INVESTIGATION OF ELECTRO-COAGULATION PROCESS FOR THE REDUCTION OF TOTAL SUSPENDED SOLIDS FROM PALM OIL MILL EFFLUENT

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Abstract

Palm oil mill effluent (POME) is characterized by high chemical oxygen demand (COD) and total suspended solids (TSS). This leads to difficulties in their treatment by conventional treatment methods thus failing to meet the minimum allowable discharge. The attractive option incorporating a pre-treatment process to reduce the values of these parameters is electrocoagulation (EC) technology. In this study, the EC process of POME (19,000 – 21,000 mg/L of TSS and 60,000 – 63,000 mg/L of COD) was investigated utilizing aluminum electrode. The effects of initial pH, current density, stirring speed, temperature and operating time on the removal efficiency of TSS and COD were examined. The experiments were conducted batch wise using 400 ml of POME per batch as the reaction mixture volume. Removal of 85.3 % of the wastewater TSS and 35.7 % of the COD were attained at the optimal operating conditions. This corresponded to the initial pH of 6, current density of 120 A/m^2, stirring speed of 100 rpm, temperature of 27 °C and operating time of 15 minutes. Limiting the current density favors low heat generation and excessive oxygen evolution during the treatment. The formations of flocks have the potential to break and release residue particles into the POME at higher stirring speeds. Chemical coagulation (CC) also conducted on POME as comparative study to EC process. As a result, EC was more efficient in removing TSS and COD through efficient Al^{3+} and operating time consumption. In conclusion, the study demonstrated that EC process is able to treat POME to the allowable discharge limit effectively through reduction of TSS and COD at the initial stage and it is suitable as an alternative preliminary process for POME treatment.

Abstrak

Air sisa kelapa sawit (POME) mempunyai kepekatan keperluan oksigen kimia (COD) dan jumlah pepejal terampai (TSS) yang agak tinggi. Hal ini menyukarkan rawatan secara konventional untuk mencapai tahap perlepasan minimum. Teknologi elektrokoagulan (EC) adalah pilihan rawatan alternative yang dapat mengurangkan nilai parameter tersebut. Dalam kajian ini, proses EC bagi POME (19,000 – 21,000 mg/L TSS dan 60,000 – 63,000 mg/L COD) telah dijalankan menggunakan elektrod aluminum. Kesan pH, ketumpatan arus, kelajuan putaran, suhu dan masa operasi ke atas pengurangan TSS dan COD dikaji. Ujikaji dijalankan menggunakan 400 ml POME bagi setiap kelompok. Pada tahap operasi optimum, pengurangan sebanyak 85.3 % TSS dan 35.7 % COD telah dicapai dan berlaku pada keadaan pH 6, ketumpatan arus 120 A/m^2, kelajuan putaran 100 rpm, suhu 27 °C dan masa operasi selama 15 minit. Didapati bahawa ketumpatan arus perlu dihadkan bagi mengelakkan peningkatan suhu dan pembebasan oksigen berlebihan semasa rawatan. Sekirannya kelajuan putaran yang tinggi dibekalkan, flok yang terbentuk berpotensi untuk pecah dan membebaskan pepejal terampai ke dalam POME. Ujikaji koagulan kimia juga dijalankan sebagai perbandingan dengan elektokoagulan. Hasilnya, rawatan menggunakan elektrokoagulan lebih cekap berbanding koagulan kimia dengan penggunaan ion Al^{3+} dan masa operasi yang lebih cekap pada pengurangan bahan tercemar yang paling optimum. Sebagai kesimpulan, kajian ini membuktikan proses EC dapat merawat POME secara efektif untuk mecapai had pelepasan yang dibenarkan melalui pengurangan TSS dan COD pada peringkat awal dan ia sesuai dijadikan rawatan alternative bagi proses permulaan rawatan POME.

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List of Abbreviations

Al   Aluminum

$Al(OH)_3$ Aluminum Hydroxide

$Al_2(SO_4)_3$ Aluminum Sulphate

Al^{3+} Aluminum ions

BOD   Biochemical Oxygen Demand (mg/L)

$CaCO_3$ Calcium Carbonate

CC   Chemical Coagulation

CO_2 Carbon Dioxide

COD   Chemical Oxygen Demand (mg/L)

EC   Electrocoagulation

Fe   Ferum/iron

$Fe(OH)_3$ Ferum Hydroxide

Fe^{2+} Ferrous ions

Fe^{3+} Ferric ions

GLC   Gel Filtration Chromatography

H_2SO_4 Sulfuric Acid

MPOB   Malaysia Palm Oil Board

NaOH   Sodium Hydroxide

O&G   Oil and Greases (mg/L)

OH^- Hydroxide ions

PCW   Potato Chips Wastewater

POME   Palm Oil Mill Effluent

POMTEC   Palm Oil Mill Technology Center

RPM   Rotation per Minutes (1/minutes)

SA/V   Electrode surface area to reactor volume

SS	Suspended Solids (mg/L)
TOC	Total Organic Carbon (mg/L)
TSS	Total Suspend Solids (mg/L)
VOC	Volatile Organic Compounds

CHAPTER 1

INTRODUCTION

1.1   Introduction

The rapid growth of industrial sectors in developed and developing countries as well as the rise in population around the world has contributed to increase a water usage (Asmal, 2000). Subsequently, the wastewaters discharged into water bodies have also increased. Wastewaters from both domestic and industrial sectors contain large amount of pollutants characterized by chemical oxygen demand (COD), biochemical oxygen demand (BOD), suspended solids (SS), toxicity and colorants which cause bacterial and algal slime growths, thermal impacts, scum formation, colour problems and loss of biodiversity and aesthetic beauty of the environment (Khansorthong & Hunsom, 2009; Katal & Pahlavanzadeh, 2011). The disposal of these effluents into nature without any proper treatment has created serious damages to the environment and constitutes a threat to human health (Rupani *et al.,* 2010; Zaied & Bellakhal, 2009).

The common wastewater treatment practised in Malaysia especially for domestic wastewater is aerated biological method (Moayedi *et al.,* 2011; Muhammad, 2009). This method was reported to produce high quality effluents with removal up to 90% of SS and BOD (Metcalf & Eddy, 2004). Although the system has been effectively utilized, it is solely limited to public sewerage systems. The plants are not suitable for the treatment of wastewater from industries due to several problems that arise such as variable settlement properties of sludge production, plant sensitive to shock loading and toxicity, and limited removal capacity for biodegradable toxic substances

(Khansorthong & Hunsom, 2009). Moreover, heavy wastewater that contains high concentration of pollutants interferes with the treatment operation units which consequently cause damages to the plant.

Among the wastewater streams contributing to major pollution of water bodies when discharged without treatment is palm oil mill effluent (POME) (Agustin *et al.,* 2008). POME is a product of extraction process where it is generated from steam sterilizer of palm fruit bunches, hydrocyclone separation and clarification of the extracted crude palm oil (Ahmad *et al.,* 2003). In Malaysia, palm oil industry is recognized for its contribution towards economic growth and development (Rupani *et al.,* 2010). However, environmental pollution due to POME production had given negative perception on milling activities as POME is characterized by high contents of contaminants which include SS, COD, BOD, oil and grease (O&G) and slightly acidic wastewater (Ahmad *et al.,* 2003). This resulted in a stricter discharge limits for POME by various environmental regulation agencies.

In the case of Malaysian regulation on discharge standard for crude palm oil mills, 400 mg/L is the minimum allowable discharge limit for SS. Yet after 1984, there is no discharge standard available for COD (Environmental Quality Act 1974, 2005). The complete of effluent discharge standard for crude palm oil mills can be found in Appendix 1. Many treatment methods have been employed by industries as part of their effort to comply with the regulation. The treatment methods might differ from each other due to the characteristics and the nature of wastewaters treated.

For POME, ponding system is a common treatment method that usually applied due to low operational cost and easy to operate (Rupani *et al.,* 2010). In addition, other

processes including aerobic and anaerobic digestion, physicochemical treatment and membrane filtration also provides possible insights into the improvement of POME (Wu *et al.,* 2010). However, the treatment methods used requires large space and long hydraulic retention time of 45 to 60 days for effective performance (Rupani *et al.,* 2010).

Back to the current conventional wastewater treatment, there are few stages of treatment involved which are primary and secondary treatment stage. Primary stage involved physically removing of debris and larger particles prior to secondary stage. Secondary stage mostly involved with biological treatment to remove or reduce the pollutants. Next, the treated wastewater is conveyed into clarifier's to clarify the water before discharging into water bodies (Wastewater Treatment, 2012). All these stages are paramount to meet the allowable discharged standards through reduction of SS, COD, BOD and O&G to the minimal requirement. Primary stage of treatment plays a major role in the removal of SS that contributes to the reduction of O&G, COD and BOD (Bhatti *et al.,* 2009). The reduction of some pollutants in the primary stage could enhance the performance of next stages of treatment due to reduction of pollutants concentration (Hatton & Simpson, 1985).

Coagulation is the usual process used in the primary stage of treatment. It is a chemical treatment process for destabilizing and aggregating colloidal particles to form flocks for the removal of pollutants. Chemicals are added to the water to promote aggregation as well as precipitation of suspended particles (Amuda & Amoo, 2007; Zaied & Bellakhal, 2009). The common metal salt used for the treatment includes aluminum sulphate (alum), aluminum chloride, ferric sulphate, ferric chloride and ferrous sulphate. Different coagulants used will affect a different degree of stabilization

of colloidal particles (Qasim, Motley, & Zhu, 2006). Coagulation technique is widely employed to treat various types of water and wastewater such as drinking water (Trinh & Kang, 2011), landfill leachate (Ntampou, Zouboulis, & Samaras, 2006), olive mill effluent (Ginos, Manios, & Mantzavinos, 2006), and paper recycling wastewater (Wang, Chen, Ge, & Yu, 2007). The treatment was proven to possess high removal efficiency in different parameters mainly SS and COD (Guida *et al.*, 2007).

However, limitation of the coagulation technique is the possible generation of secondary pollutants resulting from additional excess of chemicals during the treatment (Feng *et al.*, 2007). The excess chemicals in the water treated inhibit anaerobic digestion in the second stage of treatment (Phalakornkule *et al.*, 2010a). Moreover, an addition of chemicals could result in the increase of total dissolved solids (TDS) which will increase the cost of treatment (Alaadin, 2008). Therefore, there is a need to have an alternative process that could effectively remove SS and other related pollutants at low capital and operation costs.

Many researchers have carried out modification and development of an efficient treatment especially to treat heavy wastewater such as POME that contains high concentration of SS, COD, and BOD (Agustin *et al.*, 2008; Ahmad *et al.*, 2005; Ahmad *et al.*, 2006; Borja *et al.*, 1996). The modification is to enhance the effectiveness of existing coagulation process so that excess chemical consumption will be reduced thereby minimizing treatment cost. A possible process that can promise efficient pollutant removal is electrocoagulation (EC) (Kobya *et al.*, 2003). EC is a simple and efficient method where flocculating agent is generated by electro-oxidation of sacrificial anode, usually made of iron or aluminum (Adhoum *et al.*, 2004). No addition of chemicals is required because dissolution of metal ions performs a similar function as

the coagulant which neutralizing the charge of particulate and facilitates agglomeration of flocks towards the surface of water (Butler *et al.,* 2011). Moreover, the EC process was found to be a more efficient and practical approach to preserve the environment; it is simple in design and operation, and does not generate secondary pollution into the water treated (Agustin *et al.,* 2008; Kobya *et al.,* 2006). Therefore, treatment of POME using the EC process will be investigated in this present study with the aim to reduce total suspended solids (TSS).

1.2   Problem Statement

Suspended solids in POME are generated during extraction process of palm oil containing palms fibre (Rupani *et al.,* 2010). The extraction process requires huge amount of water as for every 1 tonne of crude palm oil produced 5 to 7.5 tonnes of water is consumed with more than 50% of the water will end up as POME (Ahmad *et al.,* 2003). POME is a colloidal suspension containing about 95-96 % of water, 0.6-0.7 % of O&G, and 4-5 % of total solids (Ahmad *et al.,* 2006). In the conventional treatment method, the suspended solids are removed by gravity settling in a pond within 24 hours (Leong *et al.,* 2002). The long retention time has called for the need of other alternative treatment processes. One of the promising treatment processes that can be examined is electrocoagulation (EC).

Studies on POME treatment using EC process are scarce in Malaysia. EC has been proven to remove suspended solids as high as 99% from wastewater without the addition of chemicals (Gürses *et al.,* 2002; Solak *et al.,* 2009). Therefore, the feasibility of EC process in treating POME for the removal of TSS and COD will be investigated together with the determination of optimum operating parameters involved during the

treatment. Understanding the whole process will help in the innovation and development of an efficient wastewater treatment which can be applied in the POME treatment plant and comply with the standard regulation. Most importantly it will also aid in preserving the environment while keeping the economy growing (Rupani *et al.,* 2010). Other than that, the performance of EC process will be compared with chemical coagulation (CC) process as CC treatment is widely used for other wastewater treatment.

1.3   Scope of Work

POME contained high concentrations of TSS, COD and BOD. However, this study will explore the feasibility of EC process in removing TSS and COD from POME. Statistics has shown that 4 - 5% of POME colloidal suspensions are SS (Ahmad *et al.,* 2006). In addition, the reduction in TSS level also has a potential to reduce other pollutants such as COD, BOD and O&G.

The effect and the optimum operational parameters namely initial pH, current density, stirring speed, temperature and operating time of EC process are investigated by examining the optimal removal efficiency of the TSS and COD. As comparison, CC process will be performed to drawn on the EC performance. The protocols outlined in standard method for examination of water and wastewater (APHA, 1992) is adopted for the determination of the TSS and COD.

1.4   Objectives of Research

The research objectives are to:

- Investigate the effect of various parameters namely initial pH, current density, stirring speed, temperature and operating time on the removal of TSS from POME using electrocoagulation process.

- Determine the optimal operating conditions of the electrocoagulation process for TSS and COD removal from POME.

- Compare the performance of electrocoagulation process with chemical coagulation process using $Al_2(SO_4)_3$ with difference dosage.

1.5   Thesis Outline

Chapter 1 introduces the background of study, problem statement, scopes of work, and research objective. Chapter 2 elaborates on the literature review of the coagulation and electrocoagulation (EC) process, mechanisms of coagulation and EC process, parameter affecting performance of EC process, merits and demerits of EC, and the application of EC in wastewater treatment.

Chapter 3 explains about the materials and methods used for the EC and CC process. Samples were taken from the middle of the supernatant after settling of 1 hour for analysis. Analysis of sample to determine the TSS and COD is carried out according to the standard method, APHA 1992. Chapter 4 will discuss and elaborate the results obtained from the experiments. Chapter 5 draws a conclusion from the findings and some recommendations for future work will be made to improve the study.

CHAPTER 2

LITERATURE REVIEW

2.1   Introduction

Electrocoagulation (EC) process in recent years has attracted attention in various kinds of effluent treatment due to its versatility and environmental compatibility (Umran *et al.,* 2009). The treatment function is similar with chemical coagulation (CC) except that the coagulant in EC process is provided from dissolution of sacrificial electrode (Butler *et al.,* 2011). EC process is efficient in removing suspended solids (SS) as well as oil and greases (O&G) in the wastewater (Xu & Zhu, 2004). Introduction of highly charged polymeric metal hydroxide species neutralizes the electrostatic charge on SS and oil droplet to facilitate agglomeration or coagulation (El-Naas *et al.,* 2009). Removal of SS and O&G can also be attributed to the removal of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) (Uğurlu *et al.,* 2008). In addition, EC is established to successfully remove other pollutants such as heavy metal (Hanay & Hasar, 2011), dyes (Adhoum & Monser, 2004; Alinsafi *et al.,* 2005), and phenol (Adhoum & Monser, 2004).

EC process is an electrochemical technique that has found many applications, especially as it relates to removal of dissolved particles and suspended mater from an aqueous solution (Emamjomeh & Sivakumar, 2009). The EC process involves applying an electrical current to an electrode material in the medium to promote aggregation of pollutants without the addition of coagulations (Butler *et al.,* 2011; Ugur *et al.,* 2008).

The electrical current provides electromotive force to drive the chemical reactions and neutralizes the particulates by formation of hydroxide complexes for the purpose of forming flocks. The flocks formed in the water are transported by gas bubbles generation at the cathode towards the surface where they can easily be removed (Khoufi *et al.,* 2007).

The EC process has remained basically the same until today, with use of different electrode materials such as cast iron (Inan *et al.,* 2004), stainless steel (Arsalan-Alaton *et al.,* 2008), aluminum (Tir & Moulai-Mostefa, 2008) or graphite (Sriransan *et al.,* 2009) for the treatment of varied types of industrial and non-industrial based effluents. Moreover, the dynamics of the process requires variation in the parameters with view of enhancing the treatment efficiencies. A vast number of scientific works have employed EC process such as textile wastewater (Kabdaşlı *et al.,* 2009; Merzouk *et al.,* 2010), pulp and paper mill wastewater (Uğurlu *et al.,* 2008; Vepsäläinen *et al.,* 2011), biodiesel wastewater (Sriransan *et al.,* 2009), oily wastewater (Inan *et al.,* 2004; Umran *et al.,* 2009) and paint manufacturing wastewater (Akyol, 2011). From the literature, it was observed that the process variables include electrode material, current density, pH, conductivity, and operating time (Akbal & Camci, 2011; Moreno-Casillas *et al.,* 2007).

Even though many wastewaters have been treated using EC process, there are limited publications on the treatment of palm oil mill effluent (POME). Recently, Phalakornkule *et al.* (2010a) reported on POME treatment using EC and found that the treatment removed 53% of SS, 72% of O&G, and 64% of COD in the optimum conditions. However, the data presented was not enough to confirm the optimal parameter involved in POME treatment. Further study is required to support the data

and to investigate other parameters that can enhance removal efficiency during treatment. The characteristic of POME which contains high concentration of SS is suitable for EC process application as reported in the literature (Agustin *et al.,* 2008; Phalakornkule *et al.,* 2010a).

2.2   Suspended Solids in Wastewater

Suspended solids (SS) are particles that are visible and in suspension in the water. They are held in the water column of a stream, river, lake or reservoir by turbulence (Bilotta & Brazier, 2008). The SS may contain up to 70% of organic solids and 30% of inorganic solids, which include floating particles consisting of sand, clay, grit, fecal solids, paper, pieces of wood, particles of food and garbage and similar materials (Vik *et al.,* 1984).

In POME, SS are made up of palm fibre and oil produced from three major processing operations such as sterilization of fresh oil palm fruit bunches, clarification of palm oil and hydrocyclone operations (Rupani *et al.,* 2010). The discharge of wastewater containing SS without treatment can cause a decrease in the transparency and reduction of dissolved oxygen in the water (Bilotta & Brazier, 2008; Inoue *et al.,* 2009). Thus, it may contribute to eutrophication and algae blooms that will affect aquatic living.

In Malaysia, there are regulatory standard that must be complied by industries before allowing their discharges into main water bodies. The regulatory standard of effluent is classified into three categories; Standard A for effluent discharged at upstream of water supply intake, Standard B for effluent discharge at downstream and

standard "C" for parameter limits other than standard A and B (Appendix 2) (Environmental Quality Act 1974, 2005). Parameter limits of effluents for SS and COD are presented in **TABLE 2.1**.

TABLE 2.1. Parameter limits of effluents of standard A, B and C (Environmental Quality Act 1974, 2005)

Parameter	Unit	Standard		
		A	B	C
SS	mg/L	50	100	400
COD	mg/L	50	100	1000

2.3   Introduction of Chemical Coagulation

Removal of SS and other pollutants are usually carried out by chemical coagulation. Chemical coagulation (CC) is a chemical treatment process used for destabilizing and aggregating colloidal particles (Ahmad *et al.,* 2006). It is widely applied in the broad range of water and wastewater treatment plant with high removal efficiency of various parameters mainly chemical oxygen demands (COD) and suspended solids (SS) (Ahmad *et al.,* 2006; Guida *et al.,* 2007; Emamjomeh & Sivakumar, 2009). The removal of pollutants through growing flocks is a result of particles collisions due to destabilization of colloidal particles (Metcalf & Eddy, 2004) where the chemicals are added to the water or wastewater to promote aggregation as well as precipitation of suspended particles (Amuda & Amoo, 2007; Zaied & Bellakhal, 2009).

Metal salt such as aluminum sulphate (alum), aluminum chloride, ferric sulphate, ferric chloride and ferrous sulphate are conventionally used as coagulant reagent (Qasim *et al.,* 2006). Different degrees of stabilization are affected by different coagulants. These coagulants provide positive charge to stabilized negative charge of

particulates. The forces acting between coagulants and colloids are illustrated in **FIGURE 2.1**.
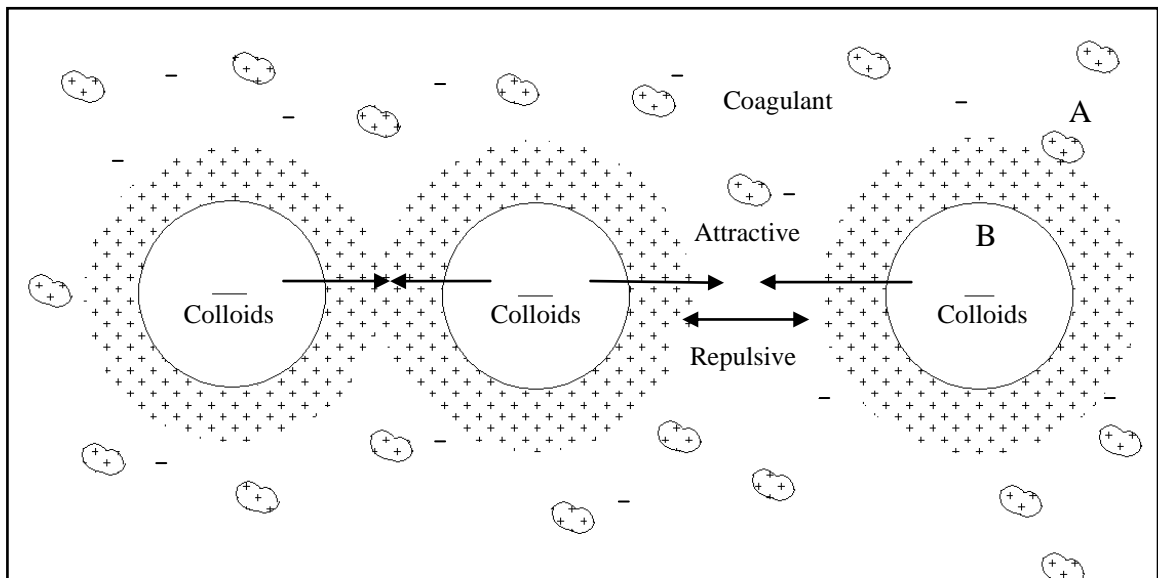
FIGURE 2.1. Reaction between coagulants and colloids (Mark & Mark, 2001).

Highly charged hydrolyzed metal ions (A) produced by metal salt reduce the repulsive force between colloids (B) by compressing the diffuse layer surrounding individual particles. With the forces of repulsion suppressed, a gentle mixing results in particle contact, and the forces of attraction cause particles to stick to each other and finally produce aggressive agglomeration (Mark & Mark, 2001). The higher the valence of the counter-ion, the more of its destabilizing effect and less dosage needed for coagulation (Al-Malack *et al.,* 1999).

In addition, to enhance the coagulation process, polymeric addition (long molecular chain organic compounds) has been utilized (Qasim *et al.,* 2006). It contained adsorbing group which help to form bridges between the flocks to increase the flocks size of the coagulated particles (bridging flocculation) (Menezes *et al.,* 1996). Furthermore, the addition of the polymer can minimize the residual metal salt in the water treated (Guida *et al.,* 2007). **FIGURE 2.2** shows agglomeration resulting from

coagulation with metal salt and polymer aid. Polymer (A) provides bridging between the particles by attaching themselves to the absorbent surfaces of colloids. The particles are attached together and larger flocculated masses are built (Mark & Mark, 2001).
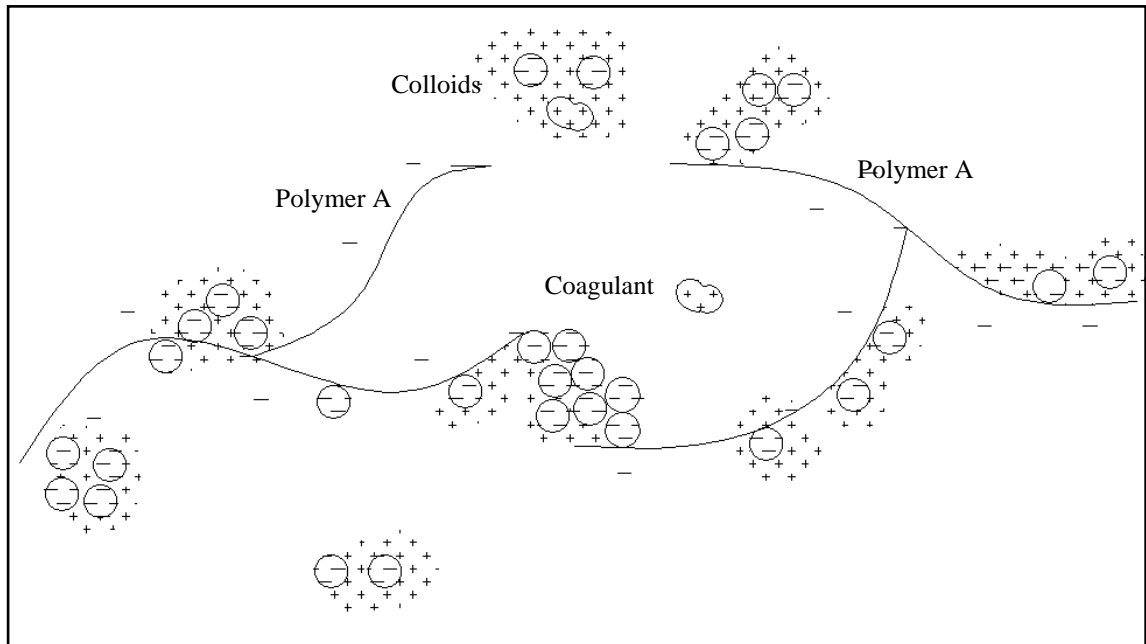
FIGURE 2.2. Agglomeration resulting from coagulation with metal salt and polymer aid (Mark & Mark, 2001).

2.3.1   Mechanisms of Chemical Coagulation Process

Several mechanisms are involved in the coagulation process, namely (i) ionic layer compression; the surface charge on a colloid attracts the opposite charge or counter-ions and finally agglomerates into flock; (ii) adsorption and charge neutralization; the counter-ion from coagulant is adsorbed onto the surface of the colloidal particles which in results neutralization between the repulsive charge on the surface of the particles and charge carried by the counter-ion; (iii) interparticle bridging; when the polymer is utilized as flocculation aid which provides specific sites of adsorption for colloidal or coagulant particles; and (iv) colloid entrapment; entrapment or enmeshment of small

particles in the hydroxide flock structure due to excessive metal salt to neutralize the colloidal particles (Ahmad *et al.,* 2006; Metcalf & Eddy, 2004).

These mechanisms are very important in forming flocks of residue oil and suspended solid which can easily settle and finally be removed (Ahmad *et al.,* 2006).

2.3.2 Application of Chemical Coagulation Process

The treatment of numerous wastewaters using CC has been reported where the removal efficiency of SS are in the range between 80% - 90% (Alaadin, 2008). Yet, report on treatment of POME using CC is scare. Ahmad *et al.* (2006) conducted a study on POME treatment using CC process with addition of chitosan, alum and PAC. The study established that the performance of chitosan was comparatively more efficient and economical as compared with alum and PAC. Chitosan is a cationic biodegradable biopolymer produced by the extensive deacetylation of chitin obtained from shrimp shell wastes. At the optimum experiment conditions, 95% of suspended solids and residue oil were removed by chitosan.

Amuda & Amoo (2007) investigated treatment of an industrial wastewater from the beverage industry using ferric chloride and polyelectrolyte. They attained with the addition of ferric chloride a removal in COD, total phosphate (TP), and TSS of 91, 99, and 97% respectively. The combined usage of coagulant and polyelectrolyte (25 mg/L) resulted in the reduction of 60% of sludge produced, compared when coagulant was solely used for the treatment.

However, the major disadvantage of chemical coagulation is the possibility of the production of secondary pollutants (chloride, sulphate in the coagulation-precipitation) in the wastewater due to additional excess of chemicals during the treatment (Akyol, 2011; Phalakornkule *et al.,* 2010a; Tchamango *et al.,* 2010). Moreover, depending on the volume of wastewater treated, the cost for treatment might be expensive (Butler *et al.,* 2011). Literature reports suggest that the cost of chemical coagulation is four times higher than EC (Phalakornkule *et al.,* 2010a). This is associated to the low efficiency in removing light and finely dispersed particles which result in an increment of total dissolved solids in the wastewater (Alaadin 2008; Chen *et al.,* 2000; Xu & Zhu, 2004).

2.3.3 Other Methods

Various treatment methods have been applied for the removal of SS from wastewater and the efficiencies of removal differed significantly. Other treatment methods that have been applied especially for POME treatment are discussed below and summarized in **TABLE 2.2**.

TABLE 2.2. Summary of other treatment method for POME.

Treatment method	Advantages	Disadvantages
Ponding System	• Easy to operate and requires low operating cost.	• Requires long treatment time and large treatment space. • Dispersion of methane gas to atmosphere and contribute to air pollution and greenhouse effect.
Biological treatment	• Minimum energy demands due to application of microbes to digest pollutants. • Less sludge production and no unpleasant odour is released. • Has a great potential for energy recovery from generated biogas.	• Does not work for wastewater containing tannins and phenolic compounds due to its potential to inhibit the anaerobic digestion efficiency. • Requires large space area for facilities and skilled technician to control the operations.
Membrane separation technology	• More uniform quality of treated wastewater and applicable for wide range of industries wastewater. • The plant is highly automated and does not require high skilled operators.	• The membrane suffering from fouling and degradation during use due to accumulation of suspended solids.

2.3.3.1 Ponding System

Most of palm oil mills employing ponding system for treatment of POME (Choong, 2012). In Malaysia, more than 85% of palm oil mills adopt this system due to their low cost and easy to operate (Wu *et al.,* 2010). However, it features have some disadvantages such as occupying a vast amount of land mass, long retention time of 45 to 60 days for effective performance, bad odour and dispersion of methane gas that contributes to air pollution and greenhouse effect (Rupani *et al.,* 2010). All those issues were arises when applying this method because there was no alternative option has been introduced to the operators for POME treatment.

2.3.3.2 Biological Treatment

Many studies have investigated the biological treatment under aerobic or anaerobic conditions in the successful removal of SS, COD and other pollutants (Adhoum & Monser, 2004; Al-Shamrani *et al.,* 2002; Vepsäläinen *et al.,* 2011). The biological treatment is suitable for wastewater containing organic substance which is generally biodegradable. The advantages of applying biological treatment is minimum energy demands, less sludge formations, no unpleasant odour, and production of methane gas due to efficient break down of organic substances by anaerobic bacteria (Rincón *et al.,* 2006). The rapid disintegration of organic matter by anaerobic digestion process has a potential for energy recovery because the generated biogas can be used in electricity generation and save fossil energy (Linke, 2006).

However, the treatment is less efficient for wastewater containing high organic load especially tannins and phenolic containing compounds because they potentially inhibit the efficiency of anaerobic digestion (Vepsäläinen *et al.,* 2011). Moreover, it requires skilled technicians to control the operations and a large space for the facilities where the typical size of an anaerobic pond with processing capacity of 54 tonnes per hour is $60.0 \times 29.6 \times 5.8$ m (length $\times$ width $\times$ depth) which is approximately half the size of a football field (Chen *et al.,* 2000; Poh & Chong 2009; Yacob *et al.,* 2006).

In the case of POME, treatment using biological method sometimes does not meet the discharged requirement standard of 400 mg/L TSS and 100 mg/L of BOD (Ibrahim, 2009; Wu *et al.,* 2010). In other words, the treatment of POME that relies on biological treatment is insufficient to remove the pollutants, thus contributing to the environmental pollution issues. Hence, a few stages of treatment that can suit with

POME are required such as treatment for SS reduction where it could enhance the efficiency of other stages.

2.3.3.3 **Membrane Separation Technology**

Membrane separation technology such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis is a process that is increasingly being used for the purpose of recovery and recycling of water (Cheryan & Rajagopalan, 1998). The advantages of this method are the quality of treated wastewater is more uniform regardless of the influent variations; it is applicable for wastewater from a wide range of industries; it has the ability to be used as *in situ* process for recycling of selected waste stream within the plant; and the plant can be highly automated and does not require high skilled operators (Cheryan & Rajagopalan, 1998).

Even though this process has potential to eliminate environmental problems, there are limitations in applying this method especially for wastewater containing high suspended solids. The membrane suffers from fouling and degradation during use and this will consequently interfere with the process flow (Ahmad *et al.,* 2003; Wu *et al.,* 2007). The application of membrane separation technology still can be applied in POME treatment but pre-treatment for TSS reduction is required. Therefore, it can be suggested that this process can be placed at the end of POME treatment before discharging into the environment since 78% of water recovery from POME was reported (Ahmad, Chong, *et al.,* 2006).

Even though this enumerated treatment methods have been applied for POME treatment, yet there are still some limitations for each treatment especially in TSS

removal such as long retention time and inefficient removal process. Thus, there is a need to have an alternative process which is more effective and practical in removing pollutants with relatively low capital and operational costs.

2.4 Introduction of Electrocoagulation

Since the application of CC during treatment can cause secondary pollutant in the treated wastewater, many researchers have proposed some modifications to enhance the efficiency of CC process (Can *et al.,* 2006; Cañizares *et al.,* 2008; Phalakornkule *et al.,* 2010a). The removal of residue particles and suspended solids in a short time and in an economic way were the purpose of the studies. Some researchers have found that the introduction of an electric current in the medium to destabilize the particles (electrocoagulation) seemed more effective than the conventional one (Cañizares *et al.,* 2008; Phalakornkule *et al.,* 2010a).

EC is a process of creating metallic hydroxide within the water by electro-dissolution of sacrificial electrode (Konstantinos *et al.,* 2011; Mouedhen *et al.,* 2008). The operation of EC is based on the fact that the stability of colloidal particles, suspension and emulsions is influenced by electrical charges (Yildiz *et al.,* 2007). In theory, the EC has advantages in removing the finest colloidal particles; the finest charged particles have a greater probability of being coagulated because of the electrical field that sets them in the motion (Gürses *et al.,* 2002). Therefore, application of this process to treat POME will be carried out by investigating the reduction of TSS and other pollutants from wastewater.

2.4.1 Electrocoagulation Reactor Set-up

A simple EC reactor is made up of electrolytic cell with one anode and one cathode, where both of them are immersed inside the medium. A DC power source supplies the current density necessary to run the process (Mollah *et al.,* 2001). The conductive metal plate, anode and cathode are made from the same or different materials where iron and aluminum are generally used. The system is also equipped with a stirrer to mix the medium homogenously. **FIGURE 2.3** illustrates the set-up of the EC reactor and the reaction during the treatment (Akbal & Camci, 2011).
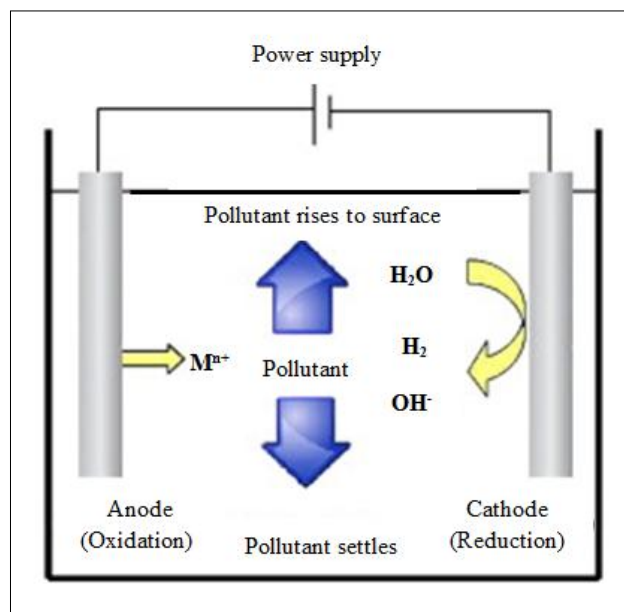
FIGURE 2.3. Set-up of EC reactor and reaction
during the treatment (Akbal & Camci, 2011).

When external power source is connected, anode material will be electrochemically corroded due to oxidation, while the cathode will be subjected to passivation (Xu & Zhu, 2004). The reaction (2.1) to (2.3) will occur during EC process:

$$\text{Anode} \quad : \qquad \qquad M \rightarrow M^{3+} + 3e^- \qquad \qquad \qquad (2.1)$$

$$\text{Cathode} : \qquad \qquad 3H_2O + 3e^- \rightarrow 3/2 \ H_2 + 3OH^- \qquad \qquad (2.2)$$

$$\text{Solution} : \qquad \qquad M + 3H_2O \rightarrow M(OH)_3 + 3H^+ \qquad \qquad (2.3)$$
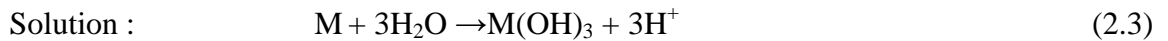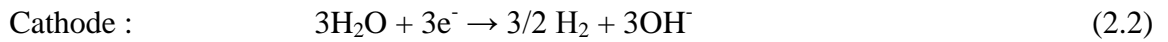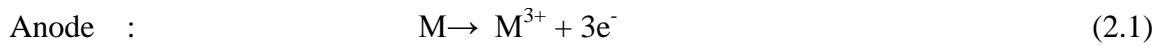
Dissolution of metal ions from sacrificial electrode will coagulate with the pollutant in the water in a manner similar to conventional method where the addition of coagulants such as alum or ferum chloride allows for aggregation of colloids and flocks formation. Gas bubbles generation at cathode helps the flocks to float towards the surface of the solution. There are three main mechanisms involved in the whole of EC process such as electrode oxidation, gas bubbles generation and flotation and sedimentation of flocks (Emamjomeh & Sivakumar, 2009; Zaied & Bellakhal, 2009).

2.4.2 Mechanisms of Electrocoagulation Process

Mechanisms of EC process have been discussed extensively in previous literature (Ilhan *et al.,* 2008; Sadeddin *et al.,* 2011). Chemical reactions during the process are shown in equation (2.4) until (2.15). When a direct current passes through anode material, (aluminum for instance) it will dissolve to Al^{3+} ions (2.4). OH^- ions will be released during cathodic reaction at the side of the cathode resulting in increases of pH in the water. In addition, vigorous H_2 bubbles production will be observed according to equation (2.5) (Inan *et al.,* 2004).

$$\text{Anode} \quad : \qquad \qquad Al \rightarrow Al^{3+} + 3e^- \qquad \qquad \qquad (2.4)$$

$$\text{Cathode} : \qquad \qquad 3H_2O + 3e^- \rightarrow 3/2 \ H_2 + 3OH^- \qquad \qquad (2.5)$$

$$\text{Solution} : \qquad \qquad Al + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \qquad \qquad (2.6)$$
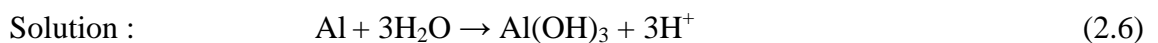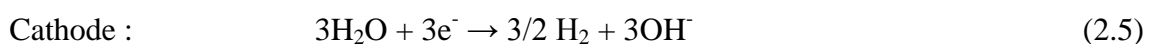
At high pH values, the cathode might be chemically attacked by OH$^-$ ions generated during H$_2$ evolution (Kobya *et al,* 2008):

$$2Al + 6H_2O + 2OH^- \rightarrow 2Al(OH)_4^- + 3H_2 \qquad (2.7)$$
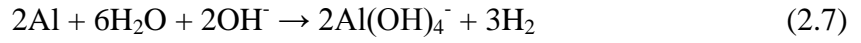
Generated Al^{3+} and OH$^-$ ions will undergo spontaneous hydrolysis reactions to form various monomeric species such as Al(OH)$^{2+}$, Al(OH)$_2^+$, Al$_2$(OH)$_2^{4+}$, Al(OH)$_4^-$ and polymeric species such as Al$_6$(OH)$_{15}^{3+}$, Al(OH)$_{17}^{4+}$, Al$_8$(OH)$_{20}^{4+}$, Al$_{13}$O$_4$(OH)$_{24}^{7+}$, Al$_{13}$(OH)$_{34}^{5+}$, which will finally transform into Al(OH)$_3$(s), according to complex precipitation kinetics (Kobya *et al.,* 2003; Zaied & Bellakhal, 2009).

Freshly formed amorphous Al(OH)$_3$(solid) known as "sweep flocks" have large specific area, which are beneficial for rapid adsorption of soluble organic compounds and trapping colloidal particles. Therefore, these flocks are removed easily from aqueous medium by sedimentation or with the help of H$_2$ flotation (Bayramoglu *et al.,* 2004; Kobya *et al.,* 2003; Zaied & Bellakhal, 2009).

Besides that, in the case of iron electrodes, it produces ferum hydroxide, Fe(OH)$_n$ upon oxidation in an electrolytic system where n is 2 or 3 by means of the following two reaction mechanisms:-

Mechanism 1

Anode :	$4Fe \rightarrow 4Fe^{2+} + 8e^-$	(2.8)
Anode :	$4Fe^{2+} + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 8H^+$	(2.9)
Cathode :	$8H^+ + 8e^- \rightarrow 4H_2$	(2.10)
Overall :	$4Fe^{2+} + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 4H_2$	(2.11)

Mechanism 2

Anode	:	$Fe \rightarrow Fe^{2+} + 2e^-$	(2.12)
Anode	:	$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$	(2.13)
Cathode	:	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	(2.14)
Overall	:	$Fe + 2H_2O \rightarrow Fe(OH)_2 + H_2$	(2.15)
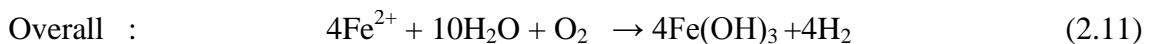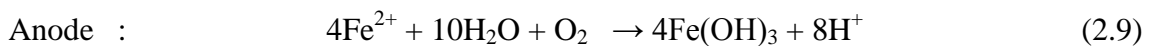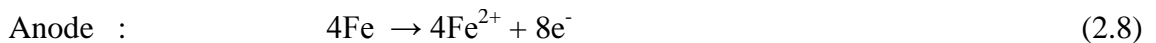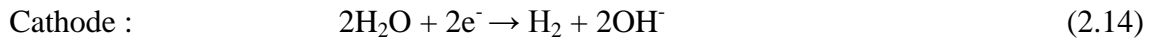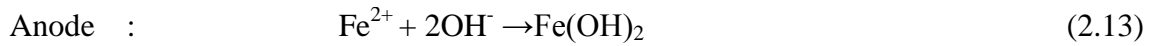
The electro parts are contributed in reaction (2.8), (2.10), (2.12) and (2.14). The rest are coagulation between the coagulant and colloidal particles. Similarly, ferric ions generated by electrochemical oxidation of iron electrode may form monomeric ions, and polymeric hydroxyl complexes, namely $Fe(H_2O)_6{}^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)_2{}^+$, $Fe_2(H_2O)_8(OH)_2{}^{4+}$, and $Fe_2(H_2O)_6(OH)_4{}^{4+}$ depending on the chemistry of the aqueous medium, especially its conductivity (Ilhan *et al.,* 2008; Zaied & Bellakhal, 2009).

Hydrolysis reactions (2.4) to (2.15) will cause the acidic surrounding of anode which attributed to the production of H^+. Meanwhile at the cathode, the evolution of hydrogen and production of OH^- ions will make the surrounding basic (Khoufi *et al.,* 2007; Mouedhen *et al.,* 2008).

The mode of action of the generated aluminum and ferum species in EC process can be explained by two mechanisms involved, charge neutralization and incorporation of impurities in the amorphous hydroxide precipitation ("sweep flocculation") (Mouedhen *et al.,* 2008). At the end of the mechanisms, the floating flocks will be removed.

2.5 Parameters Affecting Performance of Electrocoagulation Process

The optimum pollutant removal especially TSS may be achieved through optimum operating parameters of EC process. The parameters affecting performance of wastewater treatment includes electrode materials, pH, conductivity, current density, and operation time. All these parameters are explained below.

2.5.1 Electrode Material

Selection of appropriate electrode material is important to ensure effectiveness of removal during the EC treatment. Moreover, it is a key issue for reactor designs which focuses on high activation energies to avoid undesired side-reaction during the treatment process (Deng & Englehardt, 2007). Various electrode materials have been used for the treatment such as aluminum, iron, graphite, mild steel, and carbon. However, the most widely used material reported for sacrificial electrodes in EC are aluminum and iron because they are cheap, readily available and proven to be effective (Kobya *et al.,* 2003; Umran *et al.,* 2006). **TABLE 2.3** presents the advantages and limitations of two outstanding electrodes: aluminum and iron electrodes.

TABLE 2.3. Advantages and limitations of aluminum and iron electrodes.

Type	Advantages	Limitations
Aluminum	• Most effective in neutral and weak acidic medium (Bayramoglu *et al.,* 2004; Inan *et al.,* 2004). • Higher removal efficiency of suspended solids, turbidity, colour and several heavy metals such as copper and zinc (Hanay & Hasar, 2011; Katal & Pahlavanzadeh, 2011; Kobya *et al.,* 2006). To enhance removal efficiency, addition of supporting electrolyte is required (Kabdaşlı *et al.,* 2009). • Tendency of flocks settling is higher as compared with iron flocks (Kabdaşlı *et al.,* 2009)	• Waste of energy and increasing applied potential of EC due to existence of oxide film on electrode (Mouedhen *et al.,* 2008). • Less effective in alkaline medium (Inan *et al.,* 2004)
Iron	• Most effective in neutral and weak alkaline medium (Bayramoglu *et al.,* 2004; Inan *et al.,* 2004). • More efficient in energy consumption (Kobya *et al.,* 2003; Phalakornkule *et al.,* 2010a). • High removal efficiency of COD due to collective effect of EC and electro-oxidation which occur simultaneously during EC treatment (Kobya *et al.,* 2003). • Three times cheaper compared with aluminum(Kobya & Delipinar, 2008)	• Formation of yellow and brown colour in water treated resulting from iron electrode dissolution (Kobya & Delipinar, 2008; Sadeddin *et al.,* 2011; Zongo *et al.,* 2009). • Less effective in acidic medium (Inan *et al.,* 2004)

There are various findings on the best electrode material for EC treatment. According to Kobya *et al.* (2003) and Ilhan *et al.* (2008), aluminum electrode is chosen as the best and most effective removal of pollutants. It may be because of the high adsorption capacity of hydrous aluminum oxides (Emamjomeh & Sivakumar, 2009). Kobya *et al.* (2003) studied the treatment of textile wastewater using EC process and proved that the aluminum electrode is more effective as compared with iron electrode. Aluminum electrode quadruples the removal efficiency of iron electrode with respect to

turbidity due to interference from colour of dissolved iron (Kobya & Delipinar, 2008). The colour is a resulted from the *in situ* dissolution of Fe^{2+} and Fe^{3+} ions in the water treated. Due to the high solubility of Fe^{2+} at acidic or natural conditions, Fe^{2+} can easily be oxidized into Fe^{3+} in water containing oxygen (Kobya *et al.,* 2003; Kobya & Delipinar, 2008; Kobya *et al.,* 2006). Furthermore, high numbers of iron ions in the wastewater cause a high amount of sludge after the treatment (Ilhan *et al.,* 2008). In the case of aluminum, the tendency of these flocks settling is more than the iron flocks. This provides the added advantage of reusability of treated effluent water with less iron content. On the other hand, the aluminum electrodes are found to be more efficient in the removal of colour in the presence of high NaCl concentrations (Kabdaşlı *et al.,* 2009; Zongo *et al.,* 2009).

However, iron electrode is reported to be more efficient in COD reduction as compared to aluminum electrode (Katal & Pahlavanzadeh, 2011). This is because of the difference in mechanisms for COD removal between aluminum and iron electrodes. The COD removal from wastewater using aluminum electrodes are mainly by EC, but when using iron electrodes, the removal is due to the collective effect of EC and electro-oxidation (Kobya *et al.,* 2003). Furthermore, the cost of treatment using iron electrode is three times cheaper than aluminum electrode as the cost of treatment increases with the increase of operating time. However, this is argued by Akyol, (2011), where the iron electrode is found to be two times more expensive than aluminum electrode in the optimum conditions. The difference in cost is related to a high amount of electrode consumption when iron is used. A comparison of the two electrodes by Zongo *et al*., (2009) for the same treatment shows that more quantity of iron is consumed relative to aluminum.

Another electrode material like stainless steel is compared where the latter proved to be more efficient in the dye colour removal (Arslan-Alaton *et al.,* 2009). It could be because of the relatively short EC time and presence of reactive dye auxiliaries (Kabdaşlı *et al.,* 2009). Furthermore, Golder *et al.* (2010) have shown the capability of stainless steel through the removal of colour up to 90 – 98% in less than 60 minutes and the usage of lower current density as compared to aluminum electrodes. The low sludge formation after the treatment is also observed (Arsalan-Alaton *et al.,* 2008).

Meanwhile, the performance efficiency of graphite cathode and aluminum anode by Sriransan *et al.* (2009) reports a significant reduction of O&G and SS by more than 95% for biodiesel effluent. The sludge production is less as compared with the conventional methods and is easy to remove from treated wastewater.

Even though different electrode materials gives different degree of removal efficiencies, most literature reports agree that aluminum is the best electrode material to be used as anode and cathode in the EC process (El-Naas *et al.,* 2009; Emamjomeh & Sivakumar, 2009; Kobya *et al.,* 2003). This is confirmed by the removal efficiency and operating cost of treatment which is more efficient and cheaper in comparison with other electrode materials (Akyol, 2011).

2.5.2   pH of Wastewater Treatment

pH is an important factor that influences the performance of the EC process in the water and wastewater treatment (Aji *et al.,* 2011.; Kobya *et al.,* 2006). Depending on the pH of the solution, metal ions would hydrolyze to form either monomeric hydroxide ions or polymeric hydroxide complexes. These polymeric hydroxides which are highly charged

cations destabilize the negatively charged colloidal particles, allowing aggregation and formation of flocks (Alaadin, 2008).

From the literature, most of the wastewaters pH are reported to be in the range of 1.4 to 9 (Kobya & Delipinar, 2008; Umran *et al.,* 2009; Zongo *et al.,* 2009). In order to make it convenient to the electrode used, the pH is adjusted using NaOH or HCl. Precipitation of Fe^{2+} in the form of $Fe(OH)_2$ happens in pH > 6. Since the Fe^{2+} species are unstable in oxygen containing media, it will be oxidised to Fe^{3+} species and finally react with hydroxide ions to form ferric hydroxides which precipitate into flock of brownish colour (Zongo *et al.,* 2009).

Utilization of iron electrodes for the treatment of synthetically prepared waters containing high concentration of natural organics matters was studied by Yildiz *et al.,* (2007). The water was adjusted to pH 9 because the optimum pH of the solution was between 9 and 12, as expected according to the nature of the reaction of Fe^{2+} and OH^- ions. Efficiency of the treatment was increased by adding supporting electrolyte of Na_2SO_4 whereas the removal efficiency for initial humic substance concentration of 500 mg/L was 92.7% for 70 minutes. Treatment of marble processing wastewater by Solak *et al.* (2009), was successful in removing 99% of SS at optimum pH of 8 and current density of 20 A/m^2 within 2 minutes.

For aluminum electrode, the suitable pH is below 6.5 as pH higher than 6.5 decrease the removal rate. This is due to the increased amount of hydroxide ions in solution where it was probably oxidized at the anode. This action prevents the production of the same proportion of aluminum ions and therefore it results in the reduction of removal efficiency. However, at low pH of 2 - 3, cationic monomeric

species, Al^{3+} and $Al(OH)_2^+$ predominate. When pH is between 4 and 9, the Al^{3+} and OH^- ions generated by the electrodes react to form various monomeric species described in section 2.4.2 and finally transform into soluble amorphous $Al(OH)_3$ through complex precipitation kinetics (Merzouk *et al.,* 2009). Since the process leads to the formation of metal hydroxide as net final product, the pH will increase after the treatment (Kobya *et al.,* 2006; Phalakornkule *et al.,* 2010a). Therefore, amphoteric character of $Al(OH)_3$ does not precipitate at very low pH, meanwhile at high pH, it leads to the formation of $Al(OH)_4^{-}$ which is insoluble and does not contribute to wastewater treatment (Katal & Pahlavanzadeh, 2011).

pH can be adjusted to the optimum level in order to achieve higher efficiency of coagulation and flotation. The adjustment can be made depending on the electrode materials that will be used (Merzouk *et al.,* 2010). From literature, it is shown that for pH ranged between 4 to 7, aluminum electrode was recommended, while for wastewater pH in range between 7 to 9, iron electrode is recommended (Kobya *et al.,* 2006; Phalakornkule *et al.,* 2010a). Moreover, it is an advantage for the treatment if the optimal pH values are close to the raw wastewater pH, so that cost associated with pH adjustment are negated (Akyol, 2011; Kobya *et al.,* 2006).

2.5.3   Conductivity

It was reported that increasing wastewater conductivity for EC process is beneficial for the reduction of cell voltage at constant current density due to the decrease of the ohmic resistance of wastewater (Kabdaşlı *et al.,* 2009). The higher conductivity of medium accounts for the easy dissolution of metal ions, while at lower conductivity, the wastewater undergoes a longer treatment time and consequently wastes a lot of energy

(Ilhan *et al.,* 2008). Therefore, to improve conductivity of wastewater (conductivity less that 6.9 mS/cm), additional supporting electrolyte is required (Umran *et al.,* 2006). The addition is not only to increase the conductivity of wastewater but also to encourage more delivery of coagulant to the medium which results in the reduction of time and energy consumption (Umran *et al.,* 2009). There are three types of supporting electrolytes mostly used with different efficiencies as tabulated in **TABLE 2.4.**

TABLE 2.4. Supporting electrolytes mostly used.

Supporting electrolyte	Description
Na_2SO_4	• More coagulant is delivered to the medium • Provides higher electrical conductivity and contribute to highest removal rate (Yildiz *et al.,* 2007)
$NaNO_3$	• Does not contribute to the formation of flocks, but beneficial for a subsequent biological treatment. It is because $NaNO_3$ provide nitrogen source for use of microorganisms (Phalakornkule *et al.,* 2010a)
NaCl	• Benefit to disinfection of water (Yildiz et al., 2007) • Has a risk of formation of undesirable organo-chlorine compounds due to availability of high chloride ions in the solution (Kabdaşlı *et al.,* 2009; Yildiz *et al.,* 2007)

From the literature, Na_2SO_4 is found to be the most favourable supporting electrolyte because it provides higher electrical conductivity and hence contributes to the highest removal efficiency (Umran *et al.,* 2009; Yildiz *et al.,* 2007). However, the addition of supporting electrolyte may not necessarily translate to increased pollutant removal efficiency even though it may increase wastewater conductivity (Xu & Zhu, 2004). The justification advanced is that the conductivity investigated ranges between 300 to 3500 µS/cm as at this condition the optimal removal efficiency is already achieved. Although the conductivity has little effect on the treatment process it however

reduced the power consumption and operating cost by approximately 75% (Bayramoglu *et al.*, 2004; Chen *et al.,* 2000; Xu & Zhu, 2004).

Conductivity is established to decrease with time as a result of electrochemical treatment. Ilhan *et al.* (2008) studied the treatment of leachate by EC process. The authors found that the conductivity of wastewater decreased from 19.6 to 18.6 mS when the current density was 348 A/m^2 using aluminum electrodes. Therefore, to avoid a drop in the conductivity values, electrical power needs to be increased. A different result was obtained by Chen e*t al.* (2000) in the treatment of restaurant wastewater. Their finding showed the conductivity of wastewater increases and the voltages between electrodes decrease rapidly at a constant current density.

Therefore, it is essential to monitor the conductivity of wastewater so that the treatment uses efficient energy with the optimum removal efficiency of pollutants. As the conductivity increases, the voltage and power requirement decreases which directly reduced the cost and energy consumption (Bayramoglu *et al.,* 2004; Xu & Zhu, 2004). Additional supporting electrolyte is able to increase the conductivity as reported by many literatures since more coagulant is delivered to the medium (Phalakornkule *et al.,* 2010a; Umran *et al.,* 2009).

2.5.4   Current Density

The current density affects the lifespan of electrode material during the EC process (Chen *et al.,* 2000). Different current density results in different consumption rate and removal rate because it is directly related to the coagulant dosage that delivers into the wastewater (Yilmaz *et al.,* 2007). Usually, electrodes are connected to DC power supply

with potentiostatic or galvanostatic operational options for controlling current density (Merzouk *et al.,* 2009; Zongo *et al.,* 2009). Current density is regularly increased linearly with electrolysis voltage and consequently leads to an increase in power requirement (Mouedhen *et al.,* 2008).

Current density not only determines coagulant dosage rate but also H_2 bubbles production rate, size and the flocks growth, which influence the treatment efficiency and the operating cost of the EC process (Kobya & Delipinar, 2008). Increasing the current density increases the H_2 bubbles production but reduces the bubbles size (Adhoum & Monser, 2004). Reduction in bubbles size leads to the increase of specific surface area that increases the number of colloidal particles attached to gas bubbles (Phalakornkule *et al.,* 2010a). Thus, it results in a greater amount of precipitation and removal of TSS and other pollutants in the water treated (Umran *et al.,* 2009).

Moreover, increase in current density could extend the anodic dissolution of electrodes (Umran *et al.,* 2009). It is supported by Faraday's law, where the amount of coagulant or dissolved anodic metal is theoretically and directly proportional to the current density. It is shown in equation (2.16).

$$w = \frac{itM}{ZF} \qquad (2.16)$$

Where, w is the metal dissolved (g), i is the current (A), t is the operating time (s), M is the molecular weight of Al (26.98 g/mol), Z is the number of electrone involved in the redox reaction ($Z_{Al} = 3$), and F is the Faraday's constant (9.65×10^3 C/mol).

Hence, increase in current density results in increase in the amount of metal hydroxide flocks for the removal of contaminants (Chavalparit & Ongwandee, 2009). However, it is recommended to limit the current density to avoid excessive oxygen evolution as well as to eliminate other adverse effects, such as heat generation and waste of energy consumption (Khansorthong & Hunsom, 2009; Merzouk *et al.,* 2009). In addition, literature report indicates that the decrease in removal efficiency at higher current density is the result of the rapid generation of metal ions in comparison to the coagulation process (Katal & Pahlavanzadeh, 2011). The faster removal of metal hydroxide from solution by flotation leads to a reduction of probability of collision between the pollutant and coagulant (Adhoum & Monser, 2004). Therefore, it is beneficial to know the optimum current density for treatment, so that the amount of coagulant released can be controlled efficiently.

A study by Xu & Zhu, (2004) on the treatment of restaurants wastewater by EC process showed that the removal of COD and oil and greases increased with increment of current density. A reduction of 75% of COD and more than 95% of oil and greases were achieved within 30 minutes at a current density of 12 A/m^2. Moreover, Aji *et al.* (2011) reported that EC system was more efficient in a less period of time in the higher current density. It is shown in the removal of 87%, 41%, 39%, and 42% at the current density of 150 A/m^2 within 10 minutes to 90%, 59%, 63% and 66% at current density of 250 A/m^2 for Cu, Mn, Zn, and Ni, respectively.

Therefore, the optimum current density will allow fast removal of pollutants with low electrode consumption during the treatment. The short treatment time also can be achieved through the optimum current density which will consequently increase the efficiency of treatment.

2.5.5　Operating Time

The operating time for EC process varies depending on the type and characteristic of wastewater treated. It also depends on the removal efficiency that needs to be achieved. Determination of optimal operating time is paramount when considering the treatment cost and efficiency (Xu & Zhu, 2004). Beyond the optimal time, the removal efficiency may not increase but the final pH of wastewater may rise due to the greater formation of hydroxide ion at the cathode (Chavalparit & Ongwandee, 2009). **TABLE 2.5** presents various EC treatments of wastewater and respective operating times.

TABLE 2.5. Operating time for various wastewaters.

Wastewater	Operating time (minutes)	Description	References
Municipal wastewater	5	Removal efficiency depending on Fe generated from anode	(Alaadin, 2008)
Textile wastewater		With additional of PAC (Can *et al.,* 2006)	(Can *et al.,* 2006; Phalakornkule *et al.,* 2010b)
Textile wastewater	10 - 15	Al electrodes is capable to remove 40% COD, while SS electrodes remove 50% COD (Arsalan-Alaton, et al., 2008). In acidic medium, removal efficiencies of COD and turbidity using Al electrodes are higher than Fe, while in neutral and weakly alkaline medium, Fe is more efficient (Bayramoglu et al., 2004).	(Arsalan-Alaton *et al.,* 2008; Bayramoglu *et al.,* 2004; Merzouk *et al.,* 2010)
Olive mill wastewater		Using Al electrode, 52% COD removal in 30 minutes, and 90-97% colour removal in 10 minutes	(Inan *et al.,* 2004)
Dairy effluent		61% of COD is removed due to remaining lactose and some other carbohydrate which are not eliminated after treatment	(Tchamango *et al.,* 2010)
Municipal wastewater		Sludge generated decreases more than 50% after addition of H_2O_2	(Ugur *et al.,* 2008)
Pulp paper mill wastewater		Decrease in intra-resistance of solution and increase at the transfer speed of organic species to electrodes explain the higher removal efficiencies of pollutants.	(Uğurlu *et al.,* 2008)
Leachate treatment		Treatment using EC indicates higher removal efficiency compared with chemical coagulation.	(Veli *et al.,* 2008)
Biodiesel production wastewater	20 - 30	Combination using Al (anode) and graphite (cathode) give the best removal efficiency of pollutant in the optimum conditions (Sriransan *et al.,* 2009)	(Chavalparit & Ongwandee, 2009; Sriransan *et al.,* 2009)

TABLE 2.5. Continued

Wastewater	Operating time (minutes)	Description	References
Olive mill wastewater	20 - 30	Final pH of treated wastewater is nearly neutral, thus allowing it to be discharged directly into water body	(Adhoum & Monser, 2004)
Textile wastewater	30 - 40	Used Al electrodes with additional NaCl	(Kabdaşlı et al., 2009)
Vegetable oil refinery wastewater	>60	Required 90 minutes operating time with addition of polyaluminum chloride (PAC) and Na_2SO_4	(Umran et al., 2009)
Olive mill wastewater		Required 180 minutes operating time with addition of coagulant aid and H_2O_2	(Umran et al., 2006)

Therefore, from the **TABLE 2.5**, various operation treatment times are required by various kinds of wastewaters. It is because of the different characteristics of the wastewater, which will take a long time to treat and to achieve the desired level of removal. However, the treatment operation time can be reduced by enhancing the treatment efficiency through the adjustment of a few parameters which can improve the performance of EC during the treatment.

2.6   Advantages and Challenges of Electrocoagulation Treatment Process

Like any treatment process, EC process also possesses advantages and challenges when applied during treatment. The advantages and challenges were discussed below.

2.6.1   Advantages of Applying Electrocoagulation Process

The advantages of EC process compared to other conventional processes are (i) it involves simple design and equipment; (ii) easy operation and automation where it is easier to monitor and maintain; (iii) higher removal rate especially in removing suspended solids, dissolved metals, tannin and dyes; (iv) require shorter retention time; (v) high sedimentation velocities; (vi) it prevents of unnecessary ion transfer into treated wastewater; and (vii) low amount of sludge are produced and tends to be readily settable and more easily dewatered because of its composition that is mainly metallic oxides/hydroxides (Can *et al.,* 2006; Chen *et al.,* 2000; El-Naas *et al.,* 2009; Ilhan *et al.,* 2008; Merzouk *et al.,* 2009; Mollah *et al.,* 2001).

Besides that, by using EC, coagulant material used for the treatment can be minimised. The dosing of coagulant material depends on the cell potential provided (El-

Naas *et al.,* 2009). Compared to chemical coagulation, excessive coagulation dosage might occur any time as it can cause secondary pollution to the water treated (Feng *et al.,* 2007). The flocks formed by EC are similar to chemical flocks, except that EC flocks tend to be much larger, contain less bound water, is acid-resistant and more stable, and therefore, can be separated faster by filtration (El-Naas *et al.,* 2009).

2.6.2   Challenges of Applying Electrocoagulation Process

The challenges in applying EC process is that the "sacrificial electrode" used needs to be replaced regularly as a result of the oxidation (Agustin *et al.,* 2008). The cost of electrode material in some countries may be expensive which may cause the application of EC process to become unsuitable in those countries. Besides that, the use of electricity is expensive in many places and some places might not have access to electricity (Siringi *et al.,* 2012). Moreover, the initial capital costs of EC are higher compared to other technologies (Kobya *et al.,* 2003).

The formation of impermeable oxide film on the electrode may lead to the loss of efficiency of the EC unit. It could reduce the cell voltage during electrolysis and therefore reduce the removal efficiency of pollutant (Mouedhen *et al.,* 2008). The nature of wastewater also plays a role in the effectiveness of treatment where the high conductivity of the wastewater suspension is required. Addition of electrolyte is essential to achieve the required conductivity before running the EC process (El-Naas *et al.,* 2009).

The generation of gas bubbles at high current densities and/or long electrocoagulation time has set a limit on the efficiency of oil removal. It is due to the

small colloidal particles in the wastewater that cause interference in the processes of oil droplet coalescence and the attachment of oil onto flocks (Phalakornkule *et al.,* 2010a). Therefore, it would reduce the efficiency of O&G removal.

2.7 Application of Electrocoagulation for Wastewater Treatment

The EC process has been successfully used to treat oily wastewater and wastewater containing SS, with the removal efficiency as high as 99% (Can *et al.,* 2006; Solak *et al.,* 2009). Similar success is also reported on several types of wastewater. These include palm oil mill effluent (POME) (Agustin *et al.,* 2008; Phalakornkule *et al.,* 2010a), petroleum oil refinery wastewater (El-Naas *et al.,* 2009), biodiesel production wastewater (Chavalparit & Ongwandee, 2009; Jaruwat *et al.,* 2010; Sriransan *et al.,* 2009), vegetable oil refinery wastewater (Umran *et al.,* 2009), potato chips manufacturing wastewater (Kobya *et al.,* 2006), dairy wastewater (Şengil & özacar, 2006; Tchamango *et al.,* 2010), leachate (Ilhan *et al.,* 2008), marble processing wastewater (Solak *et al.,* 2009), pulp and paper mill wastewater (Khansorthong & Hunsom, 2009; Vepsäläinen *et al.,* 2011; Zaied & Bellakhal, 2009), olive mill wastewater (Adhoum & Monser, 2004; Inan *et al.,* 2004; Umran et al., 2006), refectory oily wastewater (Xu & Zhu, 2004), pharmaceutical and cosmetic wastewater (Boroski *et al.,* 2009) and textile wastewater (Can *et al.,* 2006; Merzouk *et al.,* 2009; Merzouk *et al.,* 2010; Zongo *et al.,* 2009; Phalakornkule *et al.,* 2010b).

However, a few wastewaters with high volumetric generation are constantly discharged from industrial activities to which reports in the literature of their treatment using EC are scarce. Some of these wastewaters are POME, biodiesel production wastewater, olive mill wastewater, textile wastewater, food industrial wastewater, pulp

and paper mill effluent, and leachate. **TABLE 2.6** summarizes the pollutants removal by EC process from various kinds of wastewater.

TABLE 2.6. Summary of pollutants removal by EC process.

Type of wastewater	Type of electrode	Optimal condition			Influent COD, (mg/L)	Removal COD, %	Influent SS, (mg/L)	Removal SS, %	Reference
		pH	Current density, (A/m^2)	Operating time, (min)					
POME	Al	4.3	0.65	360	36,800	30	*	*	(Agustin *et al.,* 2008)
POME	Al	5	20	5	73,200	64	67,700	43	(Phalakornkule *et al.,* 2010a)
Biodiesel wastewater	Al	6	123.4	24	30,980	55.4	340	98.4	(Chavalparit & Ongwandee, 2009)
Biodiesel wastewater	Al-Cu	6	83.2	25	30,980	55.4	*	97.8	(Sriransan *et al.,* 2009)
Petroleum refinery wastewater	Al	8	13	60	596	63	*	*	(El-Naas *et al.,* 2009)
Refectory oily wastewater	Al	6	12	30	1,500	75	*	*	(Xu & Zhu, 2004)
Olive mill wastewater	Al	6.2	200	30	48,500	52	*	*	(Inan *et al.,* 2004)
Olive mill wastewater	Fe	6.2	200	30	48,500	42	*	*	(Inan *et al.,* 2004)
Olive mill wastewater	Fe	12	750	180	45,000	86	*	*	(Umran *et al.,* 2006)
Olive mill wastewater	Al	4	750	25	75,100	76	*	*	(Adhoum & Monser, 2004)

TABLE 2.6. Continued

Type of wastewater	Type of electrode	Optimal condition			Influent COD, (mg/L)	Removal COD, %	Influent SS, (mg/L)	Removal SS, %	Reference
		pH	Current density, (A/m^2)	Operating time, (min)					
Oily wastewater	Al		250	22	62,300	90	*	*	(Tir & Moulai-Mostefa, 2008)
Vegetable oil refinery	Al	7	350	90	15,000	98.8	*	*	(Umran *et al.,* 2009)
Textile	Al	6	100	5	3,422	78	*	*	(Can *et al.,* 2006)
Textile	Al	6	150	15	3,422	65	*	*	(Kobya *et al.,* 2003)
Textile	Fe	8	100	15	3,422	77	*	*	(Kobya *et al.,* 2003)
Textile	Al	7.6	115.5	10	2,000	68	*	*	(Merzouk *et al.,* 2009)
Textile	Al	8.7	115.5	10	340	79.7	*	85.5	(Merzouk *et al.,* 2010)
Textile	SS	7.5	430	15	500	63	*	*	(Arsalan-Alaton *et al.,* 2008)
Textile	Al	<6	100	10	3,422	61-65	*	98	(Bayramoglu *et al.,* 2004)
Baker's yeast wastewater	Al	6.5	70	50	2,487	71	*	*	(Kobya & Delipinar, 2008)
Baker's yeast wastewater	Fe	7	70	50	2,487	69	*	*	(Kobya & Delipinar, 2008)

<p style="text-align:center">**TABLE 2.6**. Continued</p>

Type of wastewater	Type of electrode	Optimal condition			Influent COD, (mg/L)	Removal COD, %	Influent SS, (mg/L)	Removal SS, %	Reference
		pH	Current density, (A/m^2)	Operating time, (min)					
Leachate	Al	8.3	348	30	12,860	56	*	*	(Ilhan *et al.,* 2008)
Leachate	Fe-Cu	8.2	261	20	2,107	44.5	*	*	(Tsai *et al.,* 1997)
Leachate	Al	7.6	90	40	-	>90	*	*	(Contreras *et al.,* 2009)
Leachate	Fe	8.5	50	15	4,022	90	*	*	(Veli *et al.,* 2008)
Marble	Al	9	15	2	-	-	5,178	100	(Solak *et al.,* 2009)
Marble	Fe	8	20	2	-	-	5,178	99.94	(Solak *et al.,* 2009)
Pulp and paper mill	Fe	9.3	20.7	15	802	84	150	97	(Khansorthong & Hunsom, 2009)
Pulp and paper mill	Al		22	7.5		75	*	*	(Uğurlu *et al.,* 2008)
Pulp and paper mill	Al	5-7	700	30	1,700	>75	*	*	(Katal & Pahlavanzadeh, 2011)
Black liquor from paper industry	Al	7	14	50	7,960	98	1,160	99	(Zaied & Bellakhal, 2009)
Potato chips manufacturing	Al	6	200	40	2,800	60	*	*	(Kobya *et al.,* 2006)

TABLE 2.6. Continued

Type of wastewater	Type of electrode	Optimal condition			Influent COD, (mg/L)	Removal COD, %	Influent SS, (mg/L)	Removal SS, %	Reference
		pH	Current density, (A/m^2)	Operating time, (min)					
Dairy effluents	Al	7	43	15	-	61	*	*	(Tchamango *et al.,* 2010)
Municipal wastewater	Fe	7	182	5	143	-	*	95.4**	(Alaadin, 2008)
Municipal wastewater	Fe	7.4	16.7	8-15	380	60	*	70	(Ugur *et al.,* 2008)

* Not reported

* *Oil & greases removal

2.7.1 Palm Oil Mill Effluent (POME)

Electrocoagulation method to treat wastewater from palm oil mill effluent (POME) was studied by Agustin, Sengpracha, & Phutdhawong (2008). The wastewater was treated using aluminum electrode and NaCl was added as supporting electrolyte. The treatment was carried out continuously up to 6 hours before taking the samples for analysis. The results showed the reduction of COD and BOD was 30% and 38% respectively. For TSS removal, it was shown by the removal of turbidity of wastewater where it changed from being a dark colour to becoming a transparent solution. The electrodes used were changed regularly at every one hour during the treatment and the pH was increased from 4.3 to 7.63 after EC process due to formation of hydroxide ions according to the following reactions:-

Anode   : $$Al \rightarrow Al^{3+} + 3e^{-}$$ (2.17)

Cathode : $$3H_2O + 3e^{-} \rightarrow 3/2\ H_2 + 3OH^{-}$$ (2.18)

Solution : $$Al + 3H_2O \rightarrow Al(OH)_3 + 3H^{+}$$ (2.19)
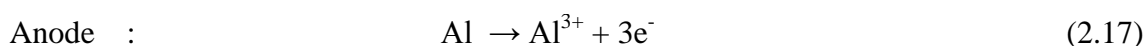
Another study on POME treatment was carried out by Phalakornkule *et al.,*(2010a) to investigate the reduction of COD, total solids (TS) and oil and greases (O&G). The results indicated that the reduction of COD, TS and O&G were 64%, 43% and 72% respectively under the optimal operating condition of pH of 5, current density of 20 A/m^2 within 5 minutes at 40°C. In addition, 8.5 g/L of NaNO$_3$ (0.1M) was added to improve the EC process.

The findings from studies of POME treatment using EC process have shown that EC is capable of treating the wastewater and changing it from dark color to clear water.

However, the time consumed for treatment was longer which was up to 6 hours even tough another study showed that the treatment could be done in 5 minutes in a temperature of 40°C. Further studies need to be carried out to improve the treatment as there is a limited study on POME treatment using EC process.

2.7.2 Biodiesel Wastewater

In a conventional biodiesel production plant, 20 L of biodiesel wastewater is discharged for every 100 L of biodiesel produced (Suehara *et al.,* 2005). The wastewater from biodiesel production is basic with pH range between 8 to 10 which contains high amount of oil and grease (O&G), chemical oxygen demand (COD), suspended solid (SS) and low content of nitrogen and phosphorus. The high pH of wastewater is due to the significant level of residual potassium hydroxide (KOH) that was added during the production of biodiesel (Jaruwat *et al.,* 2010). The characteristics of biodiesel wastewater are presented in **TABLE 2.7.**

TABLE 2.7. Characteristic of biodiesel wastewater (Ruengkong *et al.,* 2008; Sawain *et al.,* 2008; Suehara *et al.,* 2005).

Parameter	Range
pH	8.5 – 10.5
BOD_5 (mg/L)	10,5000-30,0000
COD (mg/L)	60,000-54,5000
SS (mg/L)	1,500-28,790
O&G (mg/L)	7,000-443,300

Sriransan *et al.,* (2009) carried out a treatment process with different combinations of electrode materials such as Fe-Fe, Fe-G (grapite), Al-Al, Al-G and G-G. The results indicated that optimum conditions were achieved using Al as anode and G as cathode, where the current density applied to the wastewater was 83.2 A/m^2 with initial pH of 6 for 25 minutes. The treatment had successfully removed 97.8% of O&G,

97.5% of SS and 55.7% of COD. The residual COD was still high because of the less significant removal of glycerol and methanol, which were the two main compositions of organic matters other than O&G in the biodiesel wastewater. In addition, a small amount of sludge was produced which was readily removed from the wastewater.

Chavalparit & Ongwandee, (2009) repeat this study but this time they used response surface methodology to find the significant optimum conditions of treatment. From the results, they had successfully removed 55.43% of COD, 98.59% of O&G and 96.59% of SS under the optimum condition of pH 6.06, applied voltage 18.2 V (123.4 A/m^2), and reaction time of 23.5 minutes.

Both studies have shown the ability of EC process as an efficient technology treatment for biodiesel wastewater where more than 95% of SS and O&G are removed. However, because of the less significant removal of glycerol and methanol, the residual COD still remain in the wastewater and will be removed in the next step of treatment which is biological treatment process. Therefore, the EC process is recommended for a primary treatment of biodiesel wastewater (Chavalparit & Ongwandee, 2009).

2.7.3   Olive Mill Wastewater

95% of worldwide olive oil is produced by many Mediterranean countries. It was reported that 0.8 m^3 of olive mill effluent are produced for a tonne of olive fruits treated. Olive mill effluents is difficult to treat because of the high organic loading, seasonal operation and presence of organic compounds which are hardly biodegradable, such as long-chain fatty acids and phenolic compounds (Umran *et al.,* 2006).

The EC process of olive mill wastewater was studied by Inan *et al.*, (2004) using aluminum and iron electrode. As a result, 68% of TSS and 52% of COD were removed by aluminum electrode while 65% of TSS and 42% of COD was removed by iron electrode within 20 to 30 minutes operating time. Both tests were carried out in the optimum condition with the current density of 200 A/m^2 and at pH 6.2. Another study was conducted by Umran *et al.* (2006), using aluminum and iron electrode in the presence of H_2O_2 and polyaluminum chloride (PAC) as coagulant aid. From the results obtained, iron electrode was more efficient than aluminum electrode. It was based on the removal of COD by iron electrode with 78% removal, compared with 55% by aluminum electrode. The iron electrode was more effective in this study because of the addition of coagulant aid and oxidant in the wastewater. Both electrodes successfully removed 100% of TSS and O&G at current density range of 200-750 A/m^2 depending on the concentration of H_2O_2 and coagulant aid.

Adhoum & Monser, (2004) found that the optimum pH for treatment of olive mill wastewater was in the range of 4 to 6 which allowed the wastewater to be directly treated without pH adjustment. 76% and 95% of COD and colour were removed respectively with the optimum current density of 750 A/m^2 just after 25 minutes of operation, using aluminum electrodes. Other than that, the final pH of wastewater was nearly neutral which allowed it to be discharged directly into the water body.

The treatment of olive mill wastewater using EC indicated that the removal of TSS, COD and O&G can achieve as high as 95% in the optimum operating parameter. From the literature, it has shown that the removal efficiency of treatment using iron electrode can be increased with the addition of oxidant.

2.7.4   Textile Wastewater

Large consumption of azo dyes in the dying processes has generated carcinogenic products such as aromatic amines which contains considerable strong colour, a broad range of pH ranging from 2 to 12, high COD concentration and suspended particles, and low biodegradability.

A study by Can *et al.*, (2006) on textile wastewater showed that the removal of COD increased by the addition of chemical coagulant such as polyaluminum chloride (PAC) into EC process where the removal was 80% compared to 23% with EC alone, in 5 minutes of operation. The initial presence of aluminum in the wastewater accelerated the formation of $Al(OH)_3$ flocks which absorbed particulate and soluble organic matter. In this way, the performance and the rate of EC increased, and the electrical energy consumption was also lowered with a significant decrease in the operating cost.

Comparing two electrode materials, aluminum and iron for the treatment of textile wastewater in a discontinuous system, with simultaneous variation of COD, absorbance and turbidity was carried out by Zongo et al., (2009). Both materials had totally removed turbidity and absorbance at 436 nm and COD was removed in the range of 74% to 88%. However, the most suitable material was aluminum electrode as iron electrode often resulted in the formation of very fine brown particles which were prone to settling compared to the gel flock formed with aluminum.

Another study by Merzouk *et al.*, (2009) on EC treatment for textile wastewater investigated the effects of the operating parameters, such as pH, initial concentration, duration of treatment, t, current density, j, inter-electrode distance, d, and conductivity.

Under the optimal conditions of pH 7.6, j = 115.5 A/m^2, d = 1 cm, and t =10 minutes, the removal of 83% of BOD$_5$, 68% of COD, 81.6% of turbidity, 86.5% of SS and more than 92.5% of colour were achieved. The treatment was also able to removed 70% to 99% of heavy metal when the synthetic textile wastewater concentration ranging from 50 to 600 mg/l was tested.

The results from the study shows that EC process can successfully remove colour from the wastewater. The addition of chemical coagulation enhances the removal efficiency and reduces operation time. However, application of iron electrodes is not recommended because of the formation of brown colour after the treatment.

2.7.5   Food Industry Wastewater

Wastewater discharge from food industry mainly contains high load of organic material, such as carbohydrates, starches, proteins, vitamins and sugar which are responsible for the high concentration of COD, BOD, and SS (Kobya & Delipinar, 2008; Kobya *et al.,* 2006). Moreover, fermentation product from baker's yeast produces high strength wastewaters which contain high concentrations of organic material that cannot easily be degraded by biological processes. The feasibility of EC process can be applied to treat this wastewater to comply with environmental regulation. The treatment of baker's yeast wastewater using EC process was carried out by Kobya & Delipinar (2008), using a batch reactor. The treatment was done in the constant temperature of 20 °C and 300 rpm. In each run, 800 mL of wastewater solution was placed into the electrolytic cell together with 4 electrodes (anode: iron, cathode: aluminum) connected monopolar with DC power supply. The optimal operating conditions for the removal of COD, TOC and turbidity are shown in **TABLE 2.8**.

TABLE 2.8. Optimal operating condition for removal of COD, TOC and turbidity in baker's yeast wastewater treatment.

Electrode material	pH	Current density, (A/m^2)	Operating time, (min)	Removal		
				COD, (%)	TOC, (%)	Turbidity, (%)
Al	6.5	70	50	71	53	90
Fe	7			69	52	56

From the **TABLE 2.8**, aluminum electrode showed the greatest removal of turbidity, COD and TOC compared with iron electrode due to colour interference of dissolved iron. The removal of turbidity also could be related with the removal of TSS.

Other food wastewater investigated was for potato chips manufacturing industry (PCW) by Kobya *et al.*,(2006). The characteristics of the PCW are as follows: COD, 2200-2800 mg/L; BOD, 1650-2150 mg/L; pH, 6.2-6.5; turbidity, 260-610 NTU and conductivity, 1.90-2.40 mS/cm. Aluminum electrode was used instead of iron because it was found to be more effective since the removal rate of COD, turbidity and SS were high. The removal of COD and turbidity achieved were 60% and 98% respectively, with the retention time less than 40 minutes and 0.05-1.5 kg (per kg COD removed) of dried sludge was removed.

Xu & Zhu, (2004) investigated the removal efficiency of restaurant wastewaters using iron electrode. The effect of parameter namely current density, reactive time, conductivity, electrode distance, and pH were investigated to determine the optimum conditions for treatment. It was reported that 75% of COD and 95% of O&G were removed in 30 minutes with current density range of 12 A/m^2 in the pH of 6 and 10 mm of electrode distance. Conductivity was found to have little effect on treatment

efficiency but the addition of extra salts (eg. NaCl) reduced the power consumption by approximately 75%.

The current study demonstrated that potentials of EC process in removal of pollutants from high organic containing wastewater. The method of electrode connection and mixing seems to affect the performance of operation. However, there are few studies regarding the effect of electrode connection and mixing in EC that require for further investigation.

2.7.6 Pulp and Paper Mill Effluent

The increasing paper usage around the world has increased the growth of pulp and paper industry especially in countries that has a plentiful supply of sustainable renewable forest resources and water supply. The utilization of huge amounts of water between 76 - 227 m^3 per tonne product results in the generation of large quantity of wastewater which contributes to environmental problems (Khansorthong & Hunsom, 2009).

Lafi, (2011) investigated the treatment of wastewater from paper industry using EC process with the addition of $Fe(SO_4)_3$ and Calcium Carbonate, $CaCO_3$. Six iron plates were constructed in the electrochemical reactor to perform the process. The effects of several parameters were investigated including the initial pH, current density, and operating time. As a result, with the addition of $Fe(SO_4)_3$, 95% of TSS and 96% of COD were removed, while with the addition of $CaCO_3$ resulted in 90% removal of both TSS and COD. For treatment without additional salt, 82% and 84% of TSS and COD were removed. All results were obtained in the optimum condition of initial pH of 8 and current density of 60 A/m^2 within 30 minutes.

Katal & Pahlavanzadeh, (2011) used eight electrodes which were individually connected to DC power supply. The study was conducted using different combinations of aluminum and iron electrodes. The influence of parameters such as current density, pH, electrolysis time and temperature on the removal performance was explored. As a result, with low electrode consumption, the process was able to remove >75% of COD within 30 minutes at 700 A/m^2. The optimum working pH was found to be in the range of 5 to 7, which allowed the wastewater to be treated without pH adjustment. The EC process was most effective at low temperature whereby the removal efficiency was reduced to 20% if the temperature was increased from 20°C to 60°C. Finally, it was found that a combination of Al-Al has a high efficiency in colour removal. Meanwhile, Fe-Fe was effective in COD and phenol removal.

The results from these studies indicate that the additional of iron salt is appropriate to EC process rather than the addition of $CaCO_3$. Furthermore, effect of temperature also influences the performance of EC process. Thus, further study must be carried out to verify the finding as both studies have demonstrated that EC process is the best option for treating   pulp mill wastewater.

2.7.7   Leachate Treatment

Leachate is a wastewater with complex and widely variable content generated within a landfill. They are too wet, contain a notable amount of volatile fatty acids and are not suitable to be placed into either land or water body (Redzwan & Banks, 2004). Many pretreatment and combined treatment methods have been applied to treat the leachate.

Ilhan *et al.*, (2008) carried out the treatment of leachate using EC in a batch process. Effects of treatment such as electrode material, current density, initial pH, operating time and treatment cost were investigated. As for the outcome, the selection of aluminum was an appropriate electrode material as a removal of 56% of COD was attained compared to iron electrode which was 35%. This was at the optimal condition of pH = 8.3, current density = 348.4 A/m^2 and 30 minutes of operation time. The study also did a comparison of EC process with chemical coagulation (CC) through the COD removal. The study concluded that EC process produced higher treatment performance than CC process where the COD removal efficiency of CC was only 31% compared with EC, 45%.

Another study of leachate treatment was carried out by Veli *et al.*, (2008). The authors compared electrocoagulation processes with chemical coagulation. Removal efficiencies of COD, TOC and colour were investigated. The results have shown the EC processes were more efficient than chemical coagulation where it successfully removed 90% of COD and 99% of colour by using Fe electrodes. Current density applied was in the range of 1-10mA/m^2, within 15 minutes.

Tsai *et al.* (1997) carried out the treatment using two different electrode pairs, Fe-Cu and Al-Cu. The study revealed that Fe-Cu was the most efficient electrode for the removal of COD which ranged from 30 - 50%. According to the total organic carbon (TOC) and gel-filtration chromatography (GFC) analysis, both large and small molecules were removed in this process. The larger molecules were removed by coagulation and the smaller molecules were decomposed to volatile organic compounds (VOC) or carbon dioxide (CO_2) by electrolysis. The optimum conditions of treatment were at current density of 261 A/m^2 within 20 minutes.

The results on the treatment of leachate using EC process have shown that the operation time is within 15 to 30 minutes. The comparison of EC process and CC process suggests that the EC process is more efficient in removing pollutants as the EC process can removed both suspended and dissolved solids, whereas CC is limited to mainly removal of suspended solids (Phalakornkule et al., 2010a).

2.8   Summary of Literature Review

In the application of EC process for wastewater treatment, different conclusions were reported in the literature regarding the optimal operating parameters. Findings from current research showed a strong dependence of these operating conditions on the nature of the wastewater treated. Generally, aluminum electrode was found to be the most suitable for the various wastewaters reviewed. It was due to the formation of brown colour in the water treated when using iron electrode. In addition, a slightly acidic pH to neutral pH was the best for the treatment of various wastewaters.

For biodiesel wastewater, the optimum operating parameters were found to be within an operating time of 25 minutes and 83.2 A/m^2 of current density. On the other hand, for palm oil mill effluent (POME), operating time of 5- 60 minutes, pH of 5 and current density of 20 A/ m^2 were required. The removal also improved with the addition of $NaNO_3$. For olive mill wastewater the optimum time was in the range of 10-90 minutes and current density was between 200 - 750 A/m^2. Wastewater form textile industry required 10-30 minutes operating time and a current density of between 100 - 150 A/m^2, food processing wastewater required 15 - 50 minutes operating time. For pulp and paper mill wastewater, current densities of 20 - 700 A/m^2 were sufficient.

Lastly for leachate, it required between 15-30 minutes and current density of 100-900 A/m^2. The suitability of EC treatment at pH of 6-7 was established for wastewater containing huge amounts of TSS and O&G. Studies also found the treatment can be significantly accelerated by the additional of coagulant aid.

TABLE 2.9 summarizes parameters affecting EC process performance. It was indicated that EC process was able to treat wastewater that containing TSS in the range of 150 mg/L to 68,000 mg/L and COD in the range of 140 mg/L to 75,000 mg/L. Since the TSS and COD values of POME were within the range of 15,000 mg/L to 29,000 mg/L and 45,000 mg/L to 65,000 mg/L, respectively, the application of EC process for POME treatment will be carried out (Wong et al., 2009).

TABLE 2.9. Summary of parameters that affecting EC process performance.

Electrode	pH	Current density, (A/m^2)	Operating time (minute)	Influent COD, (mg/L)	Removal COD %	Influent TSS, (mg/L)	Removal TSS, %
Aluminum	5 - 7	15 - 750	2 - 25	340 - 75,000	30 - 98	150 - 68,000	43 - 100
Iron	6 - 12	20 - 348	2 - 30	140 - 48,500	35 - 90	150 – 68,000	70 - 100

Therefore, in this study, the feasibility of EC process in treating POME will be carried out by investigating the removal efficiency of TSS and COD. Initially, the characteristic or nature of POME will be investigated before conducting the experiment. According to the information from literature, POME is acidic which means that aluminum electrode will be used since it is proven to be the best and most efficient electrode in the acidic medium. The optimum initial pH for POME treatment will be investigated. The current density of treatment will be determined and control the dosage of Al^{3+} ions supply during the treatment. The optimum operating time of POME will

also be investigated because there are limited publications on POME treatment that suggest the best operating time. In addition, the effect of motion in the reactor will be explored by providing different stirring speed. Different stirring provided will have different degree of collisions between POME particles and coagulants. Lastly, the optimum operating parameter investigated will be determined based on reduction of TSS and COD.

CHAPTER 3

METHODOLOGY

3.1   Material

POME was collected from Palm Oil Mill Technology Center (POMTEC), MPOB, Labu, Negeri Sembilan. The POME obtained was stored in a cold room maintained at 4°C. The physicochemical properties of POME are as shown in **TABLE 3.1**.

TABLE 3.1. Physicochemical properties of POME.

Characteristic	Value (Average)	Analytical method/Instrument
Temperature (°C)	80	Thermometer
COD (mg/L)	62,000	5220 c. Closed reflux, Titrimetric Method [a] (APHA, 1992)
BOD_5 (mg/L)	29,000	5210 B. 5-Days BOD Test [a]
Total suspended solid (mg/L)	20,000	2540 B. Total Solids Dried at 103-105°C [a]
Oil and greases (mg/L)	5667	5520 B. Partition-Gravitimetric Method[a]
pH	4	pH meter (METTLER TOLEDO FE20)
Conductivity (mS/cm)	10	Conductivity meter (Trans conductivity meter)

[a] According to the standard methods for examination of water and wastewater (APHA, 1992).

3.2   Experimental Set-up

The experimental set-up is shown in **FIGURE 3.1**. The system consists of DC power supply; a power control with measurement units, electrochemical reactor and digital magnetic stirrer. A 600 ml beaker was used as the electrochemical reactor, with a pair of aluminum electrodes immersed in the electrolyte and connected vertically to DC power supply (Topward 6000 Digital DC Power Supply). The dimension of the electrodes was

120 mm $\times$ 35 mm $\times$ 3 mm with a total effective area of 70 cm^2. Aluminum electrode was used due to its effectiveness in pollutant removal compared with other materials as detailed in the literature review. The dimension of the electrode was designed based on the size of the reactor used. The suitability of the electrode used was according to the electrode surface area to reactor volume (SA/V) which equal to 0.175 cm^2/mL and it was falls within the ranges of 0.069-0.430 cm^2/mL as reported by Holt, 2003. The SA/V is a measure of the potential for delivering coagulant and bubbles to a system (Holt, 2003). The gap between electrodes was kept constant at 1.0 cm to minimize the energy loss during treatment (Feng *et al.,* 2007).
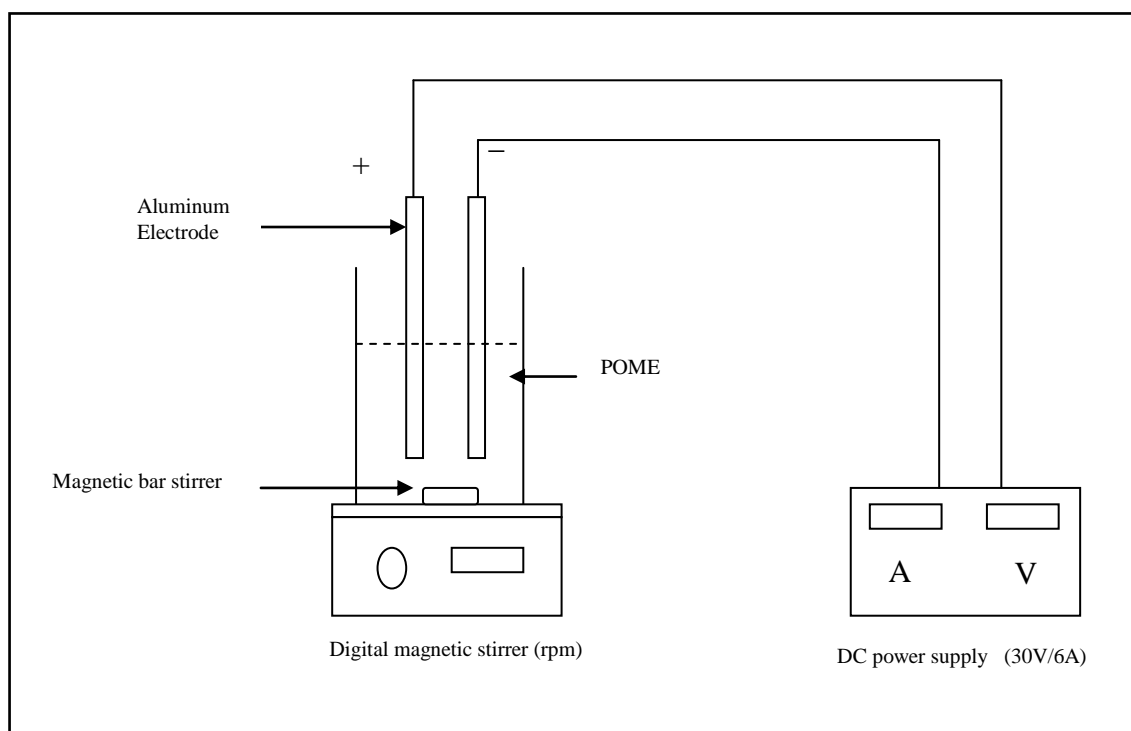

FIGURE 3.1. Experimental set-up.

The impurities and solid residue retained on the surface of electrodes were removed through washing with deionised water, dipped at least 15 minutes in HCl (1M) solution (5 %v/v), and rinsed again with deionised water (Phalakornkule *et al.,* 2010a). The electrodes were also dried and weighed at the end of the experiment. The

experiments were performed using deionised water instead of distilled water as deionised water can minimize the presence of contaminants such as carbonates which can readily passivate electrodes (Holt, 2003).

3.3 Experiments

All experimental runs were performed at the ambient temperature of 27°C except for the experiment investigating the effect of temperature. The experiments were carried out in a batch operation mode with 400 mL of POME for each run. To allow for the motion of the magnetic bar stirrer, the electrodes were immersed vertically 1 cm apart from the bottom of the reactor.

The effects of optimum parameters for electrocoagulation treatment were determined based on the reduction of TSS and COD. Before starting the analysis, the samples were left to settle for 1 hour and were drawn from the middle of the supernatant. To ensure reliability of the experiment, triplicate runs were conducted for each test. The pH and conductivity of wastewater were measured by pH meter (METTLER TOLEDO FE20) and conductivity meter (Trans conductivity meter).

3.3.1　Effect of Initial pH

The pH of sample was adjusted to the desired values of 4, 5, 6, 7, and 8, respectively by using either H_2SO_4 (1 M) or NaOH (1 M). The stirring speed of 300 rpm was used to stir the sample homogenously due to high concentrated of solution. For current density of 120 A/m^2 and operating time of 15 minutes, the values were chosen by referring to the previous study which suit with the working volume used. All those parameters were kept constant for all runs.

3.3.2　Effect of Current Density

The effect of current density was investigated, varying from 40 – 200 A/m^2. Since the optimal pH was known from previous experiments, the pH was kept constant with the stirring speed of 300 rpm, and operating time of 15 minutes.

3.3.3　Effect of Stirring Speed

The effect of stirring speed or mixing rate for TSS removal was investigated. The stirring was provided to ensure sufficient collision between pollutant particles and coagulants. The known optimum pH and current density with 15 minutes operating time was kept constant for all runs. The various stirring speed investigated ranged from 0 rpm, 100 rpm, 200 rpm, 300 rpm, and 400 rpm. The investigated value of speed was chosen based on the viscous nature of the POME (Jang & Lee, 2000).

3.3.4 Effect of Temperature

The effect of temperature was investigated starting with 27°C, 40°C, 50°C and 60 °C. The temperature was controlled using water bath. The known optimum pH, current density and 15 minutes operating time were kept constant for all runs.

3.3.5 Effect of Operating Time

The effect of operating time was studied at varied reaction time from 15 to 75 minutes. The known optimum pH, current density, mixing rate, and temperature were kept constant for all runs.

3.3.6 Chemical Coagulation Process

CC process of POME using jar test was performed as to compare its performance with EC process. 0.5 g/L to 2.5 g/L of aluminum sulphate, $Al_2(SO_4)_3$ was added into POME in step of 0.5 g/L. The suspension was stirred at 150 rpm for 5 minutes and 30 rpm for 30 minutes. The POME was left to settle for 60 minutes and a sample was pipette from the middle of supernatant for analysis.

3.4   Data Analysis

The determination of total suspended solid (TSS) and chemical oxygen demand (COD) was done according to the Standard Methods for Examination of Water and Wastewater (APHA, 1992). The removal efficiency of treatment was calculated as below:

$$\eta(\%) = \frac{(Ci - Cf)}{Ci} \times 100 \qquad (3.1)$$

Where; $\eta(\%)$: Removal efficiency (%)

C_i: Initial concentration (mg/L)

C_f: Final concentration (mg/L)

3.4.1 Total Suspended Solid Determination

TSS is the portion of total solids retained on a standard glass fibre filter paper when a sample of water is filtered and dried at 105°C over 24 hours. It contains organic and inorganic matter such as biological solids, clay, silt and other soil constituents that are common in surface water (APHA, 1992).

The glass fibre filter paper was placed on the filter apparatus and washed three times successively with 20 mL portions of distilled water. The suction continues for a further 2 minutes, until all traces of water had been removed from the paper. The filter paper was removed and placed on a tray and transferred to the oven (previously heated to 105°C). It was left to dry for 1 hour and cooled in desiccator. The dried filter paper was weighed accurately and then, placed on the filtration apparatus; 40 mL of sample was filtered under vacuum. The suction continued for a further 2 minutes to remove as much water as possible.

After the suction process, the filter paper was removed, placed on the tray and transferred to the oven and kept dry for 24 hours. Lastly, the filter paper was left to cool in desiccators and weighed. The calculation for the determination of TSS was as below:

$$\text{Total suspended solids} = \frac{(A-B)}{C} \times 1000 \text{ mg/L} \tag{3.2}$$

Where; A = weight of filter paper + residue (mg)

                B = weight of filter paper (mg)

                C = mL of sample taken

3.4.2 Chemical Oxygen Demand Determination

COD is the amount of oxygen required to oxidize the sample that is susceptible by strong chemical oxidant. The dichromate reflux method is preferred over procedures using other oxidants (for example, potassium permanganate) because of its superior oxidizing ability, applicability to a wide variety of samples and ease of manipulation. Oxidation of most organic compounds is 95-100 % of the theoretical value (APHA, 1992).

The COD of wastewater was determined by using closed reflux, titrimetric method. 2.5 mL of sample was placed into COD cell together with 1.5 mL digestion solution, Potassium Dichromate solution.

Then, 3.5 mL of sulphuric acid reagent, H_2CO_4 was added slowly inside the cell. The cells were shaken gently. All the sample cells including blank cell were heated at 150 °C in a heating block for 2 hours.

After 2 hours, the cells were taken out from the heating block and left to cool at room temperature. The excess oxidizing agent was titrated with 0.1M Ferrous Ammonium Sulphate titrant, together with two drops of ferroin as indicator. The colour

of solution changed from blue green to reddish brown during the titration. The concentration of COD was calculated as below:-

$$\text{COD as mg O}_2/\text{L} = \frac{(A - B)}{C} \times M \times 8000 \text{ mg/L} \qquad (3.3)$$

Where;   COD = Chemical Oxygen Demand

           A   = mL $Fe(NH_4)_2(SO_4)_2$ used for blank

           B   = mL $Fe(NH_4)_2(SO_4)_2$ used for sample

           C   = mL of sample

           M   = Molarity of $Fe(NH_4)_2(SO_4)_2$, 0.1M

3.5   Safety Measures

Precautionary steps were taken during the experiments starting from sample collection until apparatus cleanup. Before collecting the sample at POMTEC, all equipment required were prepared before departure. The equipment included sample containers, rope, small pail, hand gloves, and plastic funnel. Precautions were taken during sample collection due to high temperature from POME ranging from 80 to 90°C.

In conducting the experiment, it was also important to beware of the electric current that flows in the EC process. Hence, precaution was taken when connecting and disconnecting the electrodes.

After completing the experiment, the treated wastewater was placed into a disposal container meant to be collected by Quality Alam for further action. Similar action was taken with wastewater from COD test where it was placed into COD wastewater container. It could not be directly poured into a sink because it contained

mercury element from COD's sulphuric acid reagent that were added during preparation. The mercury element will retain and pollute the water body if it is simply poured into the sink.

Basic safety measures in laboratory were also given attention to avoid injury during conducting the experiments such as wearing glove while handling corrosive chemicals like H_2SO_4, NaOH and etc. For evaporable and toxics chemical, the handling activities were carried out in the fume cupboard so that the toxics fume will be expelled outside the building.

CHAPTER 4

RESULTS AND DISCUSSIONS

The effect of established operating parameters on electrocoagulation process of POME, namely: initial pH, current density, stirring speed, temperature and operating time will be investigated in this chapter. To ensure the reproducibility of experimental results, all batches were run three times and the experimental errors that obtained were agreed up to 9%. Aluminum electrodes were used for the whole experiment. A suspension settling time of 1 hour was allowed after the treatment, and samples for the analysis were taken from the middle of the supernatant. After the treatment, the colour of POME was observed visibly very dark. This could be attributed to the polymerisation of polyaromatic compounds such as phenols and tannins during the treatment. (Khoufi *et al.,* 2007; Phalakornkule *et al.,* 2010a).

4.1   Effect of Initial pH

The initial pH of wastewater in this study was modulated to be within pH range of 4 - 8 using H_2SO_4 or NaOH. In each batch, the current density, stirring speed and operating time was kept constant at 120 A/m^2, 300 rpm and 15 minutes, respectively.

FIGURE 4.1 shows removal of TSS and COD with respect to initial pH. It indicates that the TSS removal is in the range of 75.0% to 81.2% whereby the highest removal is at pH of 5. However for COD removal, increasing trends is observed at pH of 4, 5 and 6 where the removal achieved are 36.3%, 47.0% and 50.2%, respectively.

For pH higher than 6, the removal of COD decreased drastically at pH of 7 and 8 with 36.0% and 32.2% of removal, respectively.
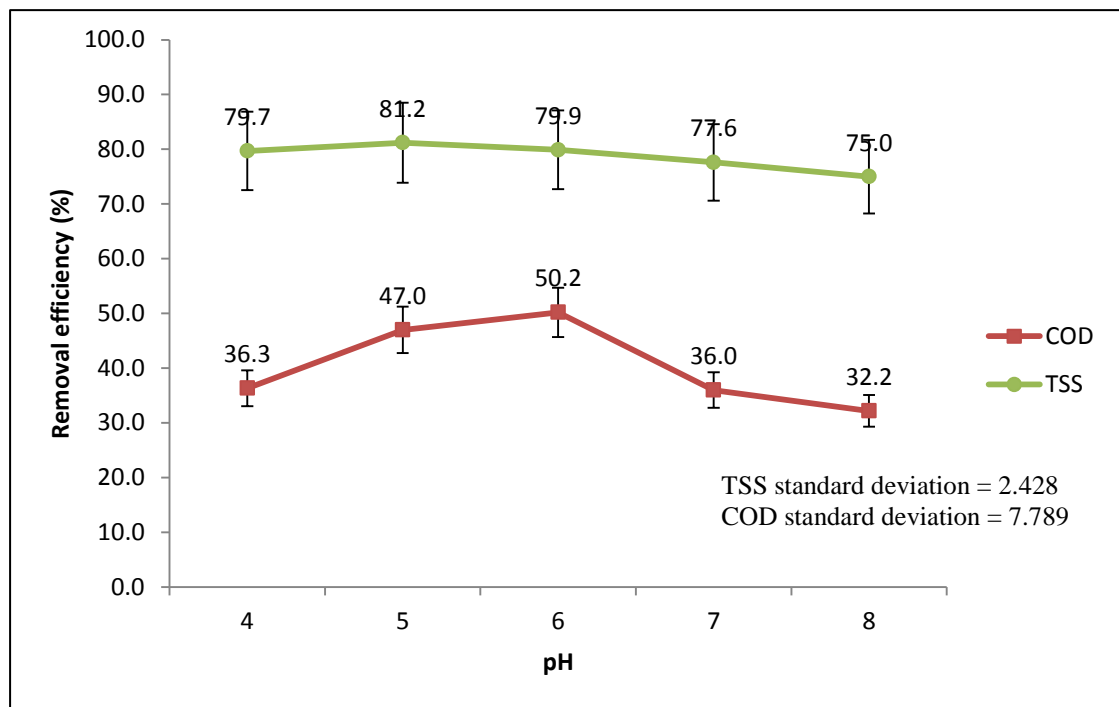

FIGURE 4.1. TSS and COD removal efficiency with respect to initial pH.

From the results obtained, pH 6 is identified as the optimum pH due to the highest removal efficiency of COD and TSS even though there are small differences with TSS removal in pH 5. The TSS removal is slightly constant due to sufficient attachment of colloidal particles with the coagulant during the treatment. The flocks formed are transported towards the surface of water by H_2 bubbles as reported by several researchers (Bayramoglu *et al.,* 2004 and Kobya *et al.,* 2003).

The efficiency of COD removal is less efficient at low and high pH. These are due to the amphoteric character of $Al(OH)_3$ which led to the solubility of Al^{3+} cations at low initial pH and monomeric anions of $Al(OH)_4^-$ at high initial pH (Adhoum *et al.,* 2004, Akyol, 2011). Both ions are unavailable for the treatment which consequently

reduces the pollutant removal efficiency (Adhoum *et al.,* 2004). When the wastewater was kept at the optimum pH of 6, all Al^{3+} cations produced at sacrificial electrode formed polymeric species and precipitated to $Al(OH)_3$ which lead to optimum removal efficiency (Katal & Pahlavanzadeh, 2011; Kobya & Delipinar, 2008).

FIGURE 4.2 shows the trend of increase in final pH after the EC process. This is due to the accumulation of OH^- ions in the POME during the process (Kobya *et al.,* 2006). The OH^- ions are generated together with the evolution of H_2 bubbles as shown in the equation (4.1).

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{4.1}$$

However, this opinion was contested by Chen *et al.* (2000) who explained this increase due to the release of CO_2 from wastewater owing to H_2 bubbles disturbance. CO_2 was over saturated at low pH and could be released during H_2 evolution, which resulted in an increase of pH. Furthermore, the authors also reported that the presence of some anions such as Cl^- and SO_4^{2-} in the wastewater could be exchanged partly with OH^- in $Al(OH)_3$ to free OH^- which consequently increase the pH.

From both opinions, the increasing in final pH was probably due to accumulation of OH^- ions in the POME. In the sufficient acidic conditions, the excess of OH^- ions was produced and a partial exchange of SO_4^{2-} ions with OH^- ions in $Al(OH)_3$ has release OH^- ions which finally increasing the final pH of wastewater (Adhoum *et al.,* 2004). The SO_4^{2-} ions was present in POME during pH adjustment with H_2SO_4.

Meanwhile in alkaline medium (pH = 8), the pH recorded dropped to 7.9 and that result is in accordance with the previous published works (Katal & Pahlavanzadeh, 2011;

Kobya *et al.,* 2003; Mouedhen *et al.,* 2008). The reduction of initial pH in the alkaline solution is due to the formation of $Al(OH)_4^-$ species together with the reaction of the cathode by OH^- ions (Adhoum *et al.,* 2004). Since there are pH increasing trend in initial acidic conditions and decreasing trend in alkaline conditions, it is suggested that EC process can act as pH neutralization during the treatment (Kobya *et al.,* 2003).
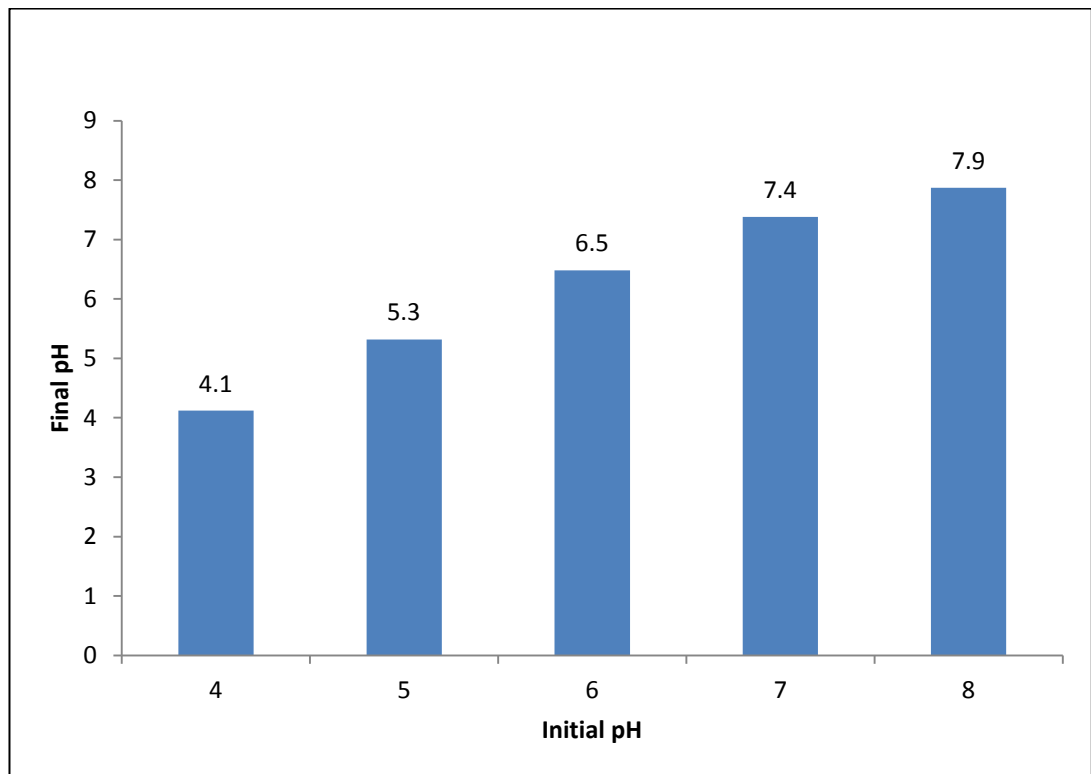

FIGURE 4.2. Results of final pH after 15 minutes of treatment.

4.2   Effect of Current Density

Many researchers observed that the current density had significant effect on the performance of EC process (Adhoum *et al.,* 2004; Feng *et al.,* 2007; Merzouk *et al.,* 2010; Uğurlu *et al.,* 2008; Umran *et al.,* 2009). Current density influenced the treatment efficiency in terms of coagulant dosage rate, bubble production rate, size and the flocs growth (Aji *et al.,* 2011; Chen *et al.,* 2000; Katal & Pahlavanzadeh, 2011). In other words, current density controlled the reaction rate during the treatment (Deng & Englehardt, 2007).

FIGURE 4.3 shows the effect of current density on the removal efficiencies of TSS and COD. According to Faraday's law, the amount of Al^{3+} ion generated is proportional to removal efficiency. It can be observed in **FIGURE 4.3**, TSS removal efficiency is attained more than 70% of removal. The highest TSS and COD removal are recorded as 83.3% and 44.7%, respectively at the current density of 120 A/m^2. This can be explained by the fact that, at high current density, the extent of anodic dissolution of Al^{3+} ions release increased, thus resulting in the precipitation of a huge amount of pollutants (Akyol, 2011). In addition, the bubbles generation increased and their size decreased with increased current density (Kobya & Delipinar, 2008). The optimum dissolution of Al^{3+} ions together with the generation of H_2 bubbles resulted in a greater upwards flux and a rapid removal of pollutant and sludge flotation (Adhoum & Monser, 2004).
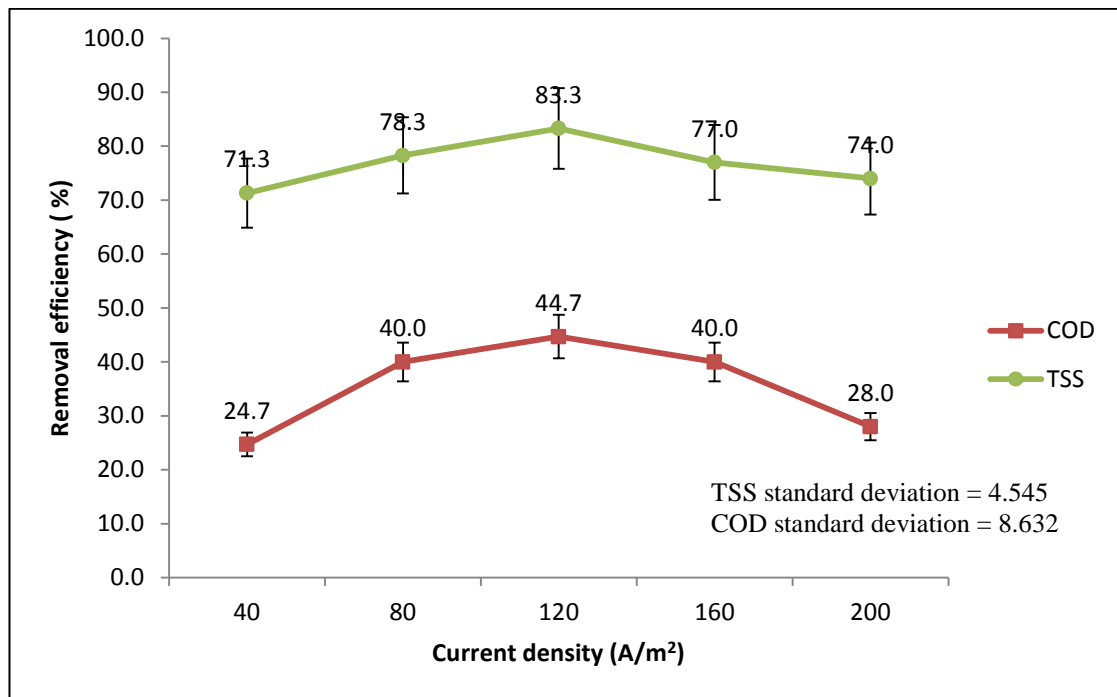
FIGURE 4.3. Effect of current density on TSS and COD removal efficiency.

Furthermore, in **FIGURE 4.3** shows steady increase in removal up to 120 A/m^2 thereafter decreased beyond the optimum current density. The increasing trend is due to continuous supply and utilisation of coagulant (Al^{3+}) released from the sacrificial anode for the coagulation process. The removal of TSS and COD at current density of 40 A/m^2 and 80 A/m^2 are less when compared to the optimum current density. This is due to limited dissolution of Al^{3+} ions for consumption of the coagulation process. Therefore, there are insufficient coagulants to react with the pollutant in order to obtain high percentage of removal.

The decrease in removal efficiencies beyond current density of 120 A/m^2 is due to the oversupply of Al^{3+} ions generation when compared to the coagulation process (Katal & Pahlavanzadeh, 2011). The rapid dissolution of Al^{3+} ions is not effectively utilised during the treatment and it led to a reduction in the probability of collision between the pollutants and coagulants (Adhoum & Monser, 2004). In addition, the high current density heated up the solution and increasing electrode consumption which

finally leading to energy waste (Khansorthong & Hunsom, 2009). Therefore, it is important to control the current density to minimise several adverse effects such as heat generation as well as avoid excessive oxygen evolution during the treatment.

In this study, the optimal current density was obtained at 120 A/m^2. This is against the backdrop that the most effective pollutant removal is at this condition. Beyond the optimum current density, the wastewater pH is increased due to the formation of OH$^-$ ions at the cathode. **FIGURE 4.4** shows the difference formation of flocks at difference current densities.

Flocks at 80 A/m^2

Flocks at 120 A/m^2

FIGURE 4.4. Different amount of flocks
with different current densities.

4.3   Effect of Stirring Speed

An effective aggregation required adequate contact between the coagulant and colloidal particles (Luu, 2000). The stirring during the treatment is necessary to allow chemical precipitation to grow large enough for pollutants removal (Adhoum & Monser, 2004). Mixing operation influences the movement of ions in the water where the negatively charged particles moved towards anode while the positively charged moved towards cathode (Ilhan *et al.,* 2008). The mixing of contaminant and coagulant between the electrodes resulted in coagulation and flotation of sludge formed by the H_2 gases (Sriransan *et al.,* 2009). In addition, the mixing is beneficial for effective utilisation of current density where Al^{3+} ions generated are dispersed uniformly in the medium.

The significance of the investigation is to observe the effect of motion and collision between coagulant and colloidal particles that influenced the removal efficiency of pollutants. Due to the appreciable concentration of suspended solids and O&G in POME, various stirring speed are introduced to promote sufficient motion. Therefore, by using optimum initial pH of 6 and current density of 120 A/m^2, the effect of stirring speed is investigated by applying 0, 100, 200, 300, and 400 rpm within 15 minutes of operating time.

FIGURE 4.5 shows the removal efficiency of TSS and COD against stirring speed. From the figure, the removal efficiency increase until 100 rpm and slowly decrease after that. The optimal stirring speed is shown at 100 rpm with the removal of 85.0% of TSS and 37.0% of COD. The highest removal was attained at this speed due to adequate aggregation and contact between coagulant and colloidal particles. From the observation, the wastewater was stirred sufficiently and gently at 100 rpm, and the

pollutants floated with the H_2 bubbles. Meanwhile at unagitated condition, there was no motion involved except within the electrode areas as a result of H_2 bubbles formation at the cathode and dissolution of Al^{3+} ions at the anode. A lot of sediment was observed after 1 hour settling time.
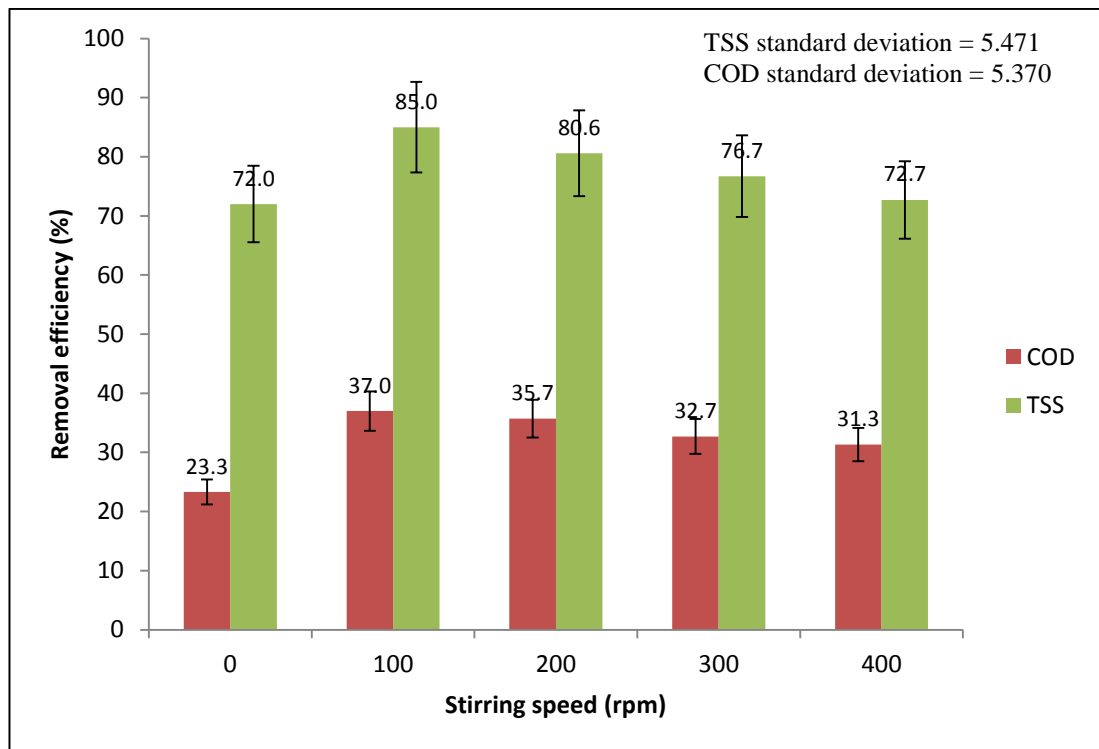

FIGURE 4.5. Effect of stirring speed on TSS and COD removal efficiency.

For stirring speed higher than 100 rpm, the removal was low because of the flocks break and residue particles release into the wastewater (Ahmad *et al.,* 2006). It is interesting to note that the removal continue to decrease with further increase in speed. High speed interferes with the process of aggregation and collision between coagulant and colloidal particles (Jang & Lee, 2000). Besides that, the rapid motion in the wastewater led to the wastage of Al^{3+} ions; because the coagulants that contribute for formation of flocks are degraded and adsorbed pollutants are desorbed (Bayar *et al.,* 2011). The pollutants are remained in the treated wastewater resulted the reduction of removal efficiencies.

Thus, mixing of POME at 100 rpm had achieved the optimal removal as it is provided sufficient movement in the wastewater to promote aggregation of flocks. The effect of stirring in removal efficiencies of pollutant was also supported by the findings of Alinsafi *et al.* (2005) and Bayar e*t al.* (2011) where high removal efficiencies were achieved.

4.4 Effect of temperature

The temperature can effect on the performance of EC process in many ways such as reaction rates, solubility of metal hydroxides, liquid conductivity and kinetics of gas bubbles, or smalls colloidal particles (Phalakornkule *et al.,* 2010a). The effect of temperature on the removal of TSS and COD from POME was performed at various temperatures namely 27°C, 40°C, 50°C and 60°C. The temperature was controlled using a water bath.

From **FIGURE 4.6**, the removal trend decrease with temperature. The highest removal was recorded at temperature of 27°C with 79.0% and 65.3% removal of TSS and COD, respectively. The removals were decrease over temperature due to the increase in kinetic energy and random motions of gas bubbles. The attachments of pollutants into flocks were interfered by this increase of motions (Phalakornkule *et al.,* 2010a). Moreover, the increase in the temperature of the wastewater results in the increasing the solubility of aluminum (El-Naas *et al.,* 2009; Katal and Pahlavanzadeh, 2011).
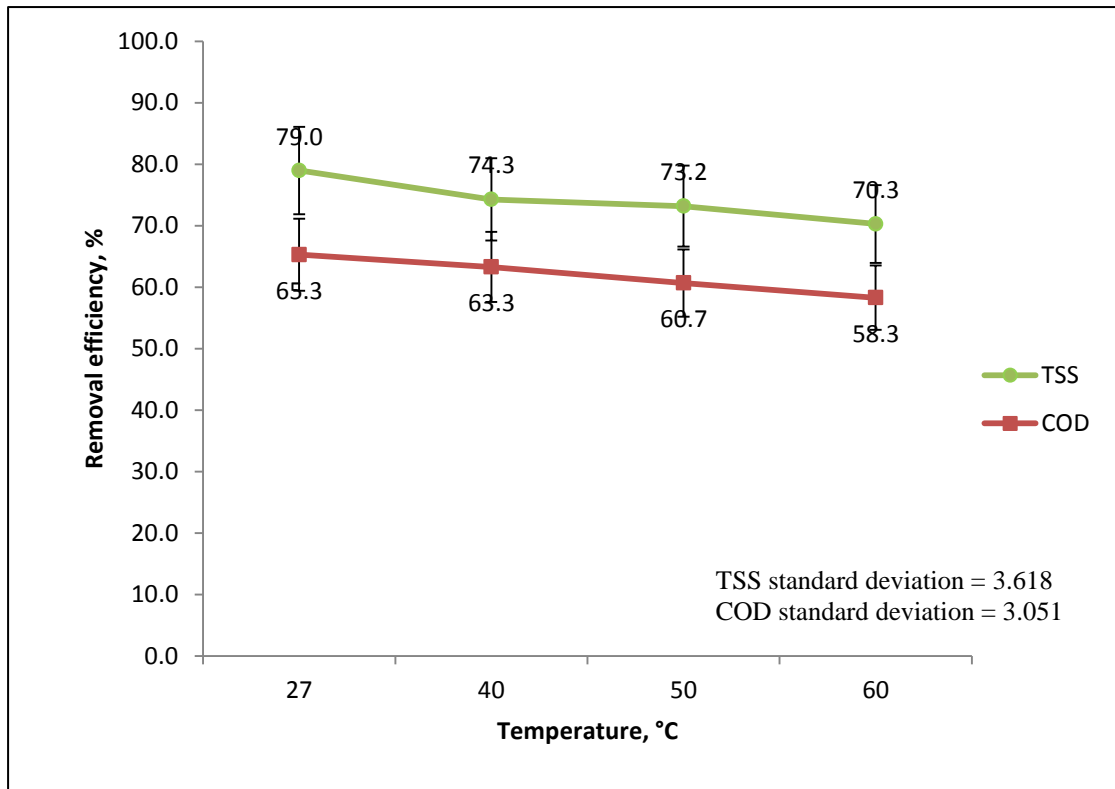
Figure 4.6. Effect of temperature on TSS and COD removal efficiency.

Therefore, the precipitation of the aluminum is enhanced at lower temperature and results in a better removal (El-Naas *et al.,* 2009). Increasing in temperature has major effect on the decrease in the removal efficiency of pollutants (Katal and Pahlavanzadeh, 2011).

4.5 Effect of Operating Time

Operating time is a main factor that reflex to the economic feasibility of the EC process. According to Faraday's law, the quantity of sacrificial electrodes released to the EC system may affect the residence time which leads to an increase in dissolution of metal ions in the system (Akyol, 2011).

FIGURE 4.7 shows the effect of operating time on removal of TSS and COD. As expected from previous studies, the removal efficiency of treatment increased with

the operating time (Bayramoglu *et al.,* 2004; Lai & Lin, 2004). The removal efficiencies of TSS and COD increased until minutes 30 and then it was almost constant in the range of 86.7% to 87.6% for TSS removal and 38.0% to 40.7% for COD removal. This is related to decreasing extent of cathodic reduction and formation of new electrocoagulant flokcs (Akyol, 2011). Moreover, increasing in reaction time may increase the temperature of wastewater which potentially increase the kinetic energy and random motion of the gas bubbles (Phalakornkule *et al.,* 2010a). The increase of random motion of gas bubbles and small colloidal particles could interfere with the process of attachment of pollutants onto flocks (Phalakornkule *et al.,* 2010a).

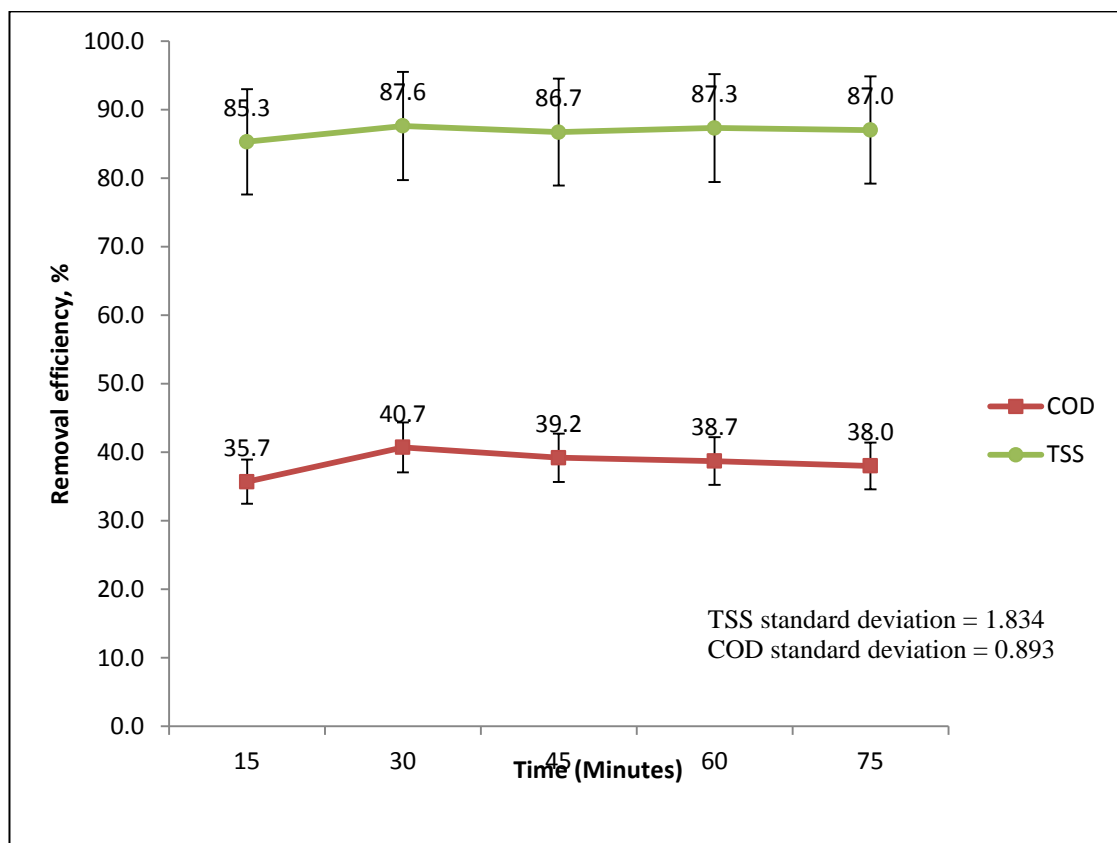**FIGURE 4.7**. Effect of operating time on TSS and COD removal efficiency.

Visible removal efficiency is observed to require only 15 minutes operating time. Even though 30 minutes operating time has given the highest removal efficiencies (87.6 % of TSS and 40.7 % of COD), however the differences of removal efficiencies are not significant when compared to 15 minutes operating time (85.3 % of TSS and

35.7 % of COD). In addition, the amounts of energy and electrode consumption for treatment were taken into consideration in deciding on the optimum operating time. According to **TABLE 4.1**, anode electrode consumption increase with increasing of operating time. The anode electrode consumption of 30 minutes is almost 55% higher than 15 minutes. It is deemed not worthwhile to further lengthen the time since there are not many changes in removal efficiency. Hence, 15 minutes is identified as the optimum time for EC process.

TABLE 4.1. Anode electrode consumption (kg Al/m^3).

Time (minutes)	Anode electrode consumption (kg Al/m^3)	Percentage difference, (%)
15	0.2750	
30	0.4250	55
45	0.6500	53
60	0.8750	35
75	1.1750	34

According to Faraday's law, the amount of Al^{3+} ions released into solution by electrolytic oxidation is proportional with operating time and current density. **FIGURE 4.8** shows the amount of metal dissolution at anode during EC proces over time. The result indicates that the experimental electrode consumption value is higher as compared to the theoretical value. This is due to the effect of mixing during treatment whereby it increased the dissolution of sacrificial electrode. As time increased, the amount of Al^{3+} ions release increased. Besides that, the pH of the solution also contributed to the increased amount of Al^{3+} ions dissolution.(Kobya & Delipinar, 2008). The percentage difference between experimental and theoretical values of metal dissolution is presented in **TABLE 4.2**.
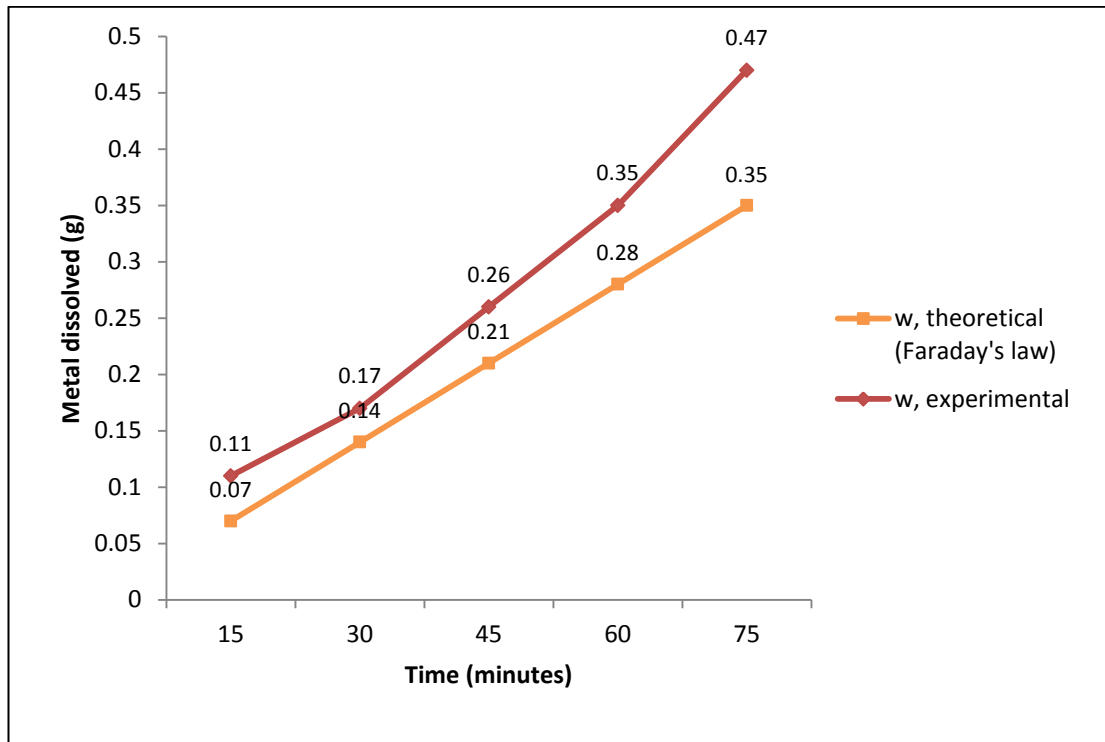
Figure 4.8. Metal dissolution after treatment over time.

TABLE 4.2. Difference percentage between experimental and theoretical values based on Faraday's law.

Time (minutes)	Percentage difference (%)
15	57
30	21
45	23
60	25
75	34

Meanwhile, little electrode consumptions were involved at the cathode. The results are shown in **TABLE 4.3**. This is resulting from the electrode reaction with OH⁻ ions and generated of H_2 bubbles as shown in equation 4.1 (Bayramoglu et al., 2004;Kobya et al., 2003).
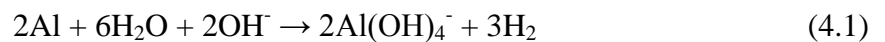
$$2Al + 6H_2O + 2OH^- \rightarrow 2Al(OH)_4^- + 3H_2 \qquad (4.1)$$

TABLE 4.3. Cathode electrode consumption (kg Al/m^3).

Time (minutes)	Cathode electrode consumption (kg Al/m^3)
15	0.0125
30	0.0375
45	0.1750
60	0.2625
75	0.4500

As time increased, cathode electrodes reacted with OH$^-$ ions increased which resulting in increasing of final pH of treated wastewater. As can be seen in **TABLE 4.3**, the cathode electrode consumption at minutes 30 is double when compared to minutes 15. The electrode consumption at cathode is similar to the anode side as it presented in **TABLE 4.1**. However there was no significant removal was attained even though the operating time was increased.

From the findings above, it can be concluded that the optimum operating time is 15 minutes as it supported by electrode consumption data. Increasing the time beyond 15 minutes did not promise the highest removal efficiency except for a little difference which is not worth the cost.

4.6 Chemical Coagulation process

Chemical coagulation process was performed using aluminum sulphate, $Al_2(SO_4)_3$ in a jar test experiments as to compare its performance with EC process. Various dosage of $Al_2(SO_4)_3$ were studied without a pH control. Interestingly after the treatment, the pH of POME was drop similar with previous study reported by Phalakornkule et al. 2010a. The reduction of POME was due to the nature of $Al_2(SO_4)_3$ which is acidic. **Figure 4.9** shows the final pH after chemical coagulation. Initially the pH was ranging from 3.65 to

3.68. After adding various dosage of $Al_2(SO_4)_3$, the pH was drop to 2.95, 2.83, 2.75 and

2.70 for 0.5 g/L, 1.5 g/L, 2.0 g/L, and 2.5 g/L of $Al_2(SO_4)_3$ dosage respectively.

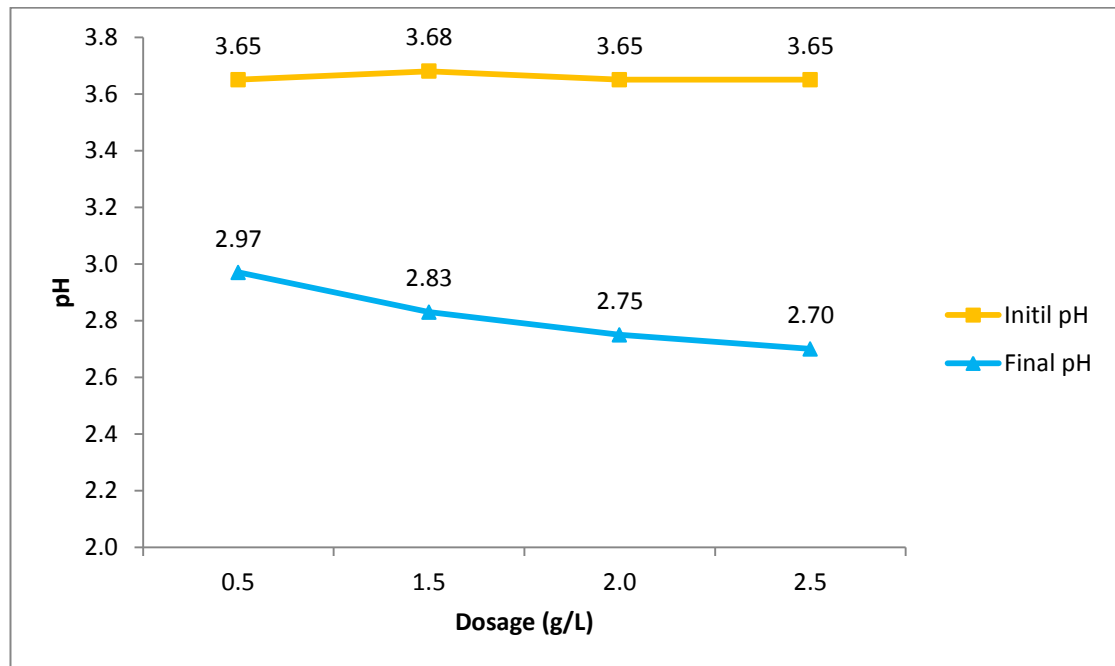**Figure 4.9**. Final pH after chemical coagulation process

Figure 4.10 shows the effects of $Al_2(SO_4)_3$ dosage on the removal of TSS and

COD. The removal efficiency of TSS and COD increased with dosage ranging from 0.5

g/L to 2.0 g/L. The highest TSS and COD removal were attained at dosage 2.0 g/L with

63.3 % and 33.3 % removal respectively. The increase in TSS removal was due to the

destabilization of the flocks influenced differing from COD removal (Guida *et al.,*

2007). At the doasage higher than 2.0 g/L, the removal of TSS and COD was slightly

dropped. This shows the restabilization of POME. At this higher dosage, a sufficient

degree of over-saturation occurs to produce a rapid precipitation of large quantity of

coagulant. A number of works on restabilization of colloidal suspensions due to

excessive treatment with polyelectrolytes have been done (Ahmad *et al.,* 2006; Pinotti *et*

al., 2001).

As a comparison with EC process at the optimum current density of 120 A/m^2 and EC time of 15 minutes, the EC process has produce 4.7 mmol of Al^{3+} whereas in the 0.4 L of POME, the dosage was equivalent to 11.75 mmole of Al^{3+}. This can be compared with removal efficiency that applying CC process with an equivalent dose of Al$_2$(SO$_4$)$_3$ of 2.0 g/L (equivalent to 11.6 mmole of Al^{3+}). As a results, it shows that the treatment using EC process was successfully to remove 85.3 % of TSS and 35.7 % of COD as compared with CC process with 63.3% and 33.3% of TSS and COD removal respectively. Moreover, EC process is able to remove both suspended and dissolved solids whereas CC process can mainly remove suspendes solids (Phalakornkule *et al.,* 2010a). In fact, CC process is potential to increase total dissolved solids in wastewater after the treatment as reported by Alaadin *et al.* 2008.
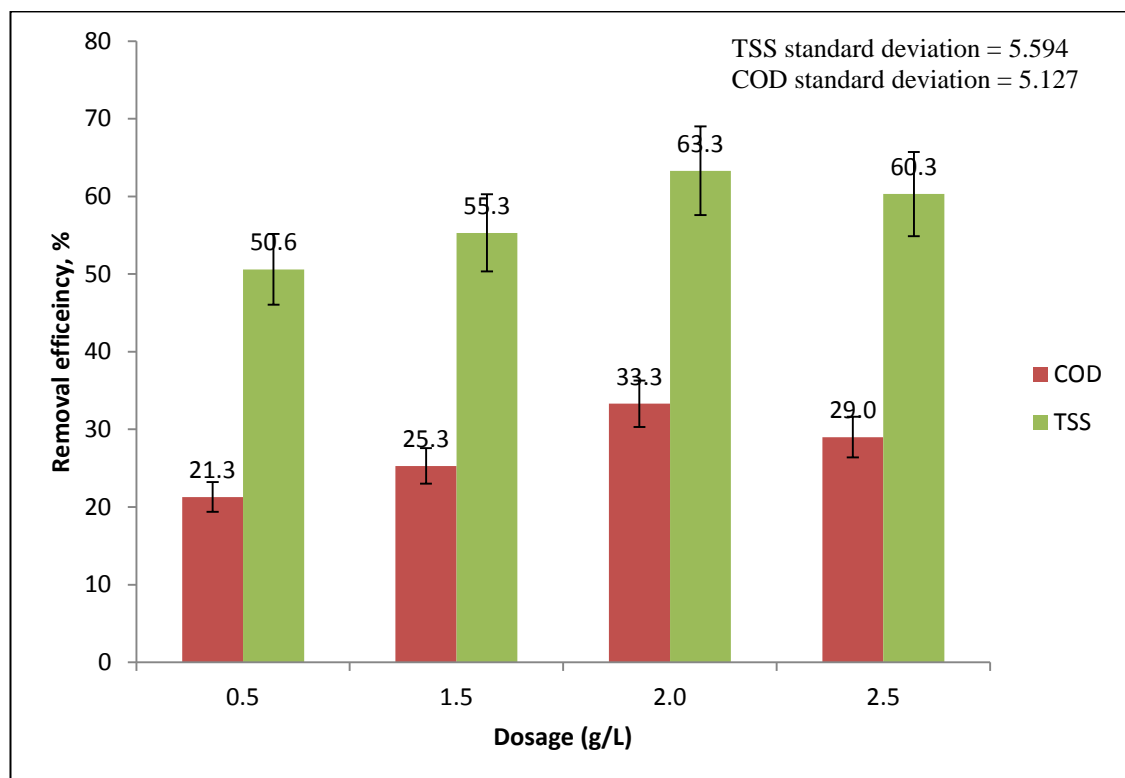

Figure 4.10. Effect of Al$_2$(SO$_4$)$_3$ dosage on TSS and COD removal efficiency

Therefore, EC process has prove its performance was better than CC process. It not only through the amount Al^{3+} consumption, but also the time consuming for the treatment which take 15 minutes for EC and 35 minutes for CC (not included 1 hour settling time).

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The present study investigated the feasibility of electrocoagulation (EC) process in treating palm oil mill effluent (POME). The POME, having 19,000 – 21,000 mg/L of TSS and 60,000 – 63,000 mg/L of COD was collected from POMTEC pond which located at MPOB, Labu, Negeri Sembilan.

From the results obtained, it can be concluded that:

1. At the optimum operating conditions of initial pH of 6, current density of 120 A/m^2, temperature of 27°C, stirring speed of 100 rpm and operating time of 15 minutes, 85.3% of TSS and 35.7 % of COD removal were attained. It was not worthwhile to increase the treatment time as there were no significant changes in the removal efficiency.

2. Limiting the current density favors low heat generation and excessive oxygen evolution during the treatment. The formation of flocks which potentially break and release residue particles into the POME was observed at higher stirring speeds.

3. Besides enhancing removal efficiency of EC process at optimal operating conditions, electrodes and energy consumption were also reduced which directlty reduced the cost of treatment.

4. The performance between electrocoagulation and chemical coagulation process were comparable. Its finally shows that the electrocoagulation process was more efficient in removing TSS and COD which not only through the amount of Al^{3+} consumption but also time consuming for the treatment.

5. The EC process effectively reduced TSS and COD prior to the next stages of treatment and it is suitable as an alternative preliminary process for POME treatment. **Table 5.1** shows the characteristics of POME before and after treatment.

Table 5.1. Characteristics of POME before and after treatment

Characteristics	Before treatment	After treatment
COD (mg/L)	62,000	39,621
BOD_5 (mg/L)	29,000	19,018
Total suspended solids (mg/L)	20,000	2,896
Oil and greases (mg/L)	5,670	1,440

5.2   Recommendations for Future Study

The following are recommendations deduced from the study for future work:

1.   Scale up the reactor used to pilot plant dimension. It may enhance the accuracy of experimental data because the results from the samples taken will be more accurate.

2. Investigate the contradictory findings from other researchers that influence some parameters such as conductivity of wastewater and electrode materials. It is because many researchers have different opinions on their finding. Therefore, the factors that affect these parameters are interesting to be investigated.

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Appendix I

Prevailing Effluent Discharge Standards for Crude Palm Oil Mills (Environmental Quality Act 1974, 2005)

Parameter	Unit	Value	Remarks
Biochemical Oxygen Demand, 3 days - 30°C	mg/L	100	
Chemical Oxygen Demand	mg/L	*	
Total Solids	mg/L	*	
Suspended Solids	mg/L	400	
Oil and Grease	mg/L	50	
Ammoniacal Nitrogen	mg/L	150	Value of filter sample
Total Nitrogen	mg/L	200	Value of filter sample
pH	-	5-9	
Temperature	°C	45	

*No discharge standard after 1984

Appendix II

PARAMETER LIMITS OF EFFLUENT OF STANDARDS A, B and "C"

Parameter	Unit	Standard A	Standard B	Standard "C"
Temperature	°C	40	40	45
pH Value	-	6.0 – 9.0	5.5 – 9.0	5.0 – 9.0
BOD_5 at 20°C	mg/L	20	50	400
COD	mg/L	50	100	1000
Suspended solids	mg/L	50	100	400
Mercury	mg/L	0.005	0.05	0.10
Cadmium	mg/L	0.01	0.02	1.0
Chromium, Hexavalent	mg/L	0.05	0.05	2.0
Arsenic	mg/L	0.05	0.10	2.0
Cyanide	mg/L	0.05	0.10	2.0
Lead		-	-	2.0
Chromium, Trivalent	mg/L	0.20	1.0	10
Copper	mg/L	0.20	1.0	10
Manganese	mg/L	0.20	1.0	10
Nickel	mg/L	0.20	1.0	10
Tin	mg/L	0.20	1.0	10
Zink	mg/L	2.0	2.0 [Am.P.U.(A) 398/2000]	10
Boron	mg/L	1.0	4.0	-
Iron (Fe)	mg/L	1.0	5.0	50
Phenol	mg/L	0.001	1.0	5.0
Free Chlorine	mg/L	1.0	2.0	-
Sulphide	mg/L	0.50	0.50	2.0
Oil and Grease	mg/L	Not detectable	10.0	100

Standard A and B – Extracted from
THIRD SCHEDULE
ENVIRONMENTAL QUALITY ACT 1974
ENVIRONMENTAL QUALITY (SEWAGE AND INDUSTRIAL EFFLUENTS)
REGULATIONS 1978
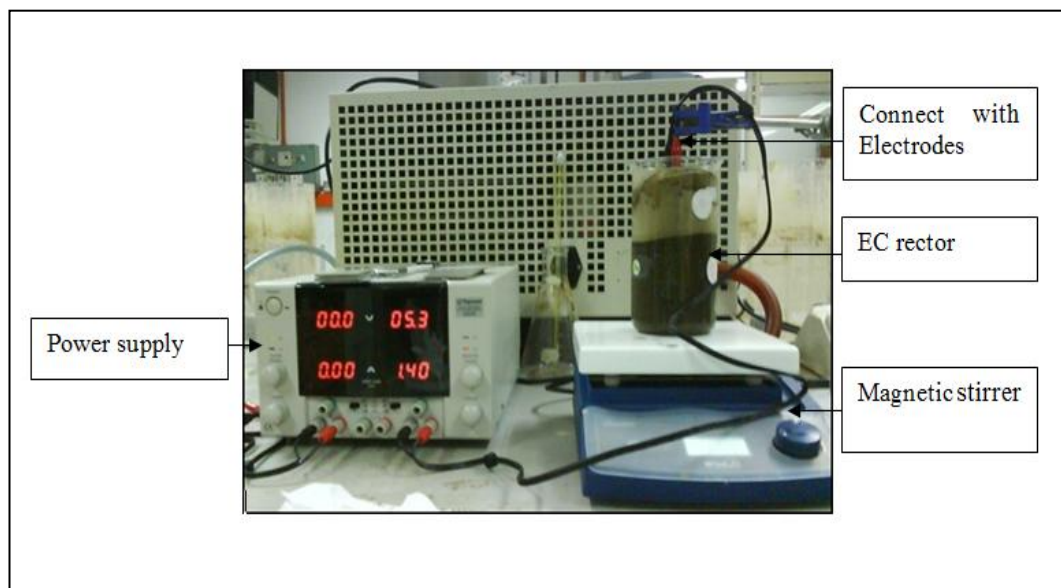[Regulation 8 (1), 8 (2), 8 (3)]

Standard "C" – Extracted from
SIXTH SCHEDULE
ENVIRONMENTAL QUALITY ACT 1974
ENVIRONMENTAL QUALITY (SEWAGE AND INDUSTRIAL EFFLUENTS)
REGULATIONS 1978
[Regulation 11 (5) (*b*)]
PARAMETER LIMITS OF EFFLUENT OTHER THAN OF STANDARD A OR B
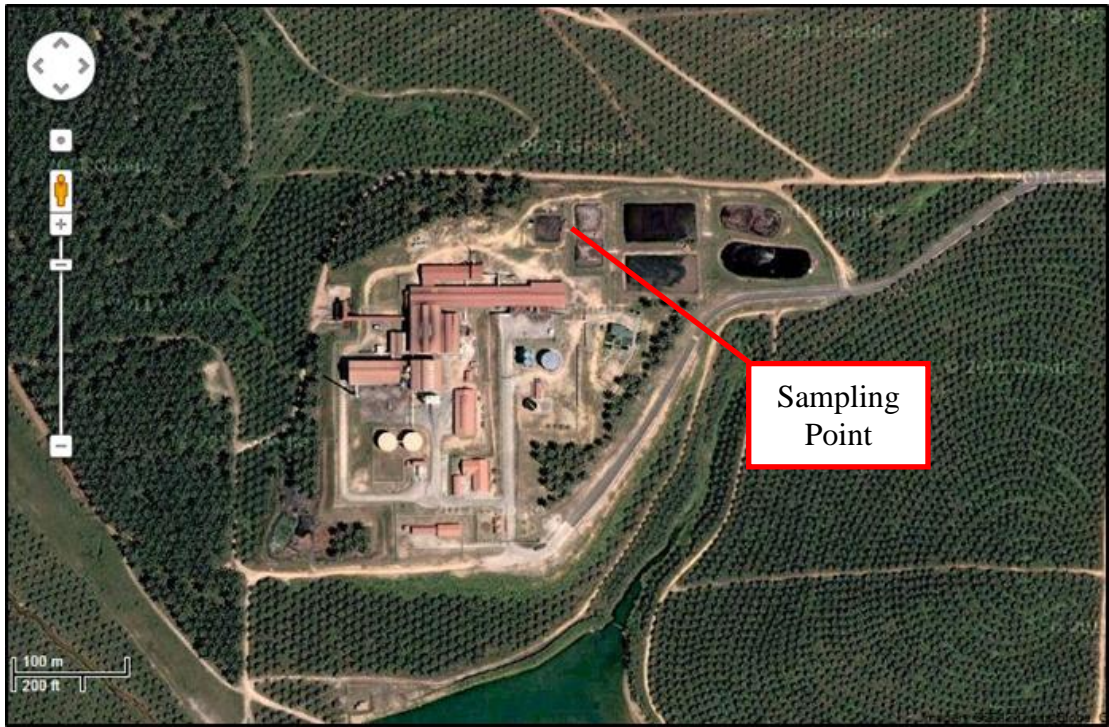
Appendix III: An aerial view of POMTEC, Labu Negeri Sembilan

Appendix IV: Sampling point

Appendix V: Experimental setup