration.

5) EC produces effluent with less total dissolved solids (TDS) content as compared with chemical treatments. If this water is reused, the low TDS level contributes to a lower water recovery cost.

6) The EC process has the advantage of removing the smallest colloidal particles, because the applied electric field sets them in faster motion, thereby facilitating the coagulation.

7) The EC process avoids uses of chemicals, and so there is no problem of neutralizing excess chemicals and no possibility of secondary pollution caused by chemical substances added at high concentration as when chemical coagulation of wastewater is used.

8) The gas bubbles produced during electrolysis can carry the pollutant to the top of the solution where it can be more easily concentrated, collected and removed.

9) The electrolytic processes in the EC cell are controlled electrically with no moving parts, thus requiring less maintenance.

10) The EC technique can be conveniently used in rural areas where electricity is not available, since a solar panel attached to the unit may be sufficient to carry out the process.

### 2.1.11 Disadvantages of EC

1) The “sacrificial electrodes” are dissolved into wastewater streams as a result of oxidation, and need to be regularly replaced.

2) The use of electricity may be expensive in many places.

3) An impermeable oxide film may be formed on the cathode leading to loss of efficiency of the EC unit.

4) High conductivity of the wastewater suspension is required.

5) Gelatinous hydroxide may tend to solubilize in some cases.

## 2.2 Petrochemical wastewater

### 2.2.1 Petrochemical industry

Petrochemical is usually confined to products that are derived from petroleum and natural gas and are made on a large scale. The petrochemical industry is a part of the chemical industry, and quite distinct from refining, except in so far as it uses some products of refining as raw materials. Many companies that make petrochemicals do not carry out oil refining, and those oil companies which make petrochemicals tend to have a separate organization for this part of the business. The oil industry's main business is fuels, with raw materials for petrochemicals as an important sideline. The petrochemical industry's main business is chemicals.

The petrochemical industry consist of 3 categories; upstream, intermediate stream and downstream. The upstream petrochemical industry is where petroleum gas such as ethane and propane or oil based products such as naphtha are converted into olefins (ethylene gas and propylene gas) and condensates are converted into aromatics (benzene, toluene and xylene) via cracking. The intermediate stream petrochemical industry is where the upstream products are processed to yield intermediate stream petrochemical products such as styrene monomer, vinyl chloride monomer, ethylene glycol and purified terephthalic acid. The downstream petrochemical industry is where intermediate petrochemical products are processed to produce downstream petrochemical products such as polymers or synthetic which can be applied as basic materials for other related industries including packing industry, electrical appliance industry, auto parts industry, textile industry, etc.

### 2.2.2 Production process & Wastewater generation

- **Petrochemical production process**

**1) Materials**

- Ethane gas

- Propane gas
- LPG gas

**2) Product**

The main products of process are ethylene and propylene after transfer to continuous petrochemical industry. In addition, in this process have side products such as, hydrogen gas, methane rich gas and fuel oil.

**3) Production process**

In petrochemical production process have main processes are Oleflexs production process and Plastic production process.

**Oleflexs production process**

Olefins are the name of unsaturated hydrocarbon such as, ethylene and propylene that are initial substance in petrochemical production process. This process starts with natural gas or crude oil and transform to new products. Olefins product is the important material in many industries, i.e., electronic equipment, computer, fabric, etc. follow the demand as show in Figure 2.5

The technology in oleflexs production have 2 processes are thermal cracking and catalyst cracking by Oleflex Reactor System. For thermal cracking process use products from natural gas to reducing size and cooling by quench water system to decrease mechanism and polymerization that is by-product. After that this product will go to charge gas compressor, chilling train and make purity by fractionators unit to get ethylene, propylene and other by-products.

For catalyst cracking process use to produce propylene done by bring propane pass though catalyst cracking by Oleflex Reactor System in this process hydrocarbon was cracked into small unit after that go to Reactor Effluent Compressor Unit to get propylene and other by-products.

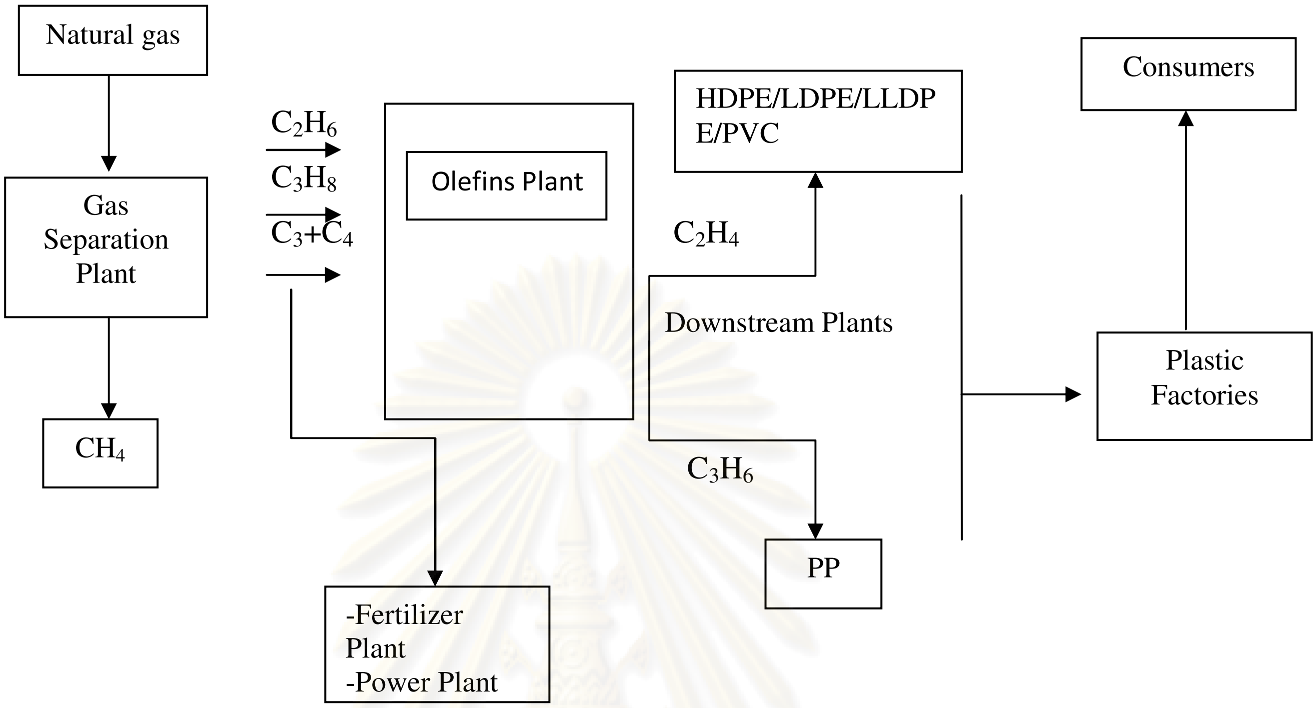


Figure 2.5 Overall of petrochemical industry (www.ftipc.or.th)

**Plastic Production Process**

In this process use raw material from olefin production process (also use Ethylene and Propylene). Types of plastics depend on raw material and production process but the majority of plastics are high density polyethylene (HDPE).

- **Source of wastewater**

  Wastewater from petrochemical plant is generated from 4 main sources:

  - Wastewater from production process consists of oleflexs production process and plastic production process.
  - Domestic wastewater.
  - Wastewater from Spent caustic is a wastewater from ethylene production process.
  - Etc., such as rain water.

### 2.2.3 Wastewater treatment for Petrochemical wastewater

Wastewater treatment of industry consist of physical treatment, chemical treatment and biological treatment

1) Oily Separator is treatment system that uses to separate oil from wastewater before treated by biological treatment process.
2) Neutralization is the system for adjust pH of wastewater before sent to Dissolve Air Floatation tank (DAF) and New DAF tank.
3) Activated Sludge in this step includes domestic wastewater that will be treated by biological treatment.
4) Final Check is the step to measure quality of wastewater before discharge into waterway of Map Ta Put Industrial Estate.

The wastewater treatment system in petrochemical industry is show in Figure 2.6

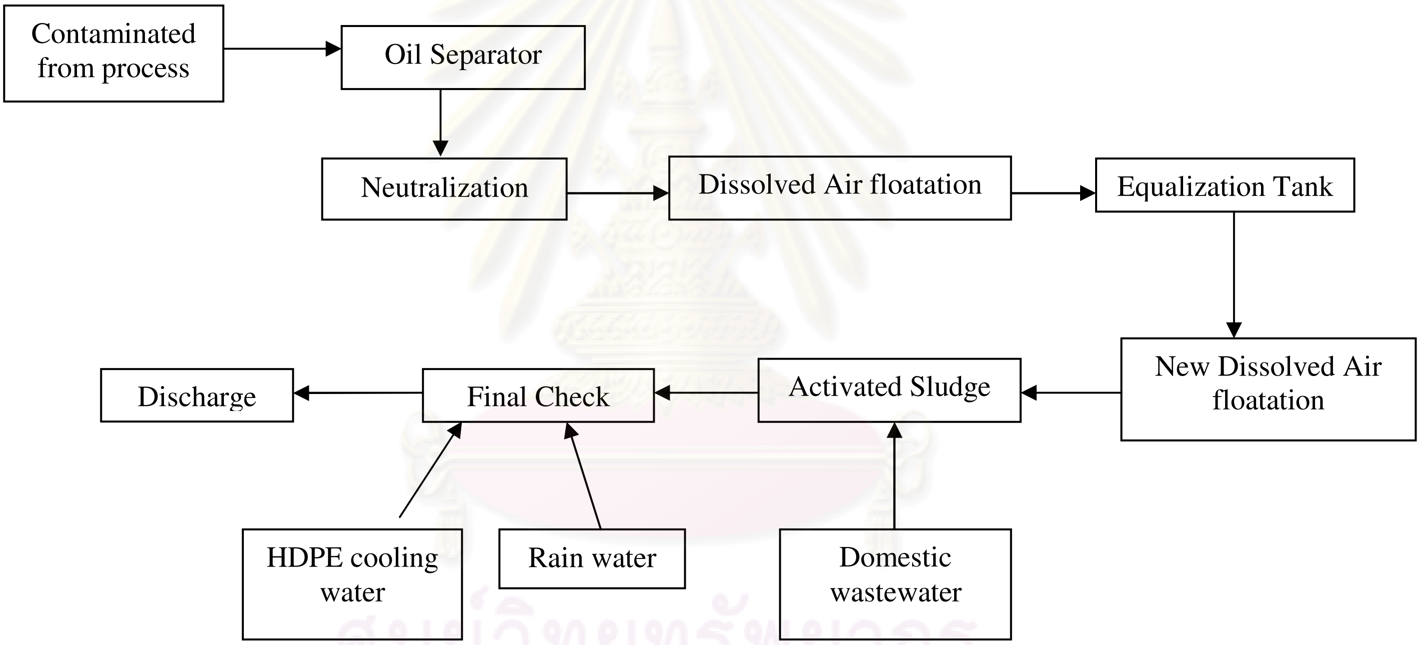


Figure 2.6 Wastewater treatment system in petrochemical industry

### 2.2.4 Wastewater characteristic of petrochemical plant case study

Petrochemical wastewater is characterized with high content of COD and oil wastewater from petrochemical product ion process contains COD and oil of 6,032 mg/L and 132.5 mg/L, respectively. Generally, petrochemical industry employs Dissolved Air Floatation (DAF) followed by activated sludge process to treat their wastewater. However, oil removal efficiency of DAF is in range of 9.69- 57.71 %

wastewater after treated by Dissolved Air Floatation still contained high COD & oil content.

Table 2.2 Wastewater characteristic after Oil separation, DAF, New DAF and Final check basin.

| Treatment Process | SS (mg/L) | COD (mg/L) | Oil & Grease (mg/L) | DO (mg/L) |
|---|---|---|---|---|
| Oil Separator | 120 | 3880 | 63 | - |
| DAF(Pretreatment) | 110 | 1818 | 42 | - |
| New DAF | 28 | 307 | 28 | - |
| Activated Sludge | 20.3 | 104.9 | 2.5 | - |
| Final Check Basin | 20 | 78 | 1.4 | 5.67 |

*Average data from petrochemical 2008-2009

### 2.3 Box-Behnken design

The Box-Behnken design, an experimental design for response surface method, was used to create a set of designed experiments by MINITAB software, version14. The Box-Behnken design was developed based on a combination of a two-level (full of fractional) factorial design with an incomplete block design. In general, a certain number of factors are put through all combinations for the factorial design in each block, while the other factors are kept at the central values. In this study, the Box-Behnken design for 3 factors, i.e, initial pH($x_1$), applied voltage ($x_2$) and reaction time ($x_3$), involved three blocks. In each of three blocks two factors were varied through the 4 possible combinations of high and low. The original factors of $x_1$, $x_2$ and $x_3$ were coded as given by Eq. 1

$$X_i = \frac{x_i - x_{cp}}{\Delta x_i} \tag{2-23}$$

Where, $X_i$ is coded level; $x_{cp}$ is the original value of the centered point; and $\Delta x_i$ is the value of variable chages step. Table 2.3 shows the levels of original and coded factors using Box-Benhken design. The values of the original variables were selected based on the preliminary experimental results. Given the three main variables and three test levels, 15 experiments were designated by MINITAB software.

Table 2.3 The Box-Behnken design for 3 factors

| RUN | $X_1$ | $X_2$ | $X_3$ |
|---|---|---|---|
| 1 | -1 | -1 | 0 |
| 2 | -1 | 1 | 0 |
| 3 | 1 | -1 | 0 |
| 4 | 1 | 1 | 0 |
| 5 | -1 | 0 | -1 |
| 6 | -1 | 0 | 1 |
| 7 | 1 | 0 | -1 |
| 8 | 1 | 0 | 1 |
| 9 | 0 | -1 | -1 |
| 10 | 0 | -1 | 1 |
| 11 | 0 | 1 | -1 |
| 12 | 0 | 1 | 1 |
| 13 | 0 | 0 | 0 |
| 14 | 0 | 0 | 0 |
| 15 | 0 | 0 | 0 |

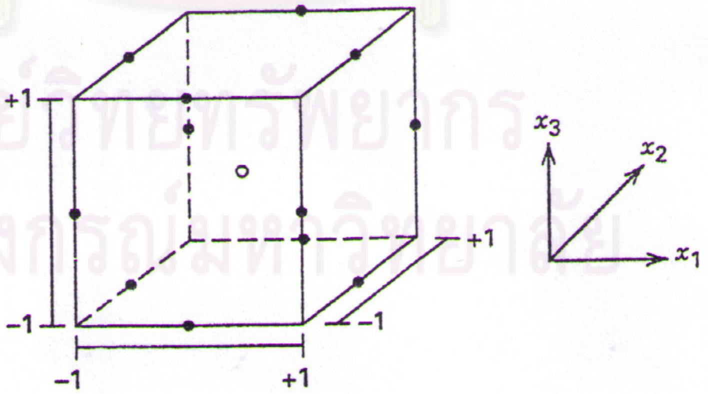


Figure 2.7 The Box-Behnken design for 3 factors (Myers and Montgomery, 2002)

## 2.4 Response Surface Methodology, RSM

RSM is a collection of mathematical and statistical techniques that are beneficial for the modeling and analysis of problems in which a response of interest is influenced by several variables to predict to targeted responses. RSM consists of an empirical modeling technique denoted to the evaluation of relations existing between a group of controlled experimental factors and the observed results. RSM is an important branch of experimental design and critical methodology in developing new processes, optimizing their performance and improving design and formulation of new products. The most extensive applications of RSM are in industrial research, particularly in situations where several input variables influence the process performance measure. This process performance measure is called the response and the input variables are called independent variables.

Figure 2.8 shows the relationship between the response surfaces yields ($y$) and the two process variables (independent variables) reaction temperature ($x_1$) and pressure range ($x_2$). The relationship is

$$y = f(x_1, x_2) + \varepsilon \qquad (2\text{-}24)$$

$\varepsilon$ as a statistic error from the experiment, often assume it $E(y) = f(x_1,x_2) = \eta$

$$\eta = f(x_1, x_2) \qquad (2\text{-}25)$$

That is “Response Surface”

In this presentation have the same yield to produce contour lines of constant response. This type of display is called a contour plot.

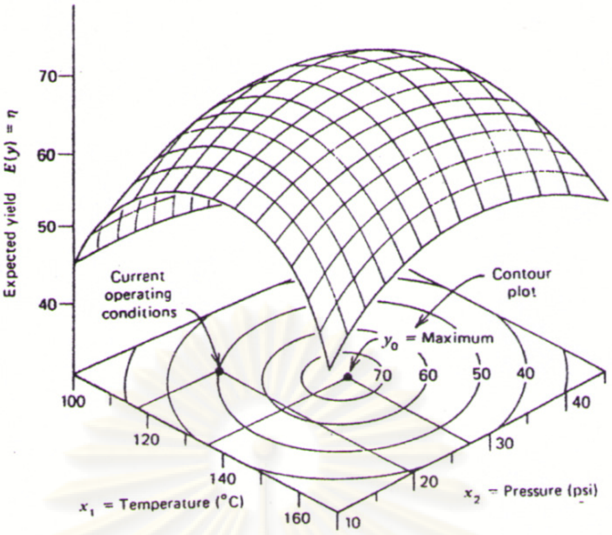


Figure 2.8 A contour plot of the theoretical response surface (Myers and Montgomery, 2002)

### 2.4.1 Response Surface Regression Analysis

Regression Analysis is the method to study the relationship between two variables are Dependent Variable: Y and Independent Variable: X, that aim to predict dependent variable with the relationship between dependent variable and independent variable is called Regression Coefficient. To perform response surface regression analysis, experimental data were fitted to 4 modals are linear modal, linear + interaction model, square model and full quadratic model was described as the following:

Linear model

$$Y = \beta_0 + \sum_{i=1}^{4} \beta_i x_i \qquad (2\text{-}26)$$

Linear + Interaction model

$$Y = \beta_0 + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{3} \sum_{j=i+1}^{4} \beta_{ij} x_{ij} \qquad (2\text{-}27)$$

Linear + Square model

$$Y = \beta_0 + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{4} \beta_{ii} x_i^2 \qquad (2\text{-}28)$$

Full Quadratic model

$$Y = \beta_0 + \sum_{i=1}^{4} \beta_i x_i + \sum_{i=1}^{4} \beta_{ii} x_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{4} \beta_{ij} x_{ij} \qquad (2\text{-}29)$$

Where, $\beta_0$, $\beta_i$, $\beta_{ii}$ and $\beta_{ij}$ are the regression coefficients for intercept, linear, quadratic and interaction terms, respectively; and $x_i$ and $x_{ij}$ are the independent variables. $Y_i$ represents COD removal ($Y_1$), G&O removal ($Y_2$) and SS removal ($Y_3$).

### 2.4.2 The fit of modal

In previous topic show the response surface regression modals in 4 forms how can we know the fit of the modal to use for decries the relationship between dependent variable and independent variable, so the appropriate modal can observe from Standard Error: SE and Coefficient of Determination: $R^2$

1. Standard Error: SE if SE has low, it means the modal is more suitable but SE has high the modal not suitable if SE = 0 is the best modal.

2. Coefficient of Determination: $R^2$ is 0-1 for the best modal $R^2$ should close to 1 or equal 1 that means independent variable can described dependent variable. $R^2_{(adj)}$ is the adjust coefficient of determination use for data less than 30 that calculate from this equation:

$$R^2_{adj} = 1 - \frac{n-1}{n-k-1} \times (1 - R^2) \qquad (2\text{-}30)$$

So,

n = amount of experiment.

k = number of modal coefficient.

### 2.4.3 Test for significance of Regression ($\beta_1$)

The test for significance of regression is a test to determine if there is a linear relationship between the responses variable y and a subset of regressor variables $x_1$, $x_2$,…, $x_k$.

1. Test for significance of regression of all independent variables in one time.

   The appropriate hypotheses are

$$H_0 : \beta_i = \beta_1 = \beta_2 = ... = \beta_k = 0$$

$$H_1 : \beta_i \neq 0$$

Rejection of $H_0$ in equation implies that at least one of the regressor variables contributes significantly to the model. For test value is F-test or *p-value*, if *p-value* higher than the number of degree of freedom (α) that can accept $H_0$, it means all of independent variable can't compute the modal and not effect on dependent variable.

2. Test for significance of regression of each independent variable.

   The appropriate hypotheses are

$$H_0 : \beta_i = 0$$

$$H_1 : \beta_i \neq 0$$

Test value is F-test or *p-value*, if *p-value* higher than the number of degree of freedom (α) that can accept $H_0$, it means independent variable not effect to dependent variable but *p-value* lower than the number of degree of freedom (α) that can reject $H_0$, it means independent variable can effect on dependent variable.

### 2.4.4 Test for Lack of fit

Response surface analysis is the test for lack of fit that the one method to test the fit of the modal because has the same experiment in the middle, so can observe from Sum of Square of the Residual Error: $SS_E$.

$$SS_E = SS_{PE} + SS_{LOF} \tag{2-31}$$

So;

$SS_{PE}$ is directly sum of square

$SS_{LOF}$ is sum of square from the lack of fit of the modal

## 2.5 Literature Reviews

- **Mohamed et al. (2008)** studied electrocoagulation process with sacrificial aluminum anode was used to separate oil from oily wastewater emulsion. Their study aims were evaluate the most accurate operating parameters, which are then used for the determination of oil removal efficiency and an experimental design using response surface method (RSM) was applied. They showed the electrocoagulation was very efficient and able to achieve 99% turbidity and 90% chemical oxygen demand (COD) in less than 22 min and current density of 25 mA $cm^{-2}$.
- **Chih et al. (2009)** have illustrated the removal efficiency of COD in the treatment of simulated laundry wastewater using electrocoagulation / electroflotation technology is described. The experiment results showed that the removal efficiency reaching to about 62%. The performance of monopolar connection of electrodes was better than that of the bipolar connection and the removal efficiency of using Al electrodes was higher in comparison with using Fe electrodes.
- **Mayank et al. (2009)** presented the chemical oxygen demand (COD) reduction of a bio-digester effluent (BDE) in a batch electrocoagulation (EC) reactor using iron electrode. A central composite (CC) experiment design employed to evaluate the indvaidual and interactive effects of four parameters on the COD removal efficiency. The parameters studied are current density, initial pH, inter-electrode distance and electrolysis time. Maximum COD and color reduction of 50.5% and 95.2%, respectively, was observed at optimum conditions.
- **Muftah et al. (2009)** investigated the removal of sulfate and COD from petroleum refinery wastewater using three types of electrodes: aluminum, stainless steel, and iron. The effect of current density, electrode

arrangement, electrolysis time, initial pH, and temperature for two wastewater samples with different concentrations of COD and sulfate. The result indicated the utilization of aluminum as, anode and cathode, was the most efficient in the reduction of both the contaminant. Although electrocoagulation was found to be most effective at 25ºC and a pH of 8.

- **Srirangsan et al. (2009)** determined the optimum condition for biodiesel wastewater treatment using an electrocoagulation process. Tested operational conditions included types of electrode, current density, retention time and initial pH. The result showed that the optimum conditions were achieved by using the electrodes of AL-C, applying the current density of 8.32 $mA/cm^2$ to the wastewater with an initial pH value of 6 for 25 min.
- **Turba (2009)** investigated the effects of different operating conditions on the removal of hexavalent chromium (Cr(VI)) by the electrocoagulation with stainless steel electrodes. The optimum conditions for complete (100%) Cr(VI) removal were established as 7.4 A applied electric current, 33.6 mM electrolyte (NaCl) concentration and 70 min application time.
- **Un et al (2009)** studied the effects of operating parameters such as pH, current density; PAC (poly aluminum chloride) dosages and $Na_2SO_4$ dosages on the removal of organics and COD removal efficiency have been investigated. The results indicated the removal efficiency of COD increased with the increasing applied current density and increasing PAC and $Na_2SO_4$ dosage and the most effective removal capacity was achieved at the pH 7 and the electrocoagulation is very efficient able to achieve 98.9% COD removal in 90 min at 35 $mAcm^{-2}$ with a specific electrical energy consumption of 42 kWh $(kg\ COD_{removed})^{-1}$.

# CHAPTER III

# RESEARCH METHODOLOGY

**Methodology:**

## 3.1 The Research methodology Framework

This study is aimed to determine optimal operating conditions for electrocoagulation process to remove oil and COD from petrochemical wastewater. The study comprises of 5 steps

**Step 1:** The optimal conditions and effects of the operating parameters were investigated using one variable at a time experiments. These parameters are as follows:

- First experiment: a study of initial pH of wastewater with 3 values, i.e., 4, 6 and 9.
- Second experiment: a study of current density with 5 values, i.e., 5.11, 8.42, 9.12, 10.93 and 12.13 mA/cm$^2$.
- Third experiment: a study of retention time with 6 values, i.e., 10, 15,20,25,30 and 40.

**Step 2:** The Box-Behnken design, an experimental design for response surface methodology (RSM), was used to create a set of designed experiments by MINITAB software, version 14. Results from step 1 were then used to calibrate quadratic regression models.

**Step 3:** Gas productions was measured.

**Step 4:** Sludge characterization was determined for both qualitative and quantitive methods.

**Step 5:** Treatment cost of the electrocoagulation system was determined.

## 3.2 Materials

### 3.2.1 Electrocoagulation Unit

Electrocoagulation experiment was conducted in a 1-L monopolar batch reactor and schematic diagram of the experimental setup is shown in Figure 3.1.

1. The reactor is connected in parallel to a digital DC Power Supply.
2. The tested electrodes are aluminum (Al) as anode and graphite (C) as cathode that has a flat and rectangular shape with an area of 50 $cm^2$

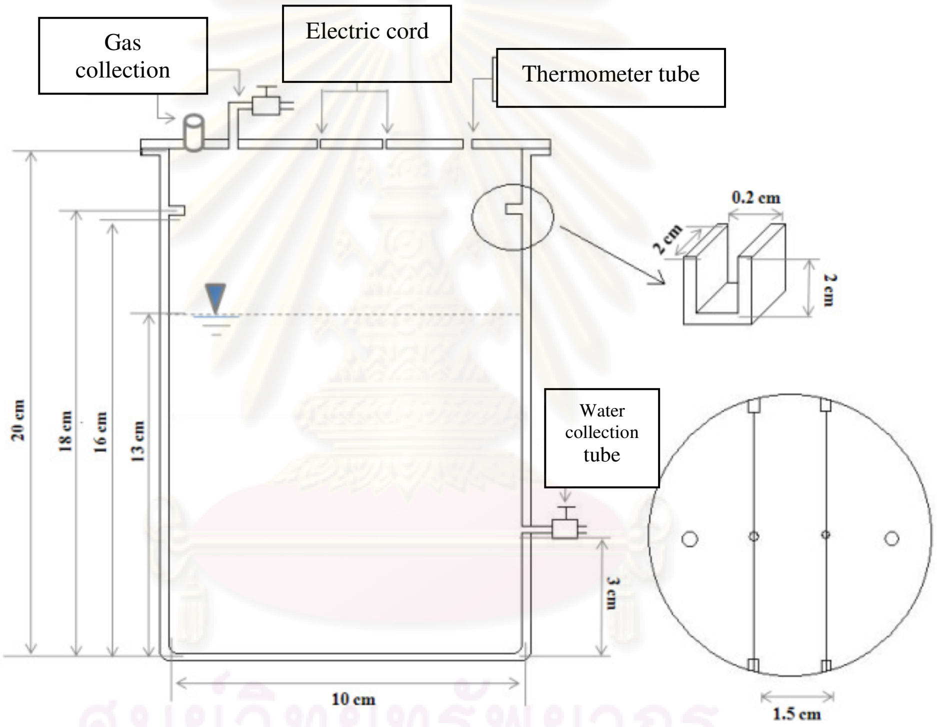


Figure 3.1 Size of reactor

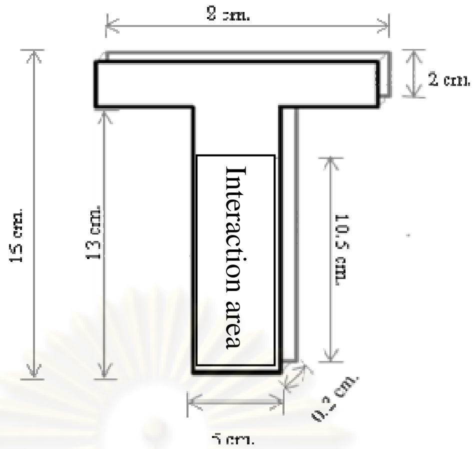


Figure 3.2 Size of electrode

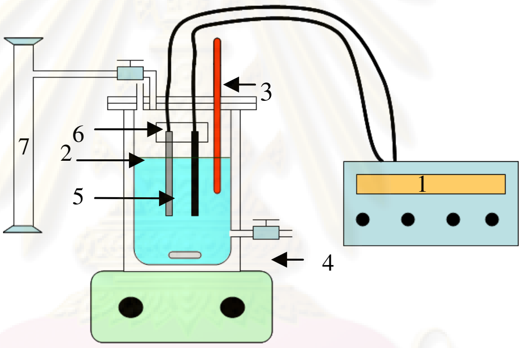


Figure 3.3 Experimental setup of the EC reactor : 1. DC power supply 2. Electrolyte 3. Thermometer 4. Stirrer Plate 5. Magnetic bar 6. Electrodes 7. Collected gas set.

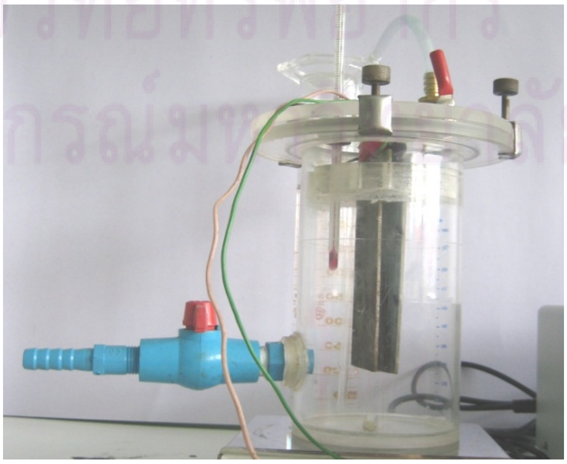


Figure 3.4 Material and reactor

## 3.3 Experiment procedure

### 3.3.1 The one variable at a time method

This experiment divides into 5 steps as shown in Figure 3.5. The experimental steps are the following:

1) Wastewater used in this study was collected from the combined wastewater sump from the wastewater treatment plant. This combined wastewater sump receives wastewater from the plant main processes.
2) Raw wastewater was characterized for pH, temperature, COD, grease & oil (G&O), and suspended solid (SS).
3) The effects of operating parameters on the petrochemical wastewater treatment by electrocoagulation process was studied as follows:
    - The initial pH of wastewater with 3 values, i.e., 4, 6 and 9.
    - The current density with 5 values, i.e., 5.11, 8.42, 9.12, 10.09 and 12.13 mA/cm$^2$.
    - The retention time periods as 10, 15, 20, 25, 30, 40 minutes.
4) The treated wastewater was tested for pH, temperature, COD, G&O and SS. Furthermore, lost weight of the used electrode, current density, type of gas production from reaction, quantity and component of sludge was determined.
5) The results from the experiments were used to evaluate the optimal conditions for the petrochemical wastewater treatment process and to estimate treatment costs such as electricity, electrodes and sludge treatment.

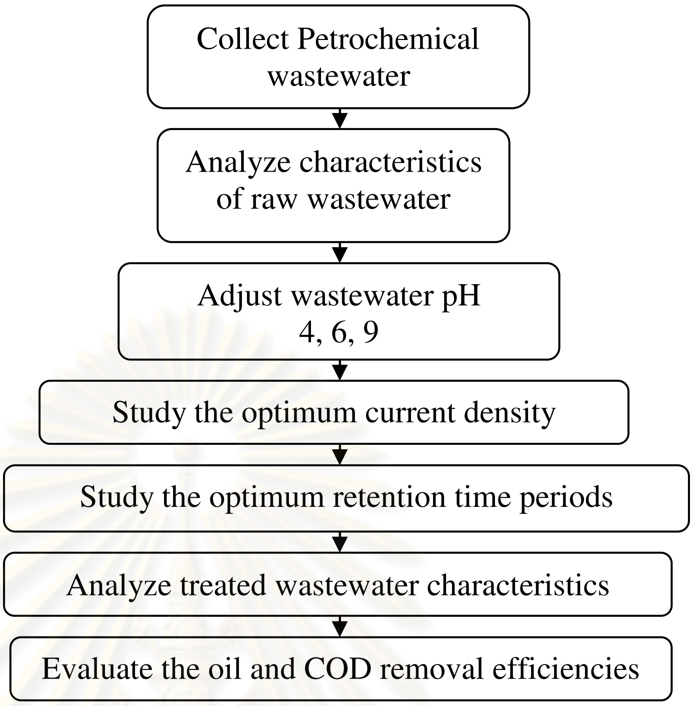


Figure 3.5 Flow chart of the experiment.

**3.3.1.1 Study the optimum pH.** The experiment steps are as followings:

1. Adjust initial pH of wastewater at 4. After that pour 1 liter of wastewater in the electrocoagulation reactor and put it on the stirring plate.
2. Put the Al-C electrodes and connect them in parallel to a DC power supply, then cover the reactor and measure gas production from the reaction, and then turn on the stirrer.
3. Turn on the DC power supply and adjust the current density to 9.12 mA/cm$^2$.
4. Let the reaction in electrocoagulation reactor run for 30 minutes.
5. Collect the gas quantity every 5 minutes.
6. After the experiment is ended, record the final electric current and temperature, then turn off the DC power supply. Let the sludge float for 30 minutes before collecting the treated wastewater sample for parameter analyses as shown in table 3.2.
7. Repeat the steps 1-6, but adjust initial pH to 6 and 9, respectively.
8. Analyze experimental results to evaluate the optimum pH that was used for the next experiment.

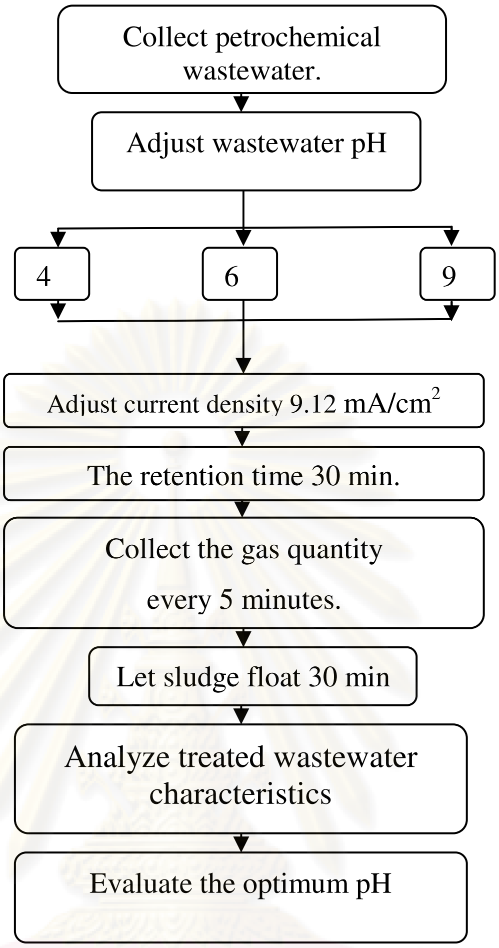


Figure 3.6 Flow chart of the optimum pH experiment.

**3.3.1.2 Study the optimum current density.** The experiment steps was following

1. Adjust initial pH of wastewater at the optimum pH from the first experiment and pour 1 liters of wastewater in electrocoagulation reactor and put it on the stir plate.
2. Put the Al-C electrodes and connect them in parallel to a DC power supply, then cover the reactor and measure gas production from the reaction, and then turn on the stirrer.
3. Turn on the DC power supply, adjust current density to 5.11 mA/cm$^2$.
4. Let the reaction in electrocoagulation reactor for 30 minutes.
5. Collect the gas quantity every 5 minutes.

6. After the experiment is ended, record the final electric current and temperature, then turn off the DC power supply. Let the sludge float for 30 minutes before collecting the treated wastewater sample for parameter analyses as shown in table 3.2.
7. Repeat the steps 1-6, but adjust current density 8.42, 9.12, 10.93 and 12.13 mA/cm$^2$, respectively
8. Analyze experimental results to evaluate the optimum current density that were used for the next experiment.

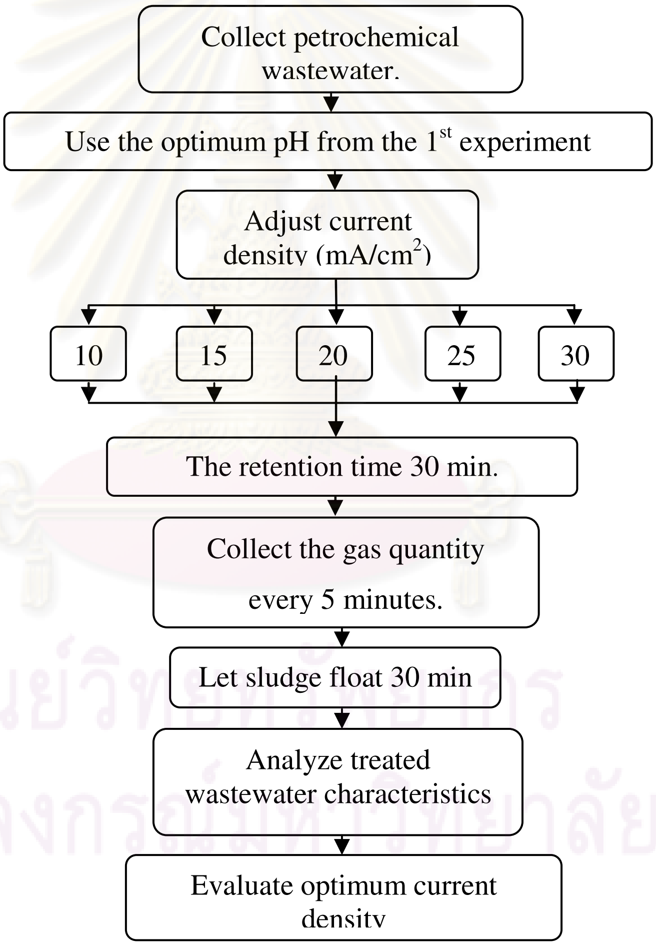


Figure 3.7 Flow chart of the optimum current density experiment

**3.3.1.3 Study the optimum retention time.** The experiment steps was following

1. Adjust initial pH of wastewater at the optimum pH from the first experiment and pour1 liters of wastewater in electrocoagulation reactor and control current density at optimum current density ($2^{nd}$ experiment).
2. Put the Al-C electrodes and connect them in parallel to a DC power supply, then cover the reactor and measure gas production from the reaction, and then turn on the stirrer.
3. Turn on the DC power supply, adjust to current density from the second experiment.
4. Let the reaction in electrocoagulation reactor for 10 minutes.
5. Collect the gas quantity every 5 minutes.
6. After the experiment is ended, record the final electric current and temperature, then turn off the DC power supply. Let the sludge float for 30 minutes before collecting the treated wastewater sample for parameter analyses as shown in table 3.2.
7. Repeat the steps 1-6, but adjust retention time to 15, 20, 25, 30 and 40 minutes, respectively.
8. Analyze experimental results to evaluate the optimum retention time that was used for the next experiment.

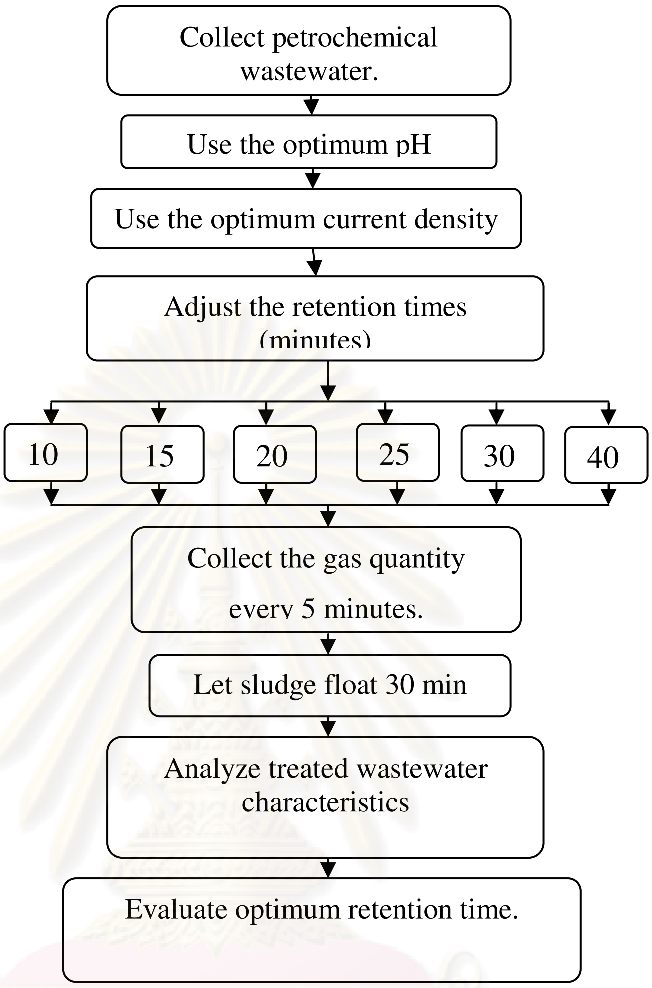


Figure 3.8 Flow chart of the optimum retention time experiment.

### 3.3.2 Box-Behnken design experiment

The Box-Behnken design, an experimental design for RSM, is used to create a set of designed experiments by MINITAB software, version 14. In this experiment study, initial pH, applied voltage and retention time are designated as three main factors. Given the three main variables and three test levels, 15 experiments were designated by MINITAB software as shown in table 3.1.

Table 3.1 Box-Behnken design with three factors by MINITAB software

| Trial | pH | Voltages (Volts) | Retention times (min) |
|---|---|---|---|
| 1 | 9.0 | 10 | 25 |
| 2 | 6.5 | 10 | 40 |
| 3 | 6.5 | 10 | 10 |
| 4 | 9.0 | 30 | 25 |
| 5 | 6.5 | 30 | 10 |
| 6 | 4.0 | 30 | 25 |
| 7 | 6.5 | 20 | 25 |
| 8 | 4.0 | 20 | 40 |
| 9 | 4.0 | 10 | 25 |
| 10 | 9.0 | 20 | 10 |
| 11 | 6.5 | 30 | 40 |
| 12 | 6.5 | 20 | 25 |
| 13 | 6.5 | 20 | 25 |
| 14 | 4.0 | 20 | 10 |
| 15 | 9.0 | 20 | 40 |

**3.3.2.1 The experiment steps for Box-Behnken design by MINITAB software** are shown in figure 3.9 and described as follows:

1. Collect wastewater sample and characterize for pH, temperature, COD, G&O and SS.
2. Perform the experiment as similar to the experiment 3.3.1 with 15 runs. Each experimental run was varying initial pH, voltages and retention times according to table 3.1.

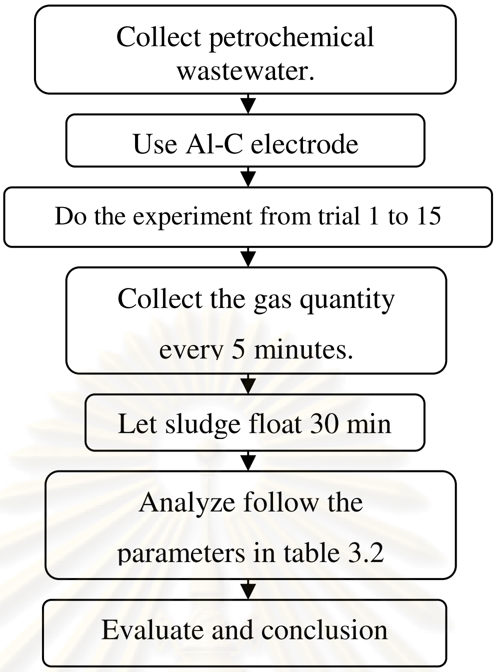


Figure 3.9 Flow chart of the experiment to optimal condition with the Box-Behnken design by MINITAB software.

### **3.4 Cost estimate for petrochemical wastewater treatment** by electrocoagulation process

In this study, cost estimate for the electrocoagulation process includes energy consumption, mass lost of electrodes, treatment chemicals, and sludge treatment. The energy consumption cost is derived as the following:

Energy cost = energy × cost/unit

1. Weight of electrode lost after experiment.
2. Cost of chemicals for adjusting pH.
3. Cost for sludge treatment

Table 3.2 Parameter and evaluate method for wastewater and sludge.

| Parameters | Method | Raw wastewater | Treated wastewater | |
|---|---|---|---|---|
| | | | Always | Optimal condition |
| 1. pH | pH meter | / | / | |
| 2. Temperature | Thermometer | / | / | |
| 3. COD | Close flux method | / | / | |
| 4. Grease & oil (G&O) | Separatory Funnel Extraction | / | / | |
| 5. SS | Suspended Solids Dried on 103-105 $^0$C | / | / | |
| 6. Electrode weight | Top pan balances | / | / | |
| 7. Electric current | DC Power Supply | | / | |
| 8. Gas quantity | Dehydration | | / | |
| 9. Gas component | Gas Chromatography (GC) | | | / |
| 10. Sludge component | Fourier Transform Infrared Spectrometer (FT-IR) | | | / |

# CHAPTER IV

# RESULTS AND DISCUSSION

## 4.1 Characterization of the studied wastewater from the petrochemical plant

Petrochemical wastewater is characterized with high contents of COD and oil at 6,032 mg/L and 132.5 mg/L, respectively. Generally, the petrochemical industry employs Dissolved Air Floatation (DAF) followed by activated sludge process for treatment of the wastewater. However, the oil removal efficiency by DAF is 9.7-57.7 %. Thus, the treated wastewater still contains the high contents of COD & oil.

Table 4.1 Characteristics of the petrochemical wastewater

| Parameter | Value |
|---|---|
| pH | 7.4 |
| Chemical oxygen demand (COD) (mg/L) | 6,032 |
| Grease and oil (G&O) (mg/L) | 132.5 |
| SS (mg/L) | 120 |

## 4.2 The one variable at a time method

### 4.2.1 Effect of initial pH.

The study was conducted by adjusting the initial pH values of the wastewater at 4, 6 and 9. The current density and retention time were set constant at 0.91 mA/cm$^2$ and 30 minutes, respectively. Table 4.2 presents removal efficiencies of COD, SS and G&O.

Table 4.2 Effect of initial pH on removal efficiencies of COD, SS and G&O

| Initial pH | Final pH | % Removal | | | Gas quantity (ml.) | Current density (mA /cm$^2$) | Electrode weight loss (g/m$^3$) | Electrodes cost (Baht/m$^3$) |
|---|---|---|---|---|---|---|---|---|
| | | COD | SS | G&O | | | | |
| 4 | 7.68 | 76.4 | 40.0 | 62.0 | 462.5 | 9.02 | 707.2 | 30.0 |
| 6 | 7.85 | 90.3 | 62.5 | 86.3 | 432.5 | 8.32 | 398.9 | 17.0 |
| 9 | 9.15 | 56.3 | 20.0 | 55.0 | 102.5 | 3.71 | 238.9 | 10.0 |

### 4.2.1.1 Effluent pH

Figure 4.1 shows the effluent pH. The treated wastewater pH increased as the initial pH values increased. The treated wastewater pH increased as the initial pH values increased. In the basic range, aluminum hydroxide ions may form negatively-charged ions such as $Al(OH)_4^-$ and $Al(OH)_2^-$, which allow less effective flocculation. Since hydroxide ions are produced along with $H_2$ bubbles at the cathode, it contributes to an increasing final pH of the treated wastewater.

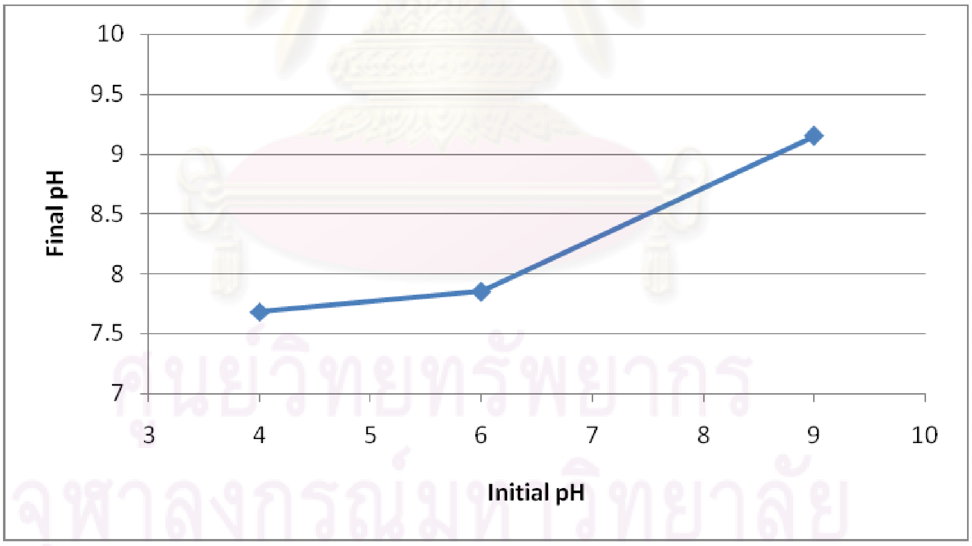


Figure 4.1 The effect of initial pH on final pH

### 4.2.1.2 Removal efficiencies of COD, SS and G&O

The tested wastewater was yellow and contained oil skimming at the surface. It is known that initial pH and current density can influence the coagulant dosage rate and bubble generation rate, which in turn affect the pollutant removal efficiencies. To determine the effect of initial pH on the removal efficiencies of COD, G&O, and SS, the pH of petrochemical wastewater was adjusted with either $H_2SO_4$ or NaOH to 4, 6, and 9. In each batch experiment, the current density and reaction time were kept constant at 9.12 mA/cm$^2$for 30 min. As shown in Figure 4.2, the pollutant removal efficiencies increased as the initial pH decreased to the acidic condition. At the pH value of 6, the highest removal efficiencies were achieved at 90.3% for COD, 86.3% for G&O, and 62.5% for SS.

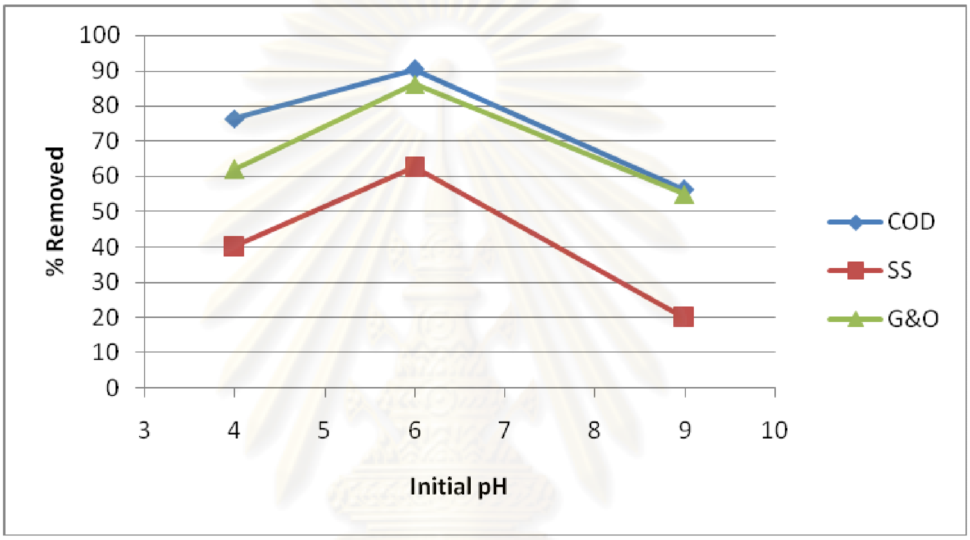


Figure 4.2 The effect of initial pH on removal efficiencies

For removal mechanisms of G&O and SS, Gürses *et al.* (2002) contributed an increasing removal efficiency of colloidal particles in the pH range of 4-7 to the formation of amorphous hydroxide precipitates and other aluminum hydroxo complexes with hydroxide ions and polymeric species. As increasing the pH to 9, the decline of the removal efficiency was observed due to less formation of the reactive flocs of aluminium hydroxide (Tir and Moulai-Mostefa, 2008).

#### 4.2.1.3 Gas Production

The gas production was measured by the water-replacement method. At the acidic condition, the EC process produced approximately 450 ml per liter of wastewater being treated as shown in figure 4.3. The gas production decreased as initial pH increased. The result showed that the initial pH can affect to gas production because pH can effect on ions in the water and affect on oxidation-reduction process. The pH of 4 yielded the highest gas production.

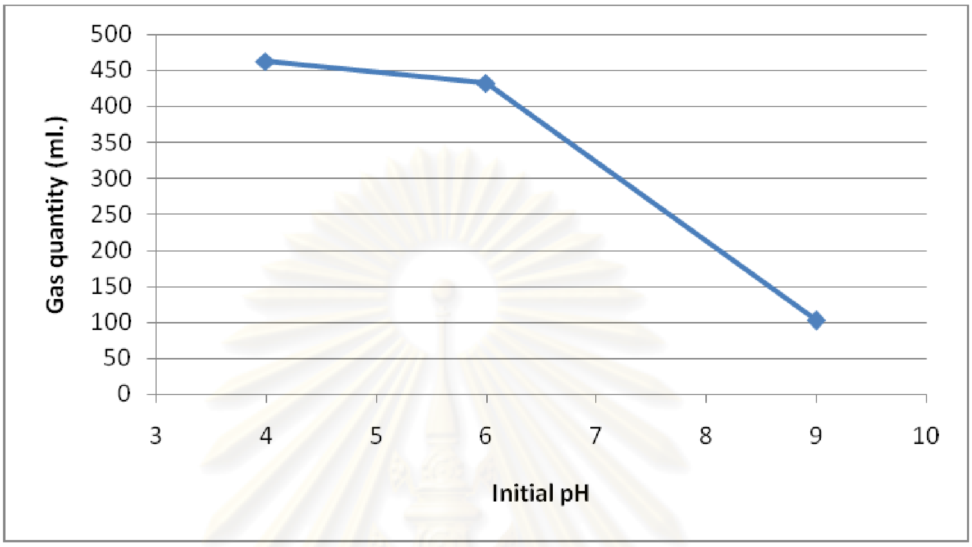


Figure 4.3 The effect of initial pH on gas production

#### 4.2.1.4 Electrode loss

In this study, aluminum and graphite were used as electrodes. The mass loss of an aluminum electrode at the operating pH of 4, 6 and 9 was 707.2, 398.9 and 238.9 g/m$^3$ as shown in Figure 4.4.

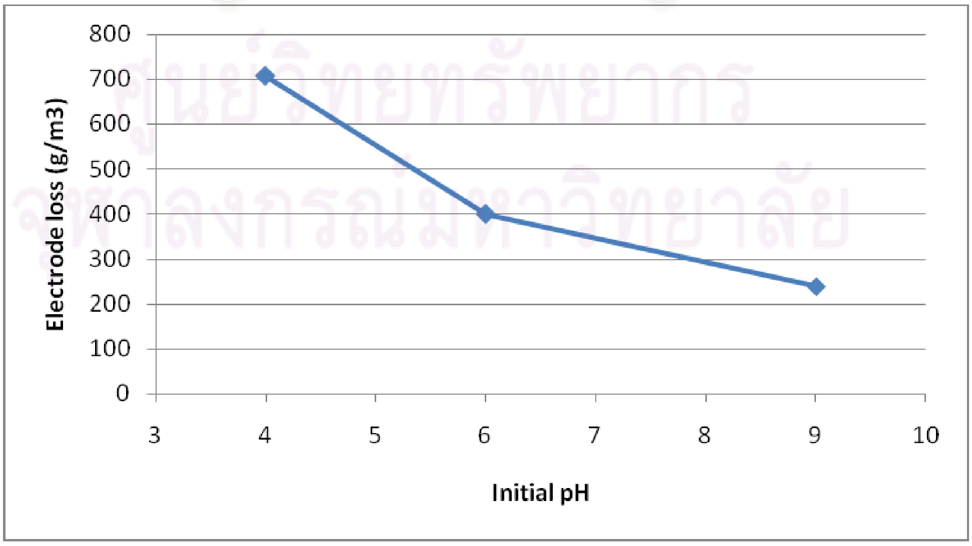


Figure 4.4 The effect of initial pH on electrode loss

#### 4.2.1.5 Summary of the initial pH effect

The result showed that the optimum wastewater pH was 6 when maintaining the current density and retention time of 9.12 mA/cm$^2$ and 30 minutes. The removal efficiencies were 90.26% for COD, 62.5% for SS and 86.25% for oil. The gas production was 432 ml per liter of wastewater being treated. The final pH was 7.85. The mass loss of an aluminum electrode was 398.9 g per cubic of wastewater being treated. The calculated cost of electrode used is 17.0 baht per cubic of wastewater. Additionally, the use of graphite as a cathode benefits less sludge production and relatively neutral pH of the effluent.

### 4.2.2 Effect of current density

The effect of applied voltage on the electrocoagulation cell was investigated by varying the current density from 5.11 to 12.13 mA/cm$^2$. Each experimental trial kept the initial pH at 6 and reaction time of 30 min. Table 4.3 presents removal efficiencies of COD, SS and G&O.

Table 4.3 The effect of current density on removal efficiencies using Al-C as electrodes and initial pH 6

| Current density (mA/cm$^2$) | Final pH | % Removal | | | Gas quantity (ml.) | Electrode weight loss (g/m$^3$) | Electrodes cost (Baht/m$^3$) |
|---|---|---|---|---|---|---|---|
| | | COD | SS | G&O | | | |
| 5.11 | 7.98 | 86.87 | 39.47 | 64.59 | 155.0 | 181.3 | 12.0 |
| 8.42 | 8.00 | 93.30 | 55.26 | 67.21 | 275.0 | 181.7 | 23.0 |
| 9.12 | 8.08 | 97.35 | 57.89 | 73.77 | 432.5 | 360.1 | 24.0 |
| 10.93 | 8.34 | 97.58 | 57.94 | 74.87 | 517.5 | 369.0 | 32.0 |
| 12.13 | 9.10 | 98.90 | 58.47 | 74.98 | 527.5 | 397.0 | 42.0 |

#### 4.2.2.1 Effluent pH

Figure 4.5 shows the effluent pH as varying the current density. The treated wastewater pH increased as the current density increased. According to Faraday’s law, the amount of coagulant or dissolved anodic metal is theoretically and directly proportional to the applied current to an electrolytic cell at a certain time. Thus, the generation rate of hydroxide ion is enhanced as well, resulting in a pH rise. As the current density increased over 9.12 mA/cm$^2$, the final pH rose greater than 8.3. As shown previously, the basic condition is ineffective at removing colloidal particles.

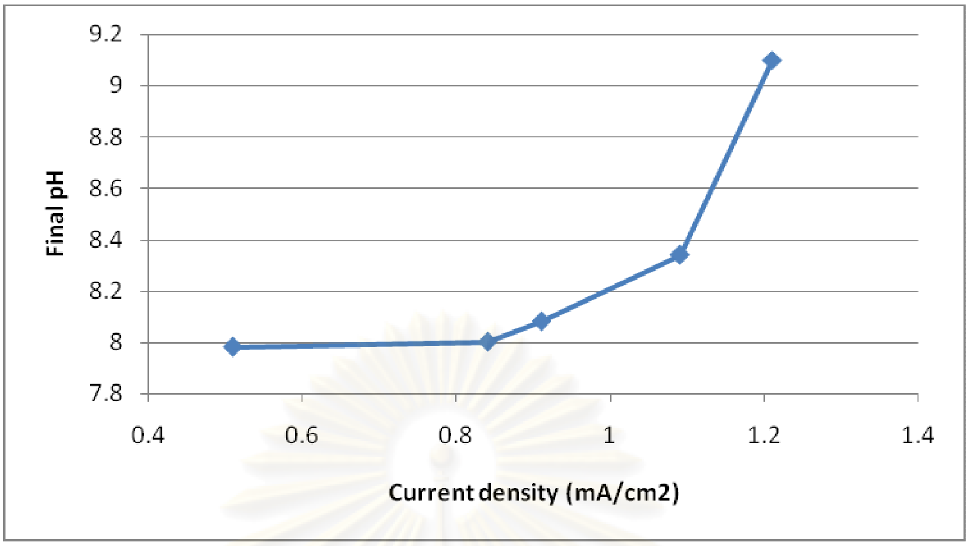


Figure 4.5 The effect of current density on final pH

### 4.2.2.2 Removal efficiencies of COD, SS and Oil

Figure 4.6 shows the variation of the removal efficiencies for COD, G&O and SS as a function of current density. The removal efficiencies of COD, SS and G&O were achieved at 86.87-98.9%, 39.47-58.47% and 64.59-74.98%, respectively. A significant increase of the removal efficiencies is observed as the current density increased from 5.11 to 9.12 mA/cm$^2$. In the voltage range of 9.12 to 12.13 mA/cm$^2$, there is a tendency for a slight increase in the percentage removal. According to Faraday's law, the amount of coagulant or dissolved anodic metal is theoretically and directly proportional to the applied current to an electrolytic cell at a certain time. Thus, increasing current density results in an increasing amount of aluminum hydroxide flocs for the removal of colloidal particles as follows:

At an anode (Oxidation): $Al_{(s)} \longrightarrow Al_{(aq)}^{3+} + 3e^-$ (4-1)

At a cathode (Reduction): $3H_2O + 3e^- \longrightarrow 3/2H_{2\,(g)} + 3OH^-$ (4-2)

In the solution: $Al_{(aq)}^{3+} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+$ (4-3)

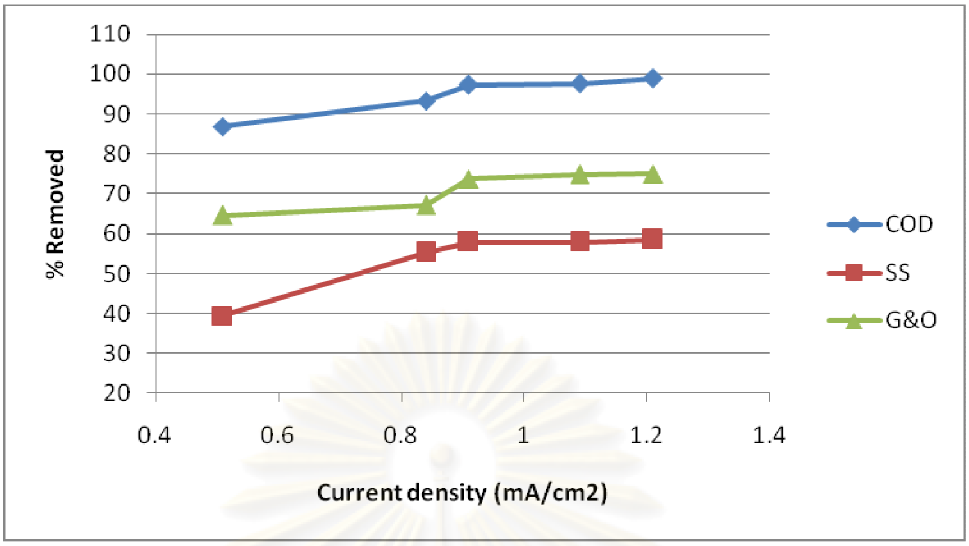


Figure 4.6 Effect of current density on the removal efficiencies for COD, G&O and SS.

### 4.2.2.3 Gas Production

Figure 4.7 shows that the gas production increased as applied voltage increased. The EC process produced approximately 155-527 ml per liter of wastewater. Increasing applied voltage can enhance the redox reaction, which generates more $H_2$ bubble production at the cathode.

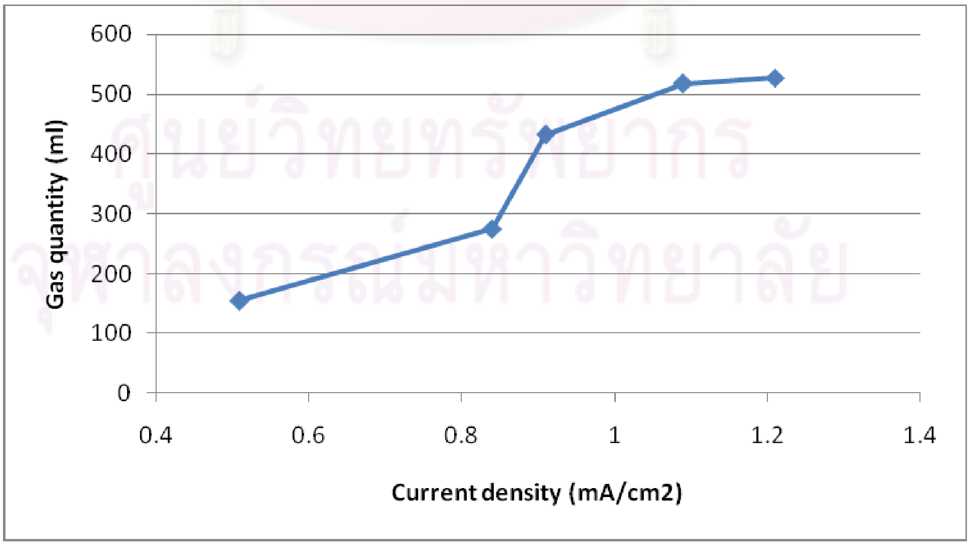


Figure 4.7 The effect of current density on gas production

#### 4.2.2.4 Electrode loss

An increasing loss of the aluminum electrode with increasing the applied voltage causes greater upwards flux. The main effect of increasing voltage is the higher rate of anode dissolution that increases the concentration of aluminum ion in the solution

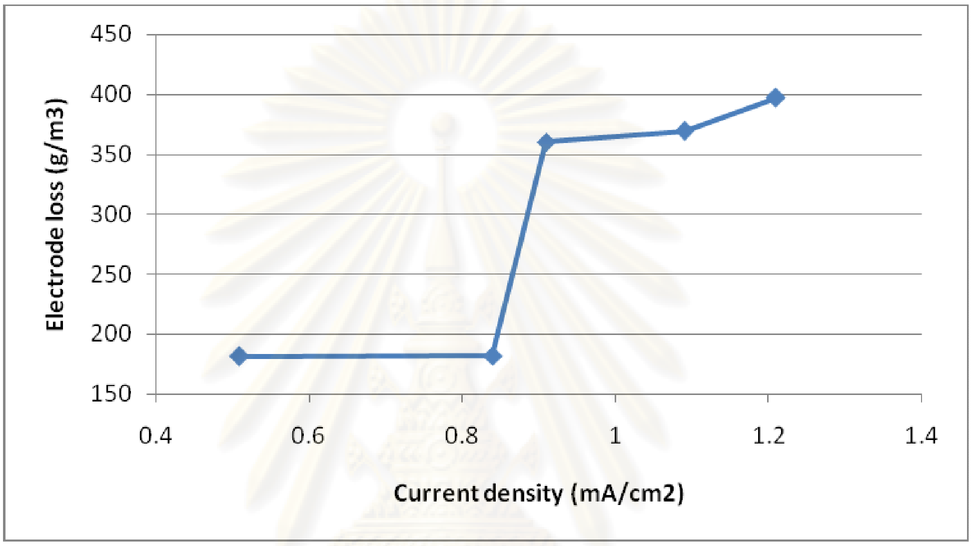


Figure 4.8 The effect of current density on electrode loss

#### 4.2.2.5 Summary of the current density effect

The result showed that the optimum current density was 9.12 mA/cm$^2$when maintaining the initial pH and retention time of 6 and 30 minutes. The removal efficiencies were 97.35% for COD, 57.89% for SS and 73.77% for oil. The gas production was 432 ml per liter of wastewater being treated. The final pH was 8.08. The mass loss of an aluminum electrode was 360.1 g per cubic of wastewater being treated. The calculated cost of electrode used is 24.0 baht per cubic of wastewater.

### 4.2.3 Effect of retention time

Shown in table 4.4 is the effect of reaction time on the pollutant removal efficiencies when the retention time was varied from 10 to 40 min. Each experimental trial kept the initial pH at 6 and current density 9.12 mA/cm$^2$. Table 4.4 presents removal efficiencies of COD, SS and G&O.

Table 4.4 The effect of retention time on removal efficiencies using Al-C as electrodes at pH 6 and 9.12 mA/cm$^2$.

| Retention Time (min) | Final pH | Current density (mA /cm$^2$) | Electrodes loss Weight (g/m$^3$) | % Removal Efficiency | | | Gas quantity (ml) | Electrode cost (Baht/m3) |
|---|---|---|---|---|---|---|---|---|
| | | | | COD | SS | G&O | | |
| 10 | 6.87 | 7.91 | 166.8 | 95.56 | 61.23 | 60.82 | 145 | 9.0 |
| 15 | 7.24 | 8.02 | 181.3 | 96.72 | 69.54 | 61.52 | 210 | 15.0 |
| 20 | 7.54 | 8.02 | 251.3 | 96.91 | 72.69 | 76.97 | 290 | 19.0 |
| 25 | 7.87 | 8.32 | 330.4 | 97.49 | 76.92 | 79.09 | 390 | 23.0 |
| 30 | 8.17 | 8.32 | 331.1 | 97.63 | 77.15 | 79.77 | 433 | 24.0 |
| 40 | 8.29 | 9.12 | 397.1 | 98.48 | 77.54 | 80.97 | 560 | 42.0 |

### 4.2.3.1 Effluent pH

Figure 4.9 shows the effluent pH as varying the retention time. An increasing pH was observed due to the greater formation of hydroxide ion at the cathode.

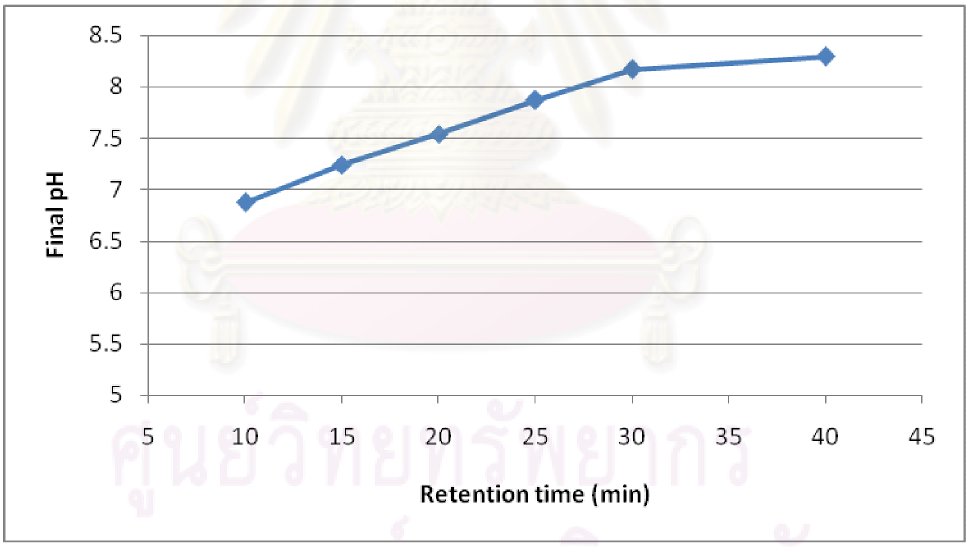


Figure 4.9 The effect of retention time on final pH

### 4.2.3.2 Removal efficiencies of COD, SS and Oil

Figure 4.10 shows that the removal efficiencies were 95.56-98.48% for COD, 61.23-77.54% for SS and 60.82-80.97% for oil. All pollutant removal efficiencies increased with respect to the reaction time. However, the allowed reaction time longer than 25 min did not enhance the removal efficiencies. According to Faraday's law, the amount of coagulant or dissolved anodic metal is theoretically and directly proportional to the applied current to an electrolytic cell at a certain time. This helps to increase the opportunity for mixing and contacting between flocs and particles. These current study results are similar to other EC studies. Xu and Zhu (2002) and Tir and Moulai-Mostefa (2008) indicated that the optimal reaction time for treatment of oily wastewater is approximately 25 min.

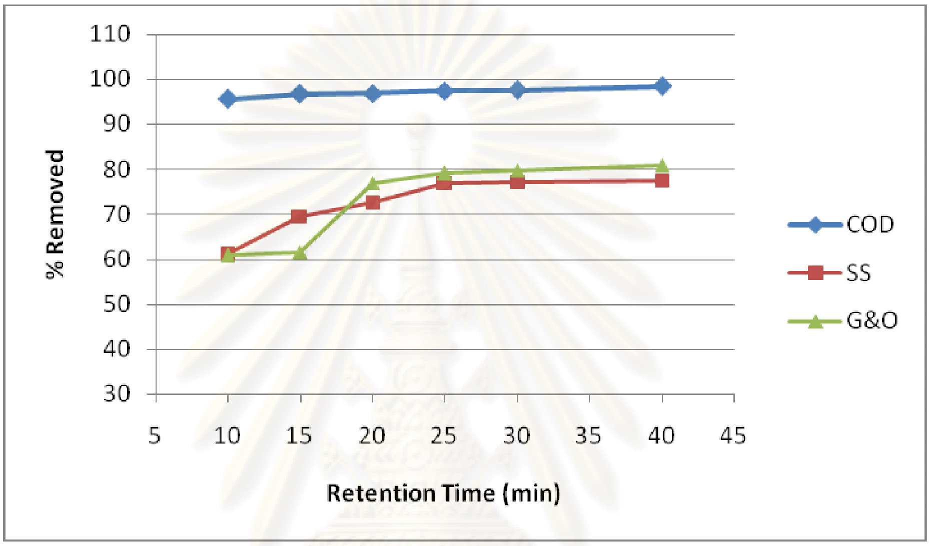


Figure 4.10 The effect of retention time on removal efficiencies

#### 4.2.3.3 Gas Production

Gas production from the EC process was approximately 145-560 ml per liter of wastewater being treated as shown in figure 4.11. The gas production increased as retention time increased because of increasing electrolysis time, which in turn increases the rate of bubble generation.

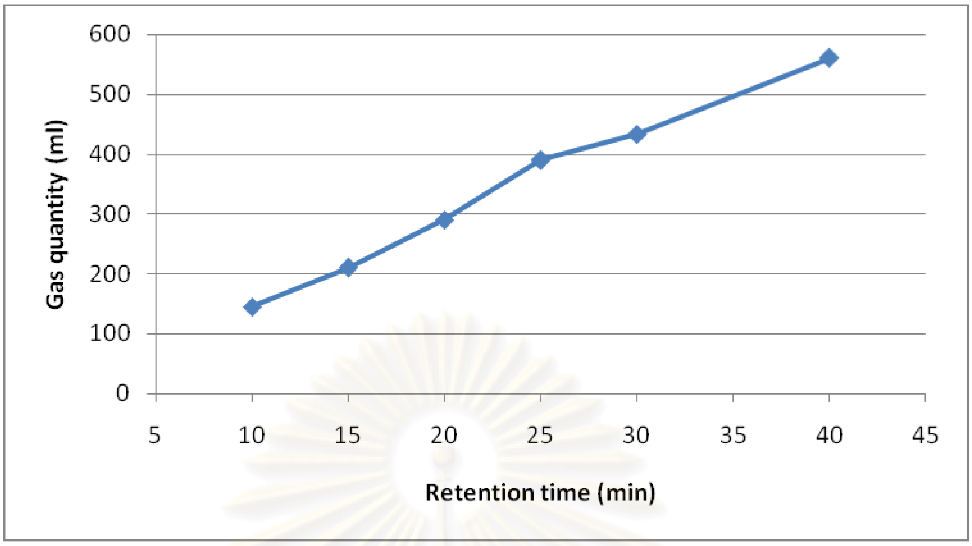


Figure 4.11 The effect of retention time on gas production

### 4.2.3.4 Electrode loss

The mass loss of an aluminum electrode at the operating retention time of 10-40 min was 166.8-397.1 g/L as shown in figure 4.12. According to Faraday's law, the amount of coagulant or dissolved anodic metal is theoretically and directly proportional to the applied current to an electrolytic cell at a certain time. It established that the rate of electrode dissolution increases with prolonging electrolysis time.

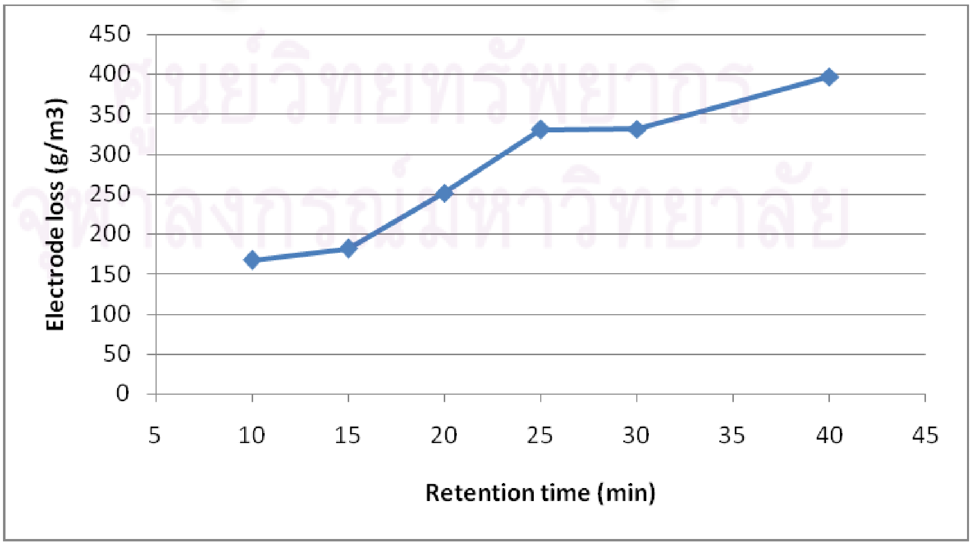


Figure 4.12 The effect of retention time on electrode loss

### 4.2.3.5 Summary of the retention time effect

The result showed that the optimum retention time was 25 minutes when maintaining the initial pH and current density of 6 and 8.32 mA/cm$^2$. The removal efficiencies were 97.49% for COD, 76.92% for SS and 79.09% for G&O. The gas production was 390 ml per liter of wastewater being treated. The final pH was 7.87. The mass loss of an aluminum electrode was 330.4 g per cubic of wastewater being treated. The calculated cost of electrode used is 23.0 baht per cubic of wastewater.

### 4.2.3.6 The summary of the optimum conditions for treatment of petrochemical wastewater by the one variable at a time method.

The results from the study of each variable effect revealed that the optimum conditions can be achieved using an aluminum anode and graphite cathode with the current density 8.32 mA/cm$^2$ at the initial pH value of 6. The removal efficiencies for COD, SS and G&O were 97.49%, 76.92% and 79.09%, respectively. The electrode consumption was 330.4 g/m$^3$ of wastewater. The gas production due to the EC process was 390 ml/L of wastewater. The approximate power requirement was 5.19 kWh/m$^3$ of wastewater. Figures 4.13(a) and (b) shows the characteristics of wet and dried sludge from the EC process. The volume of produced sludge was 54.2 ml/L and the dried sludge was 1.0852 g/L.

(a) (b)

Figure 4.13 Sludge production from the EC reaction

(a) Wet sludge (b) Dried sludge at 100 – 103 °c

Mass balance of the aluminum loss is estimated from with the mass of aluminum in the treated wastewater (0.00453 g), mass in the produced sludge (0.20587 g) and mass loss in other parts as presented below:

Aluminum weight loss (g) = Aluminum (g) (in treated wastewater + in sludge) + other (g).

0.3304 = 0.00453 + 0.20587 + 0.12

0.3304 = 0.3304

The mass of aluminum loss in other parts could be due to digestion process of the sludge. The digestion might not be able to convert aluminum hydroxide containing in the sludge to aluminum, which is a detectable form. Moreover, the aluminum loss could occur during the electrode cleaning process for dirt removal. These mechanisms could cause less mass of aluminum in the treated water and sludge than the actual loss weight.

Since the large amount of aluminum was found in the produced sludge, the pollutant removal mechanism could be due to sweep coagulation of the pollutants. Large flocs are created and used for adsorption of soluble organic compounds and for trapping of colloidal particles. Consequently, these flocs can be removed by floatation with $H_2$ bubbles.

Table 4.5 Summary of the optimum conditions for treatment of petrochemical wastewater by the one variable at a time method

| Parameter | Raw wastewater | Treated wastewater |
|---|---|---|
| COD (mg/L) | 6,032 | 151.00 |
| Grease & Oil (mg/L) | 132.50 | 27.71 |
| SS (mg/L) | 120.00 | 27.70 |
| Conductivity (µS/cm) | 350.00 | 405.00 |
| pH | 7.40 | 7.24 |

Table 4.6 Summary of cost for the optimum conditions for treatment of petrochemical wastewater by the one variable at a time method

| Parameter | Raw wastewater | Treated wastewater |
|---|---|---|
| Electrode cost (Baht/m$^3$) | - | 23.00 |
| Power Requirement (kWh/m$^3$) | - | 5.19 |
| Electric cost (Baht/ m$^3$) | - | 10.02 |
| Chemical cost (Baht/m$^3$) | - | 11.00 |

"-" denotes no detection

Table 4.5 shows that the EC process can remove COD, G&O and SS by 97.49%, 79.09%, and 76.92%, respectively. The result indicates that EC procee can be an effective method for primary treatment of petrochemical production wastewater. The reduced amount of the pollutants can reduce the pollutant loadings to a following biological treatment process.

## 4.3 Experimental design

### 4.3.1 Box-Behnken design experiment

The Box-Behnken design, an experimental design for RSM, was used to create a set of designed experiments by MINITAB software, version 14. In this study, the Box-Behnken design for 3 factors, i.e., initial pH ($x_1$), applied voltage ($x_2$), and reaction time ($x_3$), involved three blocks as shown in table 4.6. In each of the three blocks, two factors were varied through the 4 possible combinations of high and low. The values of the original variables were selected based on the preliminary experimental results. Given the three main variables and three test levels, 15 experiments were designated by MINITAB software as shown in table 4.7. The removal efficiencies for COD, SS and G&O were obtained from the one factor at a time experiment.

Table 4.7 Original and coded factors

| Factor | Original factor ($x$) | Coded factor ($X$) | | |
|---|---|---|---|---|
| | | -1 | 0 | 1 |
| Initial pH | $x1$ | 4 | 6.5 | 9 |
| Applied voltage (V) | $x2$ | 10 | 20 | 30 |
| Reaction time (min) | $x3$ | 10 | 25 | 40 |

Table 4.8 The removal efficiencies of COD, SS and G&O from the experiments designated by Box-Behnken

| Trial | Initial pH | Applied voltage (Volts) | Current density (mA/cm$^2$) | Retention time (min) | Removal efficiency (%) | | |
|---|---|---|---|---|---|---|---|
| | | | | | COD | SS | G&O |
| 1 | 9.0 | 10 | 1.20 | 25 | 62.03 | 41.55 | 39.63 |
| 2 | 6.5 | 10 | 3.21 | 40 | 91.82 | 78.30 | 88.26 |
| 3 | 6.5 | 10 | 3.30 | 10 | 80.32 | 41.36 | 59.80 |
| 4 | 9.0 | 30 | 7.51 | 25 | 74.46 | 51.36 | 49.08 |
| 5 | 6.5 | 30 | 9.32 | 10 | 93.65 | 72.05 | 80.03 |
| 6 | 4.0 | 30 | 11.82 | 25 | 92.29 | 75.63 | 75.85 |
| 7 | 6.5 | 20 | 8.42 | 25 | 95.73 | 77.16 | 87.67 |
| 8 | 4.0 | 20 | 8.62 | 40 | 94.20 | 76.88 | 76.01 |
| 9 | 4.0 | 10 | 5.11 | 25 | 84.81 | 63.75 | 63.64 |
| 10 | 9.0 | 20 | 1.90 | 10 | 76.66 | 69.38 | 55.91 |
| 11 | 6.5 | 30 | 9.42 | 40 | 97.81 | 78.86 | 88.92 |
| 12 | 6.5 | 20 | 8.22 | 25 | 95.21 | 78.30 | 88.26 |
| 13 | 6.5 | 20 | 8.52 | 25 | 95.21 | 78.30 | 88.34 |
| 14 | 4.0 | 20 | 8.32 | 10 | 86.66 | 59.38 | 55.91 |
| 15 | 9.0 | 20 | 3.91 | 40 | 71.15 | 49.09 | 47.31 |

### 4.3.2 Optimization of operating conditions

Response surface method was applied to evaluate and determine the optimum operating conditions. To develop a response surface model, various types of regression models were tested with the experimental observations of the removal efficiencies obtained from the one factor at a time experiment. The tested regression models included linear, linear and square, linear and interaction, and full quadratic models. Table 4.9 presents Standard Error (SE) and Coefficient of Determination (R$^2$) obtained from the four types of the regression models using MINITAB program.

Table 4.9 Standard Error: SE and Coefficient of Determination: $R^2$

| Parameter | Type of Model | $R^2$ (%) | $R^2$ (adj) (%) | SE |
|---|---|---|---|---|
| 1.COD | Linear | 63.2 | 53.1 | 5.557 |
| | Linear + Square | 96.3 | 93.5 | 2.065 |
| | Linear + Interaction | 66.7 | 41.7 | 6.197 |
| | Full Quadratic | 98.1 | 94.8 | 0.580 |
| 2. SS | Linear | 69.4 | 61.0 | 15.790 |
| | Linear + Square | 94.6 | 90.5 | 7.804 |
| | Linear + Interaction | 74.7 | 55.7 | 16.820 |
| | Full Quadratic | 86.0 | 84.5 | 1.451 |
| 3. G&O | Linear | 69.1 | 60.6 | 16.410 |
| | Linear + Square | 94.7 | 90.7 | 7.979 |
| | Linear + Interaction | 74.2 | 54.8 | 17.590 |
| | Full Quadratic | 96.6 | 90.5 | 2.114 |

It can be seen that a full quadratic model provided the lowest values of SE for removals of COD (0.5804), SS (1.451) and G&O (2.114) with $R^2$ of 94.8%, 84.5% and 90.5%, respectively. Thus, a full quadratic model is used to optimize the operating conditions of the EC process.

### 4.3.3 Analysis of regression coefficients ($\beta_i$)

#### 4.3.3.1 Regression coefficients

The full quadratic model used in the response ($Y_i$) was described as the following:

$$Y_i = \beta_0 + \sum_{i=1}^{4} \beta_i X_i + \sum_{i=1}^{4} \beta_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{4} \beta_{ij} X_{ij} \qquad (\ldots.)$$

$Y_1$, $Y_2$, $Y_3$ = Removal efficiencies of COD, SS, G&O

$X_1$, $X_2$, $X_3$ = Dependent variables, i.e., initial pH, applied voltage, retention time

$\beta_0, \beta_i,, \beta_{ii}, \beta_{ij}$ = regression coefficients for intercept, linear, square, interaction terms

To develop a response surface regression model, a full quadratic model was applied to experimental observations of the removal efficiencies. Calibrating with the experimental results derived from the one factor at a time experiments, the four regression coefficients can be derived as shown in table 4.10.

Table 4.10 Regression coefficients ($\beta_i$) of the full quadratic model

| Parameter | Term | Coef | StDev | *t* | *p* |
|---|---|---|---|---|---|
| 1.COD | Constant | -12.4146 | 14.1910 | -0.8750 | 0.008 |
| | pH (A) | 24.2491 | 2.9916 | 8.1060 | 0.000 |
| | Volt (B) | 2.1251 | 0.6470 | 3.2840 | 0.001 |
| | Time(C) | 1.0368 | 0.3980 | 2.6050 | 0.000 |
| | pH*pH ($A^2$) | -2.0575 | 0.2060 | -9.9900 | 0.000 |
| | Volt*Volt ($B^2$) | -0.0413 | 0.0129 | -3.2060 | 0.001 |
| | Time*Time ($C^2$) | -0.0016 | 0.0057 | -0.2770 | 0.000 |
| | pH*Volt (A*B) | 0.0495 | 0.0495 | 1.0010 | 0.001 |
| | pH*Time (A*C) | -0.0870 | 0.0330 | -2.6380 | 0.468 |
| | Volt*Time (B*C) | -0.0122 | 0.0082 | -1.4840 | 0.001 |
| 2. SS | Constant | -110.4290 | 50.4000 | -2.1910 | 0.040 |
| | pH (A) | 28.2590 | 10.6200 | 2.6600 | 0.000 |
| | Volt (B) | 5.2290 | 2.2980 | 2.2760 | 0.012 |
| | Time(C) | 3.5020 | 1.4130 | 2.4780 | 0.016 |
| | pH*pH ($A^2$) | -1.9050 | 0.7320 | -2.6040 | 0.000 |
| | Volt*Volt ($B^2$) | -0.0790 | 0.0460 | -1.7380 | 0.003 |
| | Time*Time ($C^2$) | -0.0100 | 0.0200 | -0.5100 | 0.031 |
| | pH*Volt (A*B) | -0.0210 | 0.1760 | -0.1180 | 0.000 |
| | pH*Time (A*C) | -0.2520 | 0.1170 | -2.1510 | 0.004 |
| | Volt*Time (B*C) | -0.0500 | 0.0290 | -1.7150 | 0.047 |
| 3. G&O | Constant | -162.9870 | 30.8762 | -5.2790 | 0.003 |
| | pH (A) | 54.9290 | 6.5090 | 8.4390 | 0.005 |
| | Volt (B) | 3.6410 | 1.4078 | 2.5860 | 0.049 |
| | Time(C) | 3.0920 | 0.8659 | 3.5710 | 0.040 |
| | pH*pH ($A^2$) | -4.1210 | 0.4481 | -9.1950 | 0.000 |
| | Volt*Volt ($B^2$) | -0.0530 | 0.0280 | -1.8870 | 0.001 |
| | Time*Time ($C^2$) | -0.0160 | 0.0124 | -1.2680 | 0.000 |
| | pH*Volt (A*B) | -0.0280 | 0.1076 | -0.2560 | 0.007 |
| | pH*Time (A*C) | -0.1910 | 0.0718 | -2.6660 | 0.054 |
| | Volt*Time (B*C) | -0.0330 | 0.0179 | -1.8180 | 0.000 |

Note: 1) COD S = 0.5804 R-Sq = 98.1% R-Sq(adj) = 94.8%

2) SS S = 1.4510 R-Sq = 86.0% R-Sq(adj) = 84.5%

3) G&O S = 2.1140 R-Sq = 96.6% R-Sq(adj) = 90.5%

S is standard error

Coef is regression coefficient ($\beta_i$) of variable

StDev is Standard Deviation

*t* and *p* are test value for significance of hypothesis

Therefore, the full quadratic models describing the removal efficiencies of COD, SS, G&O as functions of initial pH, applied voltage and retention time can be derived as the following equations:

$$\begin{aligned}\text{\% Removed COD} = {} & -12.4146 + 24.2491A + 2.1251B + 1.0368C - \\ & 2.0575A^2 - 0.0413B^2 - 0.0016C^2 + 0.0495AB - \\ & 0.0870AC - 0.0122BC\end{aligned}$$

$$\begin{aligned}\text{\% Removed SS} = {} & -110.4290 + 28.2590A + 5.2290B + 3.5020C - 1.9050A^2 - \\ & 0.0790B^2 - 0.0100C^2 - 0.0210AB - 0.2520AC - 0.0500BC\end{aligned}$$

$$\begin{aligned}\text{\% Removed G\&O} = {} & -162.9870 + 54.9290A + 3.6410B + 3.0920C - 4.1210A^2 \\ & -0.0530B^2 - 0.0160C^2 - 0.0280AB - 0.1910AC - 0.0330BC\end{aligned}$$

Where,

A = Initial pH
B = Applied voltage (Volt)
C = Retention time (min)

#### 4.3.3.2 Test for significance of regression coefficients

The regression coefficients were tested for significance. The relationship between each dependent variable and response variable was determined with a hypothesis of regression as describe below:

$H_0: \beta_1, \beta_2, \ldots, \beta_k = 0$ $X_i$ cannot affect on independent variable.

$H_1: \beta_1, \beta_2, \ldots, \beta_k \neq 0$ $X_i$ can affect on independent variable.

Test values for significance of hypotheses are *t* and *p*-values. If $t_0$ (from table 4.7) is greater than $t_{\alpha/2,n-k-1}$ (n = number of experiments and k = number of model coefficients) at a level of significant α, then H$_0$ is rejected. Moreover, if *p*-

*value* is less than a level of significant, then $H_0$ is rejected. The *p-value* calculated from MINITAB program with respect to each regression term is shown in table 4.10

Table 4.11 *p-value* of the full quadratic model

| Parameter | Term | *p* |
|---|---|---|
| 1. COD | Linear | 0.002 |
| | Square | 0.001 |
| | Interaction | 0.001 |
| 2.SS | Linear | 0.002 |
| | Square | 0.000 |
| | Interaction | 0.001 |
| 3.G&O | Linear | 0.004 |
| | Square | 0.002 |
| | Interaction | 0.001 |

To verify the models, the set of experiments shown in table 4.11 were conducted for 15 runs. The result shows that there was no observable difference in modeled and experimental values. Moreover, the $R^2$ values of a linear trend line between modeled and experimental values are greater than 0.996 (figures 4.16-4.18)

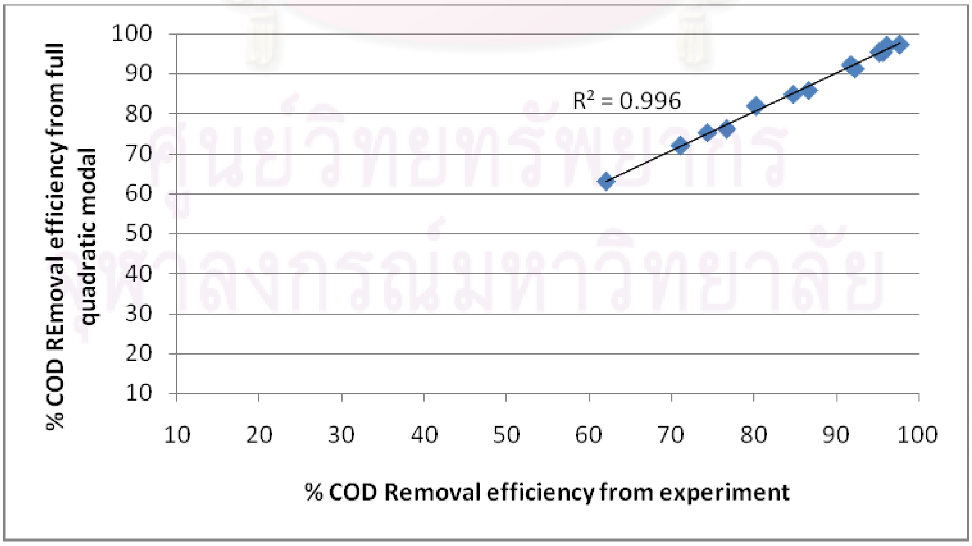


Figure 4.14 Relationship between modeled and experiment values of COD removal efficiency

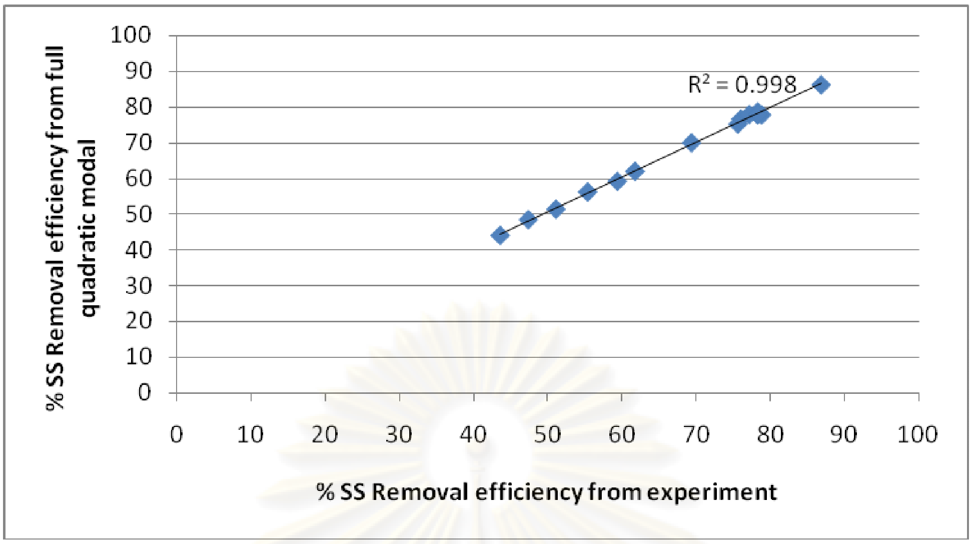


Figure 4.15 Relationship between modeled and experiment values of SS removal efficiency

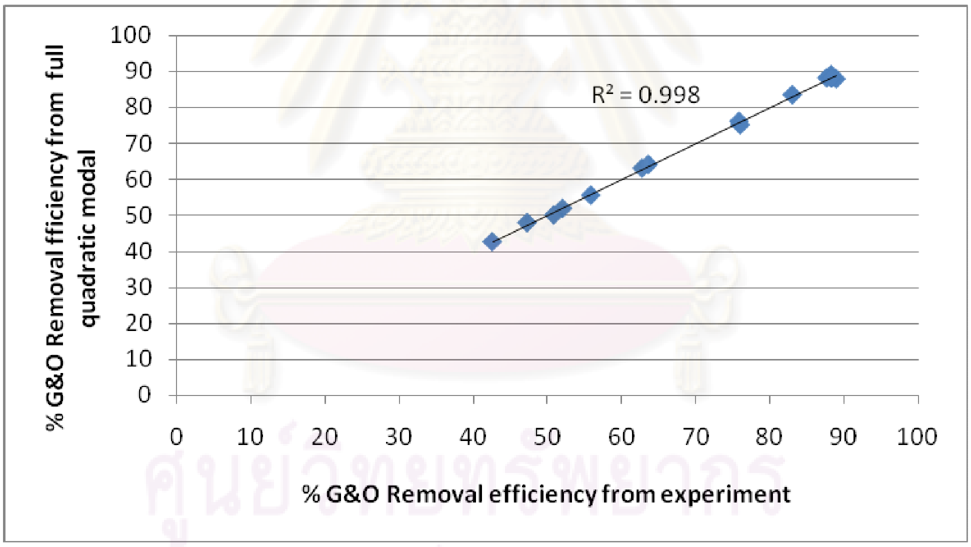


Figure 4.16 Relationship between modeled and experiment values of G&O removal efficiency

### 4.3.4 Effect of regression terms on removal efficiencies

#### 4.3.4.1 Effect on COD removal

As shown in table 4.10, the linear terms of A, B and C for the model describing COD removal efficiency have *p-value* less than 0.05. This means the relationship between the COD removal and dependent variables A, B and C is significant at 95% confidence interval. At the same time, *p-value* of the linear term presented in table 4.11 is found to be 0.002, meaning that the dependent variables A, B and C are able to predict the COD removal efficiency.

As shown in table 4.10, the square terms of $A^2$, $B^2$ and $C^2$ for the model describing COD removal efficiency have *p-value* less than 0.05. This means the relationship between the COD removal and dependent variables A, B and C is significant at 95% confidence interval. At the same time, *p-value* of the linear term presented in table 4.11 is found to be 0.001, meaning that the dependent variables $A^2$, $B^2$ and $C^2$ are able to predict the COD removal efficiency.

Finally, as shown in table 4.10, the interaction terms of AB and BC for the model describing COD removal efficiency have *p-value* less than 0.05. This means the relationship between the COD removal and dependent variables AB, AC and BC is significant at 95% confidence interval. At the same time, *p-value* of the linear term presented in table 4.11 is found to be 0.001, meaning that the dependent variables AB and BC are able to predict the COD removal efficiency.

#### 4.3.4.2 Effect on SS removal

As shown in table 4.10, the linear terms of A, B and C for the model describing SS removal efficiency have *p-value* less than 0.05. This means the relationship between the SS removal and dependent variables A, B and C is significant at 95% confidence interval. At the same time, *p-value* of the linear term presented in table 4.11 is found to be 0.002, meaning that the dependent variables A, B and C are able to predict the SS removal efficiency.

As shown in table 4.10, the square terms of $A^2$, $B^2$ and $C^2$ for the model describing SS removal efficiency have *p-value* less than 0.05. This means the relationship between the SS removal and dependent variables A, B and C is significant at 95% confidence interval. At the same time, *p-value* of the linear term presented in table 4.11 is found to be 0.000, meaning that the dependent variables $A^2$, $B^2$ and $C^2$ are able to predict the SS removal efficiency.

Finally, as shown in table 4.10, the interaction terms of AB, AC and BC for the model describing SS removal efficiency have *p-value* less than 0.05. This means the relationship between the SS removal and dependent variables AB, AC and BC is significant at 95% confidence interval. At the same time, *p-value* of the linear term presented in table 4.11 is found to be 0.001, meaning that the dependent variables AB, AC and BC are able to predict the SS removal efficiency.

#### 4.3.4.3 Effect on G&O removal

As shown in table 4.10, the linear terms of A, B and C for the model describing G&O removal efficiency have *p-value* less than 0.05. This means the relationship between the G&O removal and dependent variables A, B and C is significant at 95% confidence interval. At the same time, *p-value* of the linear term presented in table 4.11 is found to be 0.004, meaning that the dependent variables A, B and C are able to predict the G&O removal efficiency.

As shown in table 4.10, the square terms of $A^2$, $B^2$ and $C^2$ for the model describing G&O removal efficiency have *p-value* less than 0.05. This means the relationship between the G&O removal and dependent variables A, B and C is significant at 95% confidence interval. At the same time, *p-value* of the linear term presented in table 4.11 is found to be 0.002, meaning that the dependent variables $A^2$, $B^2$ and $C^2$ are able to predict the G&O removal efficiency.

Finally, as shown in table 4.10, the interaction terms of AB and BC for the model describing G&O removal efficiency have *p-value* less than 0.05. This means the relationship between the G&O removal and dependent variables AB, AC and BC is significant at 95% confidence interval. At the same time, *p-value* of the linear term presented in table 4.11 is found to be 0.001, meaning that the dependent variables AB and BC are able to predict the G&O removal efficiency.

### 4.3.5 Optimum operating conditions

Optimum operating conditions of the EC process for petrochemical wastewater treatment were determined by optimization technique with MINITAB program. Optimizing conditions for the independent variables were designated as follows:

a) Upper Limit

Upper limit is designed as the highest of removal efficiencies of COD, SS and G&O for 98%, 79% and 89%, respectively.

b) Target

This study was aimed to determine the optimum operating conditions that provided low treatment cost. Thus, the target removal efficiencies of COD, SS and G&O were designed as 95%, 78% and 88%, respectively.

c) Lower Limit

Lower limit is designed as the lowest of removal efficiencies of COD, SS and G&O for 62%, 41% and 40%, respectively.

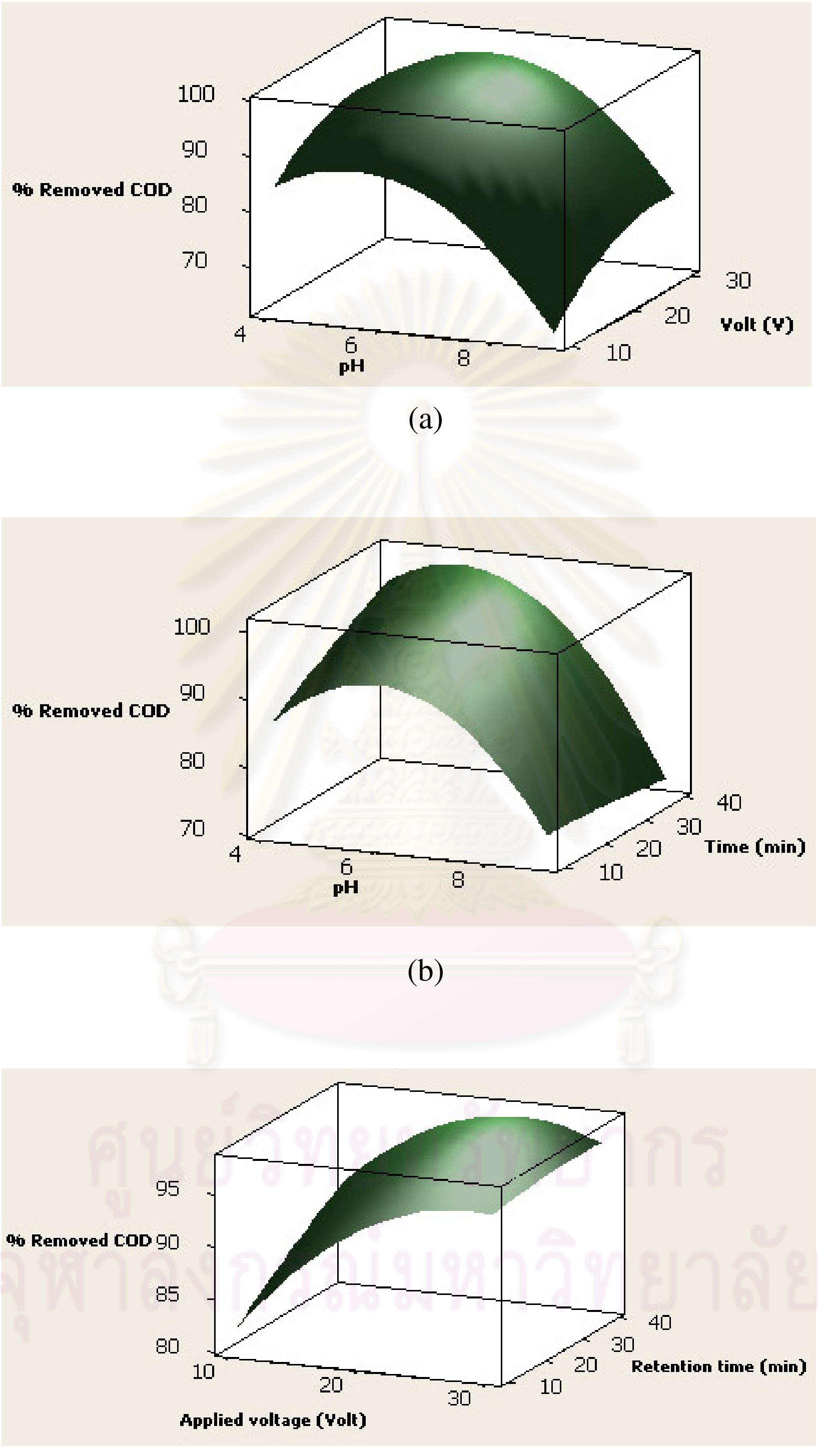
d) Weight

The degree to fix form of desirability functions in this study is 1.

With the above optimizing conditions, the calculated optimum operating conditions are initial pH of 6.73, voltage of 20.58 volt and retention time of 27.40 minutes.

### 4.3.6 3D response surface plots for the effect of each variable

Figures 4.13-4.15 show the response surface plots for the variations of COD, G&O and SS removal efficiencies according to the three independent factors, i.e., initial pH, voltage and reaction time. In each plot, two variables are varied, while the rest is kept constant. The plots are derived from the full quadratic models.

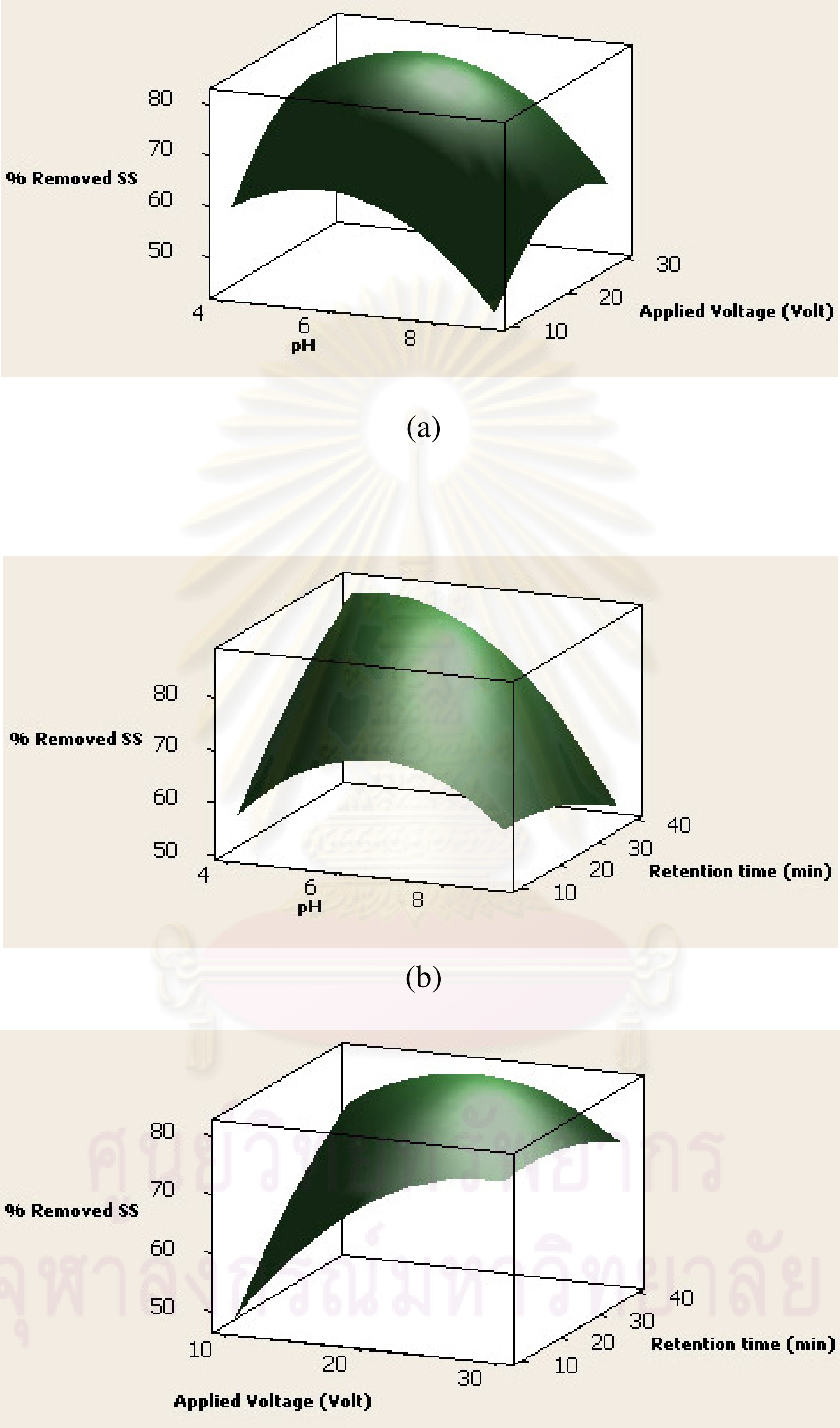


(a)

(b)

(c)

Figure 4.17 Effects of pH, voltage, and reaction time on COD removal: 3D response surface plots. (a) The reaction time was kept constant at 25 min, (b) the applied voltage was kept constant at 20 V, and (c) the initial pH was kept constant at 6.5.

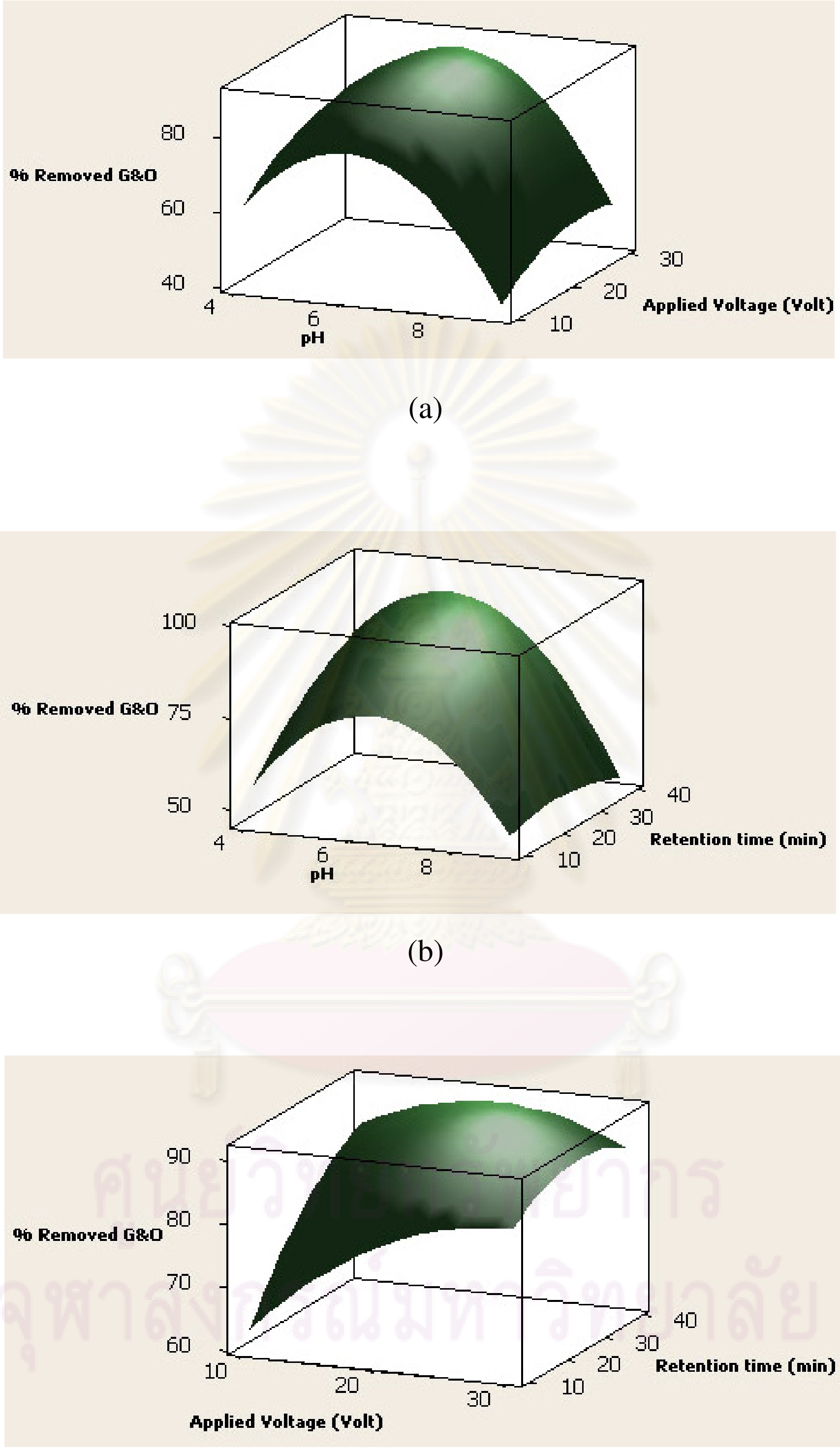


(a)

(b)

(c)

Figure 4.18 Effects of pH, voltage, and reaction time on SS removal: 3D response surface plots. (a) The reaction time was kept constant at 25 min, (b) the applied voltage was kept constant at 20 V, and (c) the initial pH was kept constant at 6.5.



(c)

Figure 4.19 Effects of pH, voltage, and reaction time on G&O removal: 3D response surface plots. (a) The reaction time was kept constant at 25 min, (b) the applied voltage was kept constant at 20 V, and (c) the initial pH was kept constant at 6.5.

It is obviously seen that the effects of pH, voltage and reaction time on the percentage removals of COD, G&O, and SS exhibit the same tendency. The surface response plots offer the maximum removal efficiencies of 94.8% for COD, 87% for G&O, and 77.8% for SS at the optimum conditions for pH of 6.73, applied voltage of 20.58 V, and reaction time of 27.40 min.

Table 4.12 Comparison of removal efficiencies between modeled and experimental values from Box-Behnken design experiment

| Trial | pH (A) | Applied voltage (B) | Time (C) (min) | % COD Removal efficiency | | % SS Removal efficiency | | % G&O Removal efficiency | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | X | Y | X | Y | X | Y |
| 1 | 9.0 | 10 | 25 | 62.03 | 63.04 | 43.55 | 43.94 | 42.63 | 42.48 |
| 2 | 6.5 | 10 | 40 | 91.82 | 92.04 | 78.30 | 78.67 | 88.26 | 88.93 |
| 3 | 6.5 | 10 | 10 | 80.32 | 81.95 | 47.36 | 48.37 | 62.80 | 62.93 |
| 4 | 9.0 | 30 | 25 | 74.46 | 75.33 | 55.36 | 56.14 | 52.08 | 51.74 |
| 5 | 6.5 | 30 | 10 | 95.65 | 95.42 | 76.05 | 76.67 | 83.03 | 83.35 |
| 6 | 4.0 | 30 | 25 | 92.29 | 91.27 | 75.63 | 75.24 | 75.85 | 75.99 |
| 7 | 6.5 | 20 | 25 | 95.73 | 95.38 | 77.16 | 77.92 | 87.67 | 88.09 |
| 8 | 4.0 | 20 | 40 | 96.20 | 96.84 | 86.88 | 86.28 | 76.01 | 75.00 |
| 9 | 4.0 | 10 | 25 | 84.81 | 84.93 | 61.75 | 61.97 | 63.64 | 63.97 |
| 10 | 9.0 | 20 | 10 | 76.66 | 76.01 | 69.38 | 69.97 | 50.91 | 49.91 |
| 11 | 6.5 | 30 | 40 | 97.81 | 97.18 | 78.86 | 77.84 | 88.92 | 87.78 |
| 12 | 6.5 | 20 | 25 | 95.21 | 95.38 | 78.30 | 77.92 | 88.26 | 88.09 |
| 13 | 6.5 | 20 | 25 | 95.21 | 95.38 | 78.30 | 77.92 | 88.34 | 88.09 |
| 14 | 4.0 | 20 | 10 | 86.66 | 85.90 | 59.38 | 59.14 | 55.91 | 55.43 |
| 15 | 9.0 | 20 | 40 | 71.15 | 71.90 | 51.09 | 51.32 | 47.31 | 47.78 |
| Optimal condition | 6.73 | 20.58 | 27.40 | 94.80 | 95.00 | 77.80 | 78.00 | 87.00 | 88.00 |

Note: X = experimental value Y = model value

### 4.3.7 Result comparison between one variable at a time method and Box-Behnken design optimiztion

According to Section 4.4.5, the optimum operating conditions obtained from Box-Behnken design optimization are initial pH of 6.73, voltage of 20.58 volt (current density 8.22 mA/cm$^2$) and retention time of 27.40 minutes. As compared with the results obtained from the one factor at a time method, the optimum conditions are pH of 6.00, current density 8.32 mA/cm$^2$ and retention time of 25.00 minutes. This implies that the full quadratic regression models reasonably optimize the operating conditions and predict the EC process efficiency for the petrochemical wastewater treatment.

Table 4.13 Comparison of optimum conditions and removal efficiencies obtained from the one factor at a time experiments and the Box-Behnken design optimization.

| Parameter | One variable at a time method | Box-Behnken design optimization |
|---|---|---|
| 1. Optimal conditions<br>• pH<br>• Applied voltage (Volt)<br>• Current density (mA/cm$^2$)<br>• Retention time (min) | <br>6.00<br>20.00<br>8.32<br>25.00 | <br>6.73<br>20.58<br>8.22<br>27.40 |
| 2. pH | 7.24 | 7.23 |
| 3. Conductivity (µS/cm) | 405.00 | 400.00 |
| 4. % COD Removal efficiency | 97.49 | 94.80 |
| 5. % SS Removal efficiency | 76.92 | 77.80 |
| 6. % G&O Removal efficiency | 79.09 | 87.00 |
| 7. Gas (ml/L) | 390.00 | 400.00 |
| 8. Electrode lost (g/m$^3$) | 330.40 | 320.0 |
| 9.Sludge quantity (ml/L) | 54.20 | 50.00 |
| 10.Electrode cost (Baht/m$^3$) | 23.00 | 20.00 |
| 11.Power Requirement (kWh/m$^3$) | 5.19 | 5.31 |
| 12.Electricity cost (Baht/ m$^3$) | 10.02 | 10.21 |
| 13.Chemical cost (Baht/m$^3$) | 11.00 | 15.00 |

Table 4.14 Comparison of the removal efficiency and power requirement of electrocoagulation process and dissolve air floatation (DAF)

| Method | % COD Removed | % SS Removed | % G&O removed | Power Requirement (kWh/m$^3$) | Electricity cost (Baht/m$^3$) |
|---|---|---|---|---|---|
| EC process | 97.49 | 76.92 | 79.09 | 5.19 | 10.02 |
| DAF | 53.14 | 7.14 | 9.69 | 9.50 | 18.34 |
| New DAF | 83.11 | 78.46 | 57.71 | 11.00 | 21.24 |

# CHAPTER V

# CONCLUSIONS AND RECOMMENDATIONS

## 5.1 Conclusions

The investigation in this work leads to the following conclusions:

This study demonstrates that the EC process using an aluminum anode and graphite cathode is effective at reducing COD, G&O, and SS more than 77% in the petrochemical processing wastewater. The EC-treated wastewater requires a further biological treatment process to meet the effluent discharge standard. Using Box-Behnken design to create a set of experimental runs can reduce a number of runs needed to optimize the operating conditions in comparison with the one fact at a time experiment method. It provides sufficient data to fit the quadratic models for pollutant removals. The calibrating models reasonably describe the removal efficiencies with the slopes of the regression lines approaching 1.00. Optimization of the models provide the optimum conditions at initial pH of 6.73, 20.58 V applied voltage, and 27.40 minutes reaction time that are in agreement with those obtained by the one factor at a time experiments. This implies that the RSM could be effectively adopted to optimize the operating multifactors in such EC complex process. The EC treatment seems competitive in comparison with conventional methods due to short process time, no chemical addition, and less sludge production.

## 5.2 Recommendations/Future works

Based on the results of this study, some recommendations for any future study are proposed as follows:

1. Electrocoagulation process with a continuously flow reactor should be studied when implementing to a real petrochemical plant.

2. In continuously flow reactor should control initial pH and current density. The total of reactor is 1.5 L. The retention time are varied more than 60 minutes.
3. The data should apply from primary treatment system to real process.
4. Use of byproduct from the EC process, such as produced hydrogen, should be considered for economical benefit.

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# APPENDICES

# APPENDIX A

## The result from all experiments

Table A-1 The result from the experiment to find optimum current density when use electrode as Al-C at pH 6 with 30 minutes.

| Applied Voltage | Trial | pH | | Conductivity (µS/cm) | | Current density (mA/cm$^2$) | Electrode weight (g/m$^3$) | COD (mg/L) | | SS (mg/L) | | G&O (mg/L) | | Gas quality (mL.) | Power Requirement (kWh/m$^3$) | Electric cost (Bath/m$^3$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Before | After | Before | After | | | Before | After | Before | After | Before | After | | | |
| 10 | 1 | 6 | 7.98 | 480 | 450 | 5.11 | 181.30 | 8184 | 1066 | 95.00 | 57.50 | 152.50 | 54.00 | 155.00 | 2.55 | 4.92 |
| | 2 | 6 | 7.99 | 480 | 440 | 5.21 | 181.00 | 8184 | 1066 | 95.00 | 55.70 | 152.50 | 53.10 | 155.00 | 2.60 | 5.00 |
| | **Avg.** | **6** | **7.98** | **480** | **445** | **5.11** | **181.30** | **8184** | **1066** | **95.00** | **56.60** | **152.50** | **53.50** | **155.00** | **2.55** | **4.96** |
| 15 | 1 | 6 | 8.00 | 480 | 440 | 8.42 | 181.70 | 8184 | 548.3 | 95.00 | 45.40 | 152.50 | 50.00 | 275.00 | 6.30 | 12.17 |
| | 2 | 6 | 8.03 | 480 | 430 | 8.32 | 181.50 | 8184 | 548.2 | 95.00 | 43.90 | 152.50 | 49.20 | 272.00 | 6.40 | 12.50 |
| | **Avg.** | **6** | **8.02** | **480** | **435** | **8.42** | **181.70** | **8184** | **548.3** | **95.00** | **44.70** | **152.50** | **49.60** | **275.00** | **6.30** | **12.10** |
| 20 | 1 | 6 | 8.08 | 490 | 410 | 9.12 | 360.10 | 8184 | 217.0 | 95.00 | 40.00 | 152.50 | 40.00 | 432.50 | 9.10 | 17.57 |
| | 2 | 6 | 8.09 | 490 | 410 | 9.02 | 360.50 | 8184 | 217.0 | 95.00 | 38.70 | 152.50 | 39.30 | 431.00 | 9.10 | 17.57 |
| | **Avg.** | **6** | **8.08** | **490** | **410** | **9.12** | **360.10** | **8184** | **217.0** | **95.00** | **39.40** | **152.50** | **39.70** | **432.50** | **9.10** | **17.57** |
| 25 | 1 | 6 | 8.34 | 480 | 410 | 10.93 | 369.00 | 8184 | 198.0 | 95.00 | 40.00 | 152.50 | 38.30 | 517.50 | 13.63 | 26.10 |
| | 2 | 6 | 8.36 | 480 | 410 | 11.03 | 368.90 | 8184 | 198.0 | 95.00 | 38.80 | 152.50 | 37.70 | 518.00 | 13.40 | 26.40 |
| | **Avg.** | **6** | **8.35** | **480** | **410** | **10.93** | **369.00** | **8184** | **198.0** | **95.00** | **39.30** | **152.50** | **38.00** | **517.50** | **13.52** | **26.30** |
| 30 | 1 | 6 | 9.10 | 480 | 400 | 12.13 | 397.00 | 8184 | 90.0 | 95.00 | 39.50 | 152.50 | 38.20 | 527.50 | 18.15 | 35.05 |
| | 2 | 6 | 9.14 | 480 | 400 | 12.23 | 396.80 | 8184 | 90.0 | 95.00 | 38.20 | 152.50 | 37.50 | 526.00 | 18.45 | 35.10 |
| | **Avg.** | **6** | **9.12** | **480** | **400** | **12.13** | **397.00** | **8184** | **90.0** | **95.00** | **38.90** | **152.50** | **37.80** | **527.50** | **18.30** | **18.30** |

Table A-2 The result from the experiment to find optimum retention time period when use electrode as Al-C current density 9.12 mA/cm$^2$ (20 V) at pH 6.

| Retention time | Trial | pH | | Conductivity (µS/cm) | | Current density (mA/cm$^2$) | Electrode weight (g/m$^3$) | COD (mg/L) | | SS (mg/L) | | G&O (mg/L) | | Gas quality (mL.) | Power Requirement (kWh/m$^3$) | Electric cost (Bath/m$^3$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Before | After | Before | After | | | Before | After | Before | After | Before | After | | | |
| 10 | 1 | 6 | 6.93 | 480 | 440 | 7.91 | 166.8 | 8184 | 363.4 | 95.00 | 37.00 | 152.5 | 60.00 | 145.00. | 1.98 | 3.69 |
| | 2 | 6 | 6.80 | 480 | 430 | 7.91 | 166.9 | 8184 | 363.3 | 95.00 | 36.00 | 152.5 | 59.00 | 155.00 | 1.98 | 3.69 |
| | **Avg.** | **6** | **6.87** | **480** | **435** | **7.91** | **166.8** | **8184** | **363.4** | **95.00** | **37.00** | **152.5** | **59.50** | **145.00** | **1.98** | **3.69** |
| 15 | 1 | 6 | 7.24 | 480 | 440 | 8.02 | 181.3 | 8184 | 268.4 | 95.00 | 29.00 | 152.5 | 58.60 | 210.00 | 3.01 | 5.8 |
| | 2 | 6 | 7.25 | 480 | 440 | 8.02 | 181.7 | 8184 | 268.4 | 95.00 | 28.00 | 152.5 | 58.00 | 210.00 | 3.00 | 5.79 |
| | **Avg.** | **6** | **7.24** | **480** | **440** | **8.02** | **181.3** | **8184** | **268.4** | **95.00** | **28.50** | **152.5** | **58.30** | **210.00** | **3.00** | **5.79** |
| 20 | 1 | 6 | 7.54 | 480 | 430 | 8.02 | 251.3 | 8184 | 252.8 | 95.00 | 26.00 | 152.5 | 35.10 | 290.00 | 4.03 | 7.75 |
| | 2 | 6 | 7.53 | 480 | 430 | 7.91 | 251.1 | 8184 | 253.0 | 95.00 | 25.00 | 152.5 | 34.50 | 300.00 | 4.00 | 7.72 |
| | **Avg.** | **6** | **7.54** | **480** | **430** | **8.02** | **251.3** | **8184** | **253.0** | **95.00** | **25.50** | **152.5** | **35.00** | **290.00** | **4.00** | **7.72** |
| 25 | 1 | 6 | 7.90 | 480 | 400 | 8.32 | 330.4 | 8184 | 205.4 | 95.00 | 22.00 | 152.5 | 32.00 | 385 | 5.19 | 10.02 |
| | 2 | 6 | 7.80 | 480 | 410 | 8.32 | 331.1 | 8184 | 205.4 | 95.00 | 21.00 | 152.5 | 31.30 | 395 | 5.19 | 10.02 |
| | **Avg.** | **6** | **7.87** | **480** | **405** | **8.32** | **330.4** | **8184** | **205.4** | **95.00** | **22.00** | **152.5** | **31.70** | **390** | **5.19** | **10.02** |
| 30 | 1 | 6 | 8.20 | 490 | 410 | 8.32 | 331.1 | 8184 | 194.0 | 95.00 | 21.00 | 152.5 | 31.00 | 435 | 6.24 | 12.04 |
| | 2 | 6 | 8.10 | 490 | 410 | 8.32 | 351.8 | 8184 | 194.0 | 95.00 | 21.00 | 152.5 | 30.30 | 430 | 6.23 | 12.03 |
| | **Avg.** | **6** | **8.17** | **490** | **410** | **8.32** | **331.1** | **8184** | **194.0** | **95.00** | **21.00** | **152.5** | **30.70** | **433** | **6.23** | **12.03** |
| 40 | 1 | 6 | 8.30 | 480 | 400 | 9.02 | 397.1 | 8184 | 124.3 | 95.00 | 20.70 | 152.5 | 29.00 | 550 | 9.1 | 17.57 |
| | 2 | 6 | 8.20 | 480 | 400 | 9.22 | 400.9 | 8184 | 124.4 | 95.00 | 20.50 | 152.5 | 28.50 | 570 | 9.1 | 17.57 |
| | **Avg.** | **6** | **8.29** | **480** | **400** | **9.12** | **397.1** | **8184** | **124.4** | **95.00** | **20.60** | **152.5** | **28.80** | **560** | **9.1** | **17.57** |

Table A-3 The result from Box-Benhken design experiment.

| Trials | Time | pH | | Conductivity (µS/cm) | | Current density (mA/cm$^2$) | Electrode weight (g/m$^3$) | COD (mg/L) | | SS (mg/L) | | G&O (mg/L) | | Gas quality (mL.) | Power Requirement (kWh/m$^3$) | Electric cost (Bath/m$^3$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Before | After | Before | After | | | Before | After | Before | After | Before | After | | | |
| 1 | 1 | 9.0 | 9.31 | 390 | 310 | 1.40 | 19.7 | 8184 | 3107.5 | 95 | 53.6 | 152.5 | 87.5 | 70 | 0.58 | 1.13 |
| | 2 | 9.0 | 9.26 | 390 | 320 | 1.00 | 17.1 | 8184 | 3107.1 | 95 | 52 | 152.5 | 86.1 | 65 | 0.42 | 0.80 |
| | **Avg.** | 9.0 | **9.29** | **390** | **315** | **1.20** | **18.4** | **8184** | **3107.3** | **95** | **52.8** | **152.5** | **86.8** | **67.5** | **0.50** | **0.97** |
| 2 | 1 | 6.5 | 7.92 | 430 | 370 | 3.20 | 53.6 | 8184 | 669.5 | 95 | 20.6 | 152.5 | 17.9 | 240 | 2.13 | 4.12 |
| | 2 | 6.5 | 7.87 | 430 | 370 | 3.20 | 76.8 | 8184 | 669.4 | 95 | 20 | 152.5 | 17.6 | 240 | 2.13 | 4.12 |
| | **Avg.** | **6.5** | **7.89** | **430** | **370** | **3.20** | **65.2** | **8184** | **669.5** | **95** | **20.3** | **152.5** | **17.8** | **240** | **2.13** | **4.12** |
| 3 | 1 | 6.5 | 7.07 | 430 | 370 | 3.20 | 14.0 | 8184 | 1610.6 | 95 | 50 | 152.5 | 56.7 | 55 | 0.53 | 1.03 |
| | 2 | 6.5 | 6.96 | 430 | 360 | 3.41 | 15.7 | 8184 | 1610.4 | 95 | 48.4 | 152.5 | 55.8 | 60 | 0.57 | 1.09 |
| | **Avg.** | **6.5** | **7.02** | **430** | **365** | **3.31** | **15.1** | **8184** | **1610.5** | **95** | **49.2** | **152.5** | **56.3** | **57.5** | **0.55** | **1.06** |
| 4 | 1 | 9 | 9.52 | 390 | 300 | 7.61 | 110.5 | 8184 | 2090.2 | 95 | 42.4 | 152.5 | 73.1 | 275 | 9.50 | 18.34 |
| | 2 | 9 | 9.43 | 390 | 320 | 7.31 | 97.0 | 8184 | 2090 | 95 | 41.1 | 152.5 | 71.9 | 265 | 9.13 | 17.62 |
| | **Avg.** | **9** | **9.47** | **390** | **310** | **7.51** | **103.7** | **8184** | **2090.1** | **95** | **41.8** | **152.5** | **72.5** | **270** | **9.3125** | **17.98** |
| 5 | 1 | 6.5 | 7.52 | 430 | 360 | 9.62 | 70.9 | 8184 | 356 | 95 | 22.8 | 152.5 | 25.9 | 170 | 4.80 | 9.27 |
| | 2 | 6.5 | 7.43 | 430 | 370 | 9.00 | 65.0 | 8184 | 356 | 95 | 22.4 | 152.5 | 25.5 | 175 | 4.50 | 8.69 |
| | **Avg.** | **6.5** | **7.47** | **430** | **365** | **9.32** | **67.95** | **8184** | **356** | **95** | **22.6** | **152.5** | **25.7** | **172.5** | **4.65** | **8.98** |
| 6 | 1 | 4 | 6.88 | 640 | 460 | 11.22 | 195.1 | 8184 | 630.9 | 95 | 21.7 | 152.5 | 36.8 | 385 | 14.00 | 27.03 |
| | 2 | 4 | 7.19 | 640 | 460 | 12.43 | 231.7 | 8184 | 630.9 | 95 | 21 | 152.5 | 36.2 | 400 | 15.50 | 29.93 |
| | **Avg.** | **4** | **7.03** | **640** | **460** | **11.81** | **213.4** | **8184** | **630.9** | **95** | **21.4** | **152.5** | **36.5** | **392.5** | **14.75** | **28.48** |

Table A-3 The result from Box-Benhken design experiment (con).

| Trials | Time | pH |  | Conductivity (µS/cm) |  | Current density (mA/cm$^2$) | Electrode weight (g/m$^3$) | COD (mg/L) |  | SS (mg/L) |  | G&O (mg/L) |  | Gas quality (mL.) | Power Requirement (kWh/m$^3$) | Electric cost (Bath/m$^3$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | Before | After | Before | After |  |  | Before | After | Before | After | Before | After |  |  |  |
| 7 | 1 | 6.5 | 8.27 | 430 | 340 | 8.22 | 141.6 | 8184 | 349.5 | 95 | 21.7 | 152.5 | 18.8 | 345.0 | 6.83 | 13.20 |
|  | 2 | 6.5 | 8.28 | 430 | 340 | 8.62 | 147.1 | 8184 | 349.4 | 95 | 21.0 | 152.5 | 18.5 | 360.0 | 7.17 | 13.84 |
|  | **Avg.** | **6.5** | **8.28** | **430** | **340** | **8.42** | **144.4** | **8184** | **349.5** | **95** | **21.4** | **152.5** | **18.7** | **352.5** | **7.00** | **13.52** |
| 8 | 1 | 4 | 7.27 | 640 | 440 | 8.42 | 228.5 | 8184 | 311.0 | 95 | 12.5 | 152.5 | 36.6 | 600.0 | 11.20 | 21.63 |
|  | 2 | 4 | 7.54 | 640 | 450 | 8.82 | 256.1 | 8184 | 311.0 | 95 | 12.1 | 152.5 | 36.0 | 590.0 | 11.73 | 22.66 |
|  | **Avg.** | **4** | **7.41** | **640** | **445** | **8.62** | **242.3** | **8184** | **311.0** | **95** | **12.3** | **152.5** | **36.3** | **595.0** | **11.47** | **22.14** |
| 9 | 1 | 4 | 6.15 | 640 | 480 | 5.21 | 121.6 | 8184 | 1243.1 | 95 | 36.3 | 152.5 | 56.4 | 240.0 | 2.17 | 4.18 |
|  | 2 | 4 | 6.39 | 640 | 490 | 5.00 | 87.9 | 8184 | 1243.0 | 95 | 35.2 | 152.5 | 55.4 | 225.0 | 2.08 | 4.02 |
|  | **Avg.** | **4** | **6.27** | **640** | **485** | **5.10** | **104.7** | **8184** | **1243.1** | **95** | **35.8** | **152.5** | **55.9** | **232.5** | **2.13** | **4.10** |
| 10 | 1 | 9 | 9.14 | 390 | 330 | 2.00 | 29.0 | 8184 | 1910.1 | 95 | 29.1 | 152.5 | 74.9 | 40.0 | 0.67 | 1.29 |
|  | 2 | 9 | 9.25 | 390 | 320 | 1.80 | 18.2 | 8184 | 1910.0 | 95 | 28.2 | 152.5 | 74.0 | 40.0 | 0.60 | 1.16 |
|  | **Avg.** | **9** | **9.20** | **390** | **325** | **1.90** | **23.6** | **8184** | **1910.1** | **95** | **28.7** | **152.5** | **74.5** | **40.0** | **0.63** | **1.22** |
| 11 | 1 | 6.5 | 9.63 | 430 | 340 | 9.62 | 302.1 | 8184 | 179.2 | 95 | 20.1 | 152.5 | 16.9 | 640.0 | 19.20 | 37.08 |
|  | 2 | 6.5 | 9.53 | 430 | 330 | 9.22 | 329.1 | 8184 | 179.2 | 95 | 19.4 | 152.5 | 16.6 | 660.0 | 18.40 | 35.53 |
|  | **Avg.** | **6.5** | **9.58** | **430** | **335** | **9.42** | **315.6** | **8184** | **179.2** | **95** | **19.8** | **152.5** | **16.8** | **650.0** | **18.80** | **36.30** |
| 12 | 1 | 6.5 | 7.88 | 430 | 340 | 8.22 | 135.6 | 8184 | 392.0 | 95 | 20.6 | 152.5 | 17.9 | 370.0 | 6.83 | 13.20 |
|  | 2 | 6.5 | 8.06 | 430 | 350 | 8.22 | 146.6 | 8184 | 391.9 | 95 | 20.0 | 152.5 | 17.6 | 360.0 | 6.83 | 13.20 |
|  | **Avg.** | **6.5** | **7.97** | **430** | **345** | **8.22** | **141.1** | **8184** | **392.0** | **95** | **20.3** | **152.5** | **17.8** | **365.0** | **6.83** | **13.20** |

Table A-3 The result from Box-Benhken design experiment (con).

| Trials | Time | pH | | Conductivity (µS/cm) | | Current density (mA/cm$^2$) | Electrode weight (g/m$^3$) | COD (mg/L) | | SS (mg/L) | | G&O (mg/L) | | Gas quality (mL.) | Power Requirement (kWh/m$^3$) | Electric cost (Bath/ m$^3$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Before | After | Before | After | | | Before | After | Before | After | Before | After | | | |
| 13 | 1 | 6.5 | 8.09 | 430 | 360 | 8.42 | 140.6 | 8184 | 392.0 | 95 | 20.6 | 152.5 | 17.8 | 355 | 7.00 | 13.52 |
| | 2 | 6.5 | 8.15 | 430 | 350 | 8.62 | 185.8 | 8184 | 392.0 | 95 | 20.0 | 152.5 | 17.5 | 355 | 7.17 | 13.84 |
| | **Avg.** | **6.5** | **8.12** | **430** | **355** | **8.52** | **163.2** | **8184** | **392.0** | **95** | **20.3** | **152.5** | **17.7** | **355** | **7.08** | **13.68** |
| 14 | 1 | 4 | 5.12 | 640 | 480 | 7.81 | 58.4 | 8184 | 1091.7 | 95 | 38.6 | 152.5 | 67.2 | 120 | 2.60 | 5.02 |
| | 2 | 4 | 5.29 | 640 | 500 | 8.72 | 70.3 | 8184 | 1091.6 | 95 | 37.4 | 152.5 | 66.8 | 130 | 2.90 | 5.60 |
| | **Avg.** | **4** | **5.21** | **640** | **490** | **8.32** | **64.4** | **8184** | **1091.7** | **95** | **38.0** | **152.5** | **67.0** | **125** | **2.75** | **5.31** |
| 15 | 1 | 9 | 8.80 | 390 | 320 | 4.31 | 77.2 | 8184 | 2361.1 | 95 | 46.5 | 152.5 | 80.4 | 125 | 5.73 | 11.07 |
| | 2 | 9 | 8.77 | 390 | 320 | 3.51 | 88.0 | 8184 | 2360.8 | 95 | 45.0 | 152.5 | 79.1 | 115 | 4.67 | 9.01 |
| | **Avg.** | **9** | **8.79** | **390** | **320** | **3.90** | **82.6** | **8184** | **2361.0** | **95** | **45.8** | **152.5** | **79.8** | **120** | **5.20** | **10.04** |

Table A-4 The result of optimum condition from the one variable at a time method with Al-C pH 6 current density 8.32 mA/cm$^2$(20 V) at 25 min.

| Trial | pH | | Conductivity (μS/cm) | | Current density (mA/cm$^2$) | Electrode weight (g/m$^3$) | COD (mg/L) | | SS (mg/L) | | G&O (mg/L) | | Gas quality (mL.) | Power Requirement (kWh/m$^3$) | Electric cost (Baht/ m$^3$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Before | After | Before | After | | | Before | After | Before | After | Before | After | | | |
| 1 | 6 | 7.2 | 480 | 400 | 8.32 | 330.4 | 8184 | 205.4 | 95 | 22.0 | 152.5 | 31.9 | 385 | 5.10 | 9.80 |
| 2 | 6 | 7.28 | 480 | 410 | 8.32 | 330.4 | 8184 | 205.4 | 95 | 21.2 | 152.5 | 31.4 | 395 | 5.20 | 10.05 |
| **Avg.** | **6** | **7.24** | **480** | **405** | **8.32** | **330.4** | **8184** | **205.4** | **95** | **21.6** | **152.5** | **31.7** | **390** | **5.19** | **10.02** |

Table A-5 The result of optimum condition from the Box-Benhken design experiment with Al-C pH 6.73 20.58 V at 27.4 min.

| Trial | pH | | Conductivity (μS/cm) | | Current density (mA/cm$^2$) | Electrode weight (g/m$^3$) | COD (mg/L) | | SS (mg/L) | | G&O (mg/L) | | Gas quality (mL.) | Power Requirement (kWh/m$^3$) | Electric cost (Baht/ m$^3$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Before | After | Before | After | | | Before | After | Before | After | Before | After | | | |
| 1 | 6.73 | 7.23 | 460 | 400 | 8.02 | 320 | 8184 | 425.6 | 95 | 21.1 | 152.5 | 19.8 | 400 | 5.25 | 10.10 |
| 2 | 6.73 | 7.23 | 460 | 410 | 8.42 | 310 | 8184 | 425.5 | 95 | 20.4 | 152.5 | 19.5 | 400 | 5.36 | 10.32 |
| **Avg.** | **6.73** | **7.23** | **460** | **405** | **8.22** | **320** | **8184** | **425.5** | **95** | **20.8** | **152.5** | **19.7** | **400** | **5.31** | **10.21** |

# APPENDIX B

## Figure of Experiments

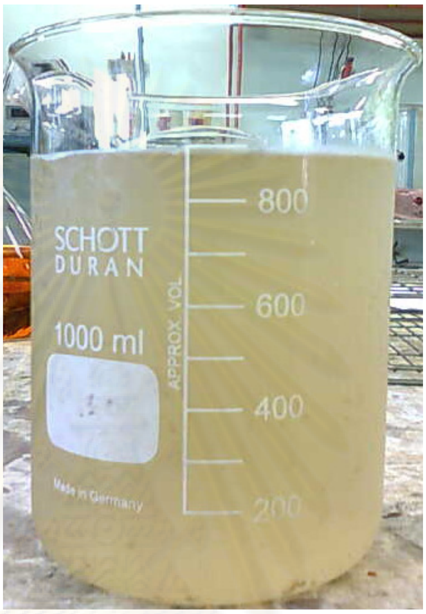

Figure B-1 Petrochemical wastewater characteristic

**The characteristic of treated wastewater with tested condition**

1. Treated wastewater from 1st experiment.

Figure B-2 (a) pH 4 (b) pH 6 (c) pH 9

2. Treated wastewater from 2nd experiment.

Figure B-3 (a) 10 Volts (b) 15 Volts (c) 20 Volts

(d) 25 Volts (e) 30 Volts

3. Treated wastewater from 3rd experiment.

Figure B-4 (a) 10 min (b) 15 min (c) 20 min

(d) 25 min (e) 30 min (f) 40 min

# APPENDIX C

## The analysis of sludge

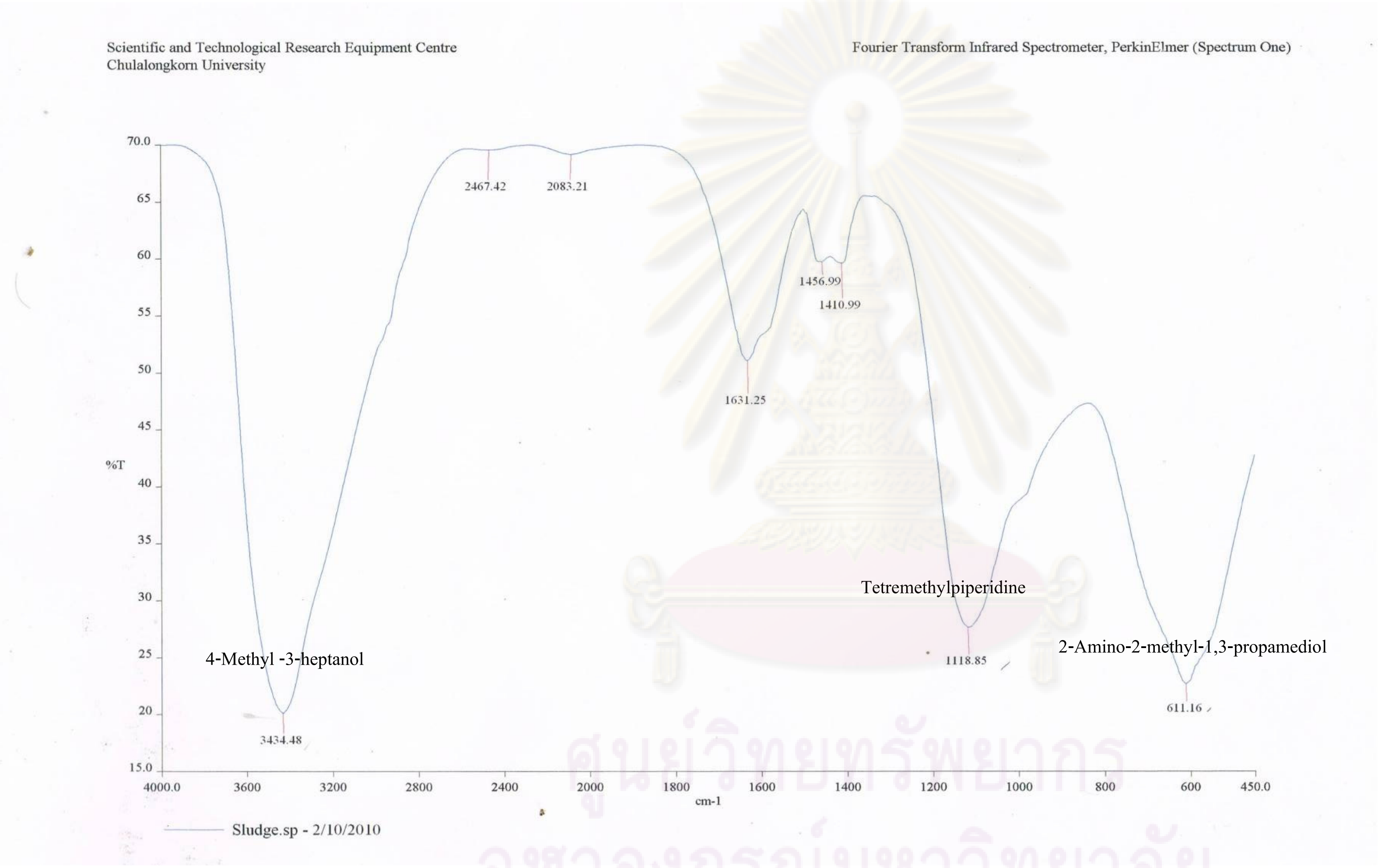

Figure C-1 The analysis result of sludge with Fourier Transform Infrared Spectrometer (FT-IR) of petrochemical treated wastewater using initial pH of 6, voltage of 20 V and retention time of 25 minutes.

# APPENDIX D

## Standard Electrode at 25 ºc

Table D-1 Standard Electrode at 25 ºc

| Half Reaction | Standard Electrode (Volts) |
|---|---|
| $I_{3-} + 2e \leftrightarrow 3I^-$ | 0.536 |
| $I_2(s) + 2e \leftrightarrow 2I^-$ | 0.5355 |
| $I_2(aq) + 2e \leftrightarrow 2I^-$ | 0.620 |
| $Cu^+ + e \leftrightarrow Cu(s)$ | 0.521 |
| $H_2SO_3 + 4H^+ + 4e \leftrightarrow S(s) + 3H_2O$ | 0.45 |
| $Ag_2CrO_4(s) + 2e \leftrightarrow 2Ag(s) + CrO_4^{2-}$ | 0.446 |
| $VO^{2+} + 2H^+ + e \leftrightarrow V^{3+} + H_2O$ | 0.361 |
| $Fe(CN)_6^{3-} + e \leftrightarrow Fe(CN)_6^{4-}$ | 0.36 |
| $Cu^{2+} + 2e \leftrightarrow Cu(s)$ | 0.337 |
| $UO_2^{2+} + 4H^+ + 2e \leftrightarrow U^{4+} + 2H_2O$ | 0.334 |
| $BiO^+ + 2H^+ + 3e \leftrightarrow Bi(s) + H_2O$ | 0.32 |
| $Hg_2Cl(s) + 2e \leftrightarrow 2Hg(l) + 2Cl^-$ | 0.368 |
| $AgCl(s) + e \leftrightarrow Ag(s) + Cl^-$ | 0.222 |
| $SO_4^{2-} + 4H^+ + 2e \leftrightarrow H_2SO_3 + H_2O$ | 0.17 |
| $BiCl_4^- + 3e \leftrightarrow Bi(s) + 4Cl^-$ | 0.16 |
| $Sn^{4+} + 2e \leftrightarrow Sn^{2+}$ | 0.154 |
| $Cu^{2+} + e \leftrightarrow Cu^+$ | 0.153 |
| $S(s) + 2H^+ + 2e \leftrightarrow H_2S(g)$ | 0.141 |
| $TiO^{2+} + 2H^+ + e \leftrightarrow Ti^{3+} + H_2O$ | 0.1 |
| $AgBr(s) + e \leftrightarrow Ag(s) + Br^-$ | 0.095 |
| $S_4O_6^{2} + 2e \leftrightarrow 2S_2O_3^{2-}$ | 0.08 |
| $Ag(S_2O_3)_2^{3-} + e \leftrightarrow Ag(s) + 2S_2O_3^{2-}$ | 0.010 |
| $2H^+ + 2e \leftrightarrow H_2(g)$ | 0.000 |
| $Pb^{2+} + 2e \leftrightarrow Pb(s)$ | -0.126 |
| $Sn^{2+} + 2e \leftrightarrow Sn(s)$ | -0.136 |
| $AgI(s) + e \leftrightarrow Ag(s) + I^-$ | -0.151 |
| $CuI(s) + e \leftrightarrow Cu(s) + I^-$ | -0.185 |
| $N_2(g) + 5H^+ + 4e \leftrightarrow N_2H_5^+$ | -0.23 |
| $Ni^{2+} + 2e \leftrightarrow Ni(s)$ | -0.250 |
| $V^{3+} + e \leftrightarrow V^{2+}$ | -0.255 |
| $Co^{2+} + 2e \leftrightarrow Co(s)$ | -0.277 |
| $Ag(CN)_2^- + e \leftrightarrow Ag(s) + 2CN^-$ | -0.31 |
| $Tl^+ + e \leftrightarrow Tl(s)$ | -0.336 |
| $PbSO_4(s) + 2e \leftrightarrow Pb(s) + SO_4^{2-}$ | -0.356 |
| $Ti^{3+} + e \leftrightarrow Ti^{2+}$ | -0.37 |
| $Cd^{+2} + 2e \leftrightarrow Cd(s)$ | -0.403 |
| $Cr^{+3} + 2e \leftrightarrow Cr^{+2}$ | -0.41 |
| $2CO_2\ (g) + 2H^+ + 2e \leftrightarrow H_2C_2O_4$ | -0.49 |
| $Cr^{3+} + 3e \leftrightarrow Cr(s)$ | -0.74 |
| $Zn^{2+} + 2e \leftrightarrow Zn(s)$ | -0.763 |
| $Mn^{2+} + 2e \leftrightarrow Mn(s)$ | -1.18 |
| $Al^{3+} + 3e \leftrightarrow Al(s)$ | -1.66 |
| $Mg^{2+} + 2e \leftrightarrow Mg(s)$ | -2.37 |
| $Na^+ + e \leftrightarrow Na(s)$ | -2.714 |
| $Ca^{2+} + 2e \leftrightarrow Ca(s)$ | -2.87 |
| $Ba^{2+} + 2e \leftrightarrow Ba(s)$ | -2.90 |
| $K^+ + e \leftrightarrow K(s)$ | -2.925 |
| $Li^+ + e \leftrightarrow Li(s)$ | -3.045 |

Table D-1 Standard Electrode at 25 ºc

| Half Reaction | Standard Electrode (Volts) |
|---|---|
| $F_2(g) + 2H^+ + 2e \leftrightarrow 2HF(aq)$ | 3.06 |
| $O_3(g) + 2H + 2e \leftrightarrow O_2(g) + H_2O$ | 2.07 |
| $S_2O_8^{2-} + 2e \leftrightarrow 2SO_4^{2-}$ | 2.01 |
| $Co^{3+} + e \leftrightarrow Co^{2+}$ | 1.842 |
| $H_2O_2 + 2H^+ + 2e \leftrightarrow 2H_2O$ | 1.776 |
| $MnO_4^- + 4H^+ + 3e \leftrightarrow MnO_2(s) + 2H_2O$ | 1.695 |
| $Ce^{4+} + e \leftrightarrow Ce^{3+}$ | |
| $HClO + H^+ + e \leftrightarrow ½Cl_2(g) + H_2O$ | 1.63 |
| $H_5IO_6 + H_+ + 2e \leftrightarrow IO_3^- + 3H_2O$ | 1.60 |
| $BrO_3^- + 6H^+ + 5e \leftrightarrow ½Br_2(l) + 3H_2O$ | 1.52 |
| $MnO_4 + 8H^+ + 5e \leftrightarrow Mn^{2+} + 4H_2O$ | 1.51 |
| $Mn^{3+} + e \leftrightarrow Mn^{2+}$ | |
| $ClO_3^- + 6H^+ + 5e \leftrightarrow ½Cl_2(g) + 3H_2O$ | 1.47 |
| $PbO_2(s) + 4H^+ + 2e \leftrightarrow Pb^{2+} + 2H_2O$ | 1.455 |
| $Cl_2(g) + 2e \leftrightarrow 2Cl^-$ | 1.359 |
| $Cr_2O_7^{2-} + 14H^+ + 6e \leftrightarrow 2Cr^{3+} + 7H_2O$ | 1.33 |
| $Tl^{3+} + 2e \leftrightarrow Tl^+$ | 1.25 |
| $IO_3^- + 2Cl^- + 6H^+ + 4e \leftrightarrow ICl_{2-} + 3H_2O$ | 1.24 |
| $MnO_2(s) + 4H^+ + 2e \leftrightarrow Mn^{2+} + 2H_2O$ | 1.23 |
| $O_2(g) + 4H^+ + 4e \leftrightarrow 2H_2O$ | 1.229 |
| $IO_3^- + 6H^+ + 5e \leftrightarrow ½I_2(s) + 3H_2O$ | 1.195 |
| $IO_3^- + 6H^+ + 5e \leftrightarrow ½I_2(aq) + 3H_2O$ | 1.178 |
| $SeO_4^{2-} + 4H^+ + 2e \leftrightarrow 2H_2SeO_3 + H_2O$ | 1.15 |
| $Br_2(l) + 2e \leftrightarrow 2Br^-$ | 1.065 |
| $Br_2(aq) + 2e \leftrightarrow 2Br^-$ | 1.087 |
| $ICl_2^- + e \leftrightarrow ½I_2(s) + 2Cl^-$ | 1.06 |
| $V(OH)_4^+ + 2H^+ + e \leftrightarrow VO^{2+} + H_2O$ | 1.00 |
| $HNO_2 + H^+ + e \leftrightarrow NO(g) + H_2O$ | 1.00 |
| $Pd^{2+} + 2e \leftrightarrow Pd(s)$ | 0.987 |
| $NO_3^- + 3H^+ + 2e \leftrightarrow HNO_2 + H_2O$ | 0.94 |
| $2Hg^{2+} + 2e \leftrightarrow Hg_2^{2+}$ | 0.920 |
| $HO_2^- + H_2O + 2e \leftrightarrow 3OH^-$ | 0.88 |
| $Cu^{2+} + I^- + e \leftrightarrow CuI(s)$ | 0.86 |
| $Hg^{2+} + 2e \leftrightarrow Hg(l)$ | 0.854 |
| $Ag^+ + e \leftrightarrow Ag(s)$ | 0.799 |
| $Hg_2^{2+} + 2e \leftrightarrow 2Hg(l)$ | 0.789 |
| $Fe^{3+} + e \leftrightarrow Fe^{2+}$ | 0.771 |
| $H_2SeO_3 + 4H^+ + 4e \leftrightarrow Se(s) + 3H_2O$ | 0.740 |
| $PtCl_4^{2-} + 2e \leftrightarrow Pt(s) + 4Cl^-$ | 0.73 |
| $C_6H_4O_2(quinone) + 2H^+ + 2e \leftrightarrow C_6H_4(OH)_2$ | 0.699 |
| $O_2(g) + 2H^+ + 2e \leftrightarrow H_2O_2$ | 0.682 |
| $PtCl_6^{2-} + 2e \leftrightarrow PtCl_4^{2-} + 2Cl^-$ | 0.68 |
| $Hg_2SO_4(s) + 2e \leftrightarrow 2Hg(l) + SO_4^{2-}$ | 0.615 |
| $Sb_2O_5(s) + 6H^+ + 4e \leftrightarrow 2SbO^+ + 3H_2O$ | 0.581 |
| $MnO_4^- + e \leftrightarrow MnO_4^{2-}$ | 0.564 |
| $H_3AsO_4 + 2H^+ + 2e \leftrightarrow H_3AsO_3 + H_2O$ | 0.559 |

# APPENDIX E

## The calculation for electricity cost

For example: Wastewater 1L. Size of electrode is 10.5 cm × 5 cm × 2mm the distance between electrode 1.5 cm and applied voltage 20 V current 0.82 Amp. The retention time is 3 minute.

1. Electricity in Faraday's unit

Electricity = I (amp)*t (sec)

= 0.82*(30/60)*60*60

= 1.476 Coulomb/mole

= 0.015 Faraday

2. Calculation of current density

C = I/A

= (0.82*1000)/((1.5+0.4)*10.5*5)

= 8.22 mA/cm$^2$

3. Calculation of power requirement

W = Vlt/1000v

= (20*0.82*(30/60))/(1000*(1.0/1000)

= 8.2 kWh/m$^3$

4. Calculation of electricity cost

Electricity cost = energy × cost/unit

= 8.2*1.8047*1.07

= 15.38 Baht/m$^3$

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