

EFFECTIVENESS MAGNESIUM AMMONIUM PHOSPHATE (MAP) PRECIPITATION AND FILTRATION METHOD IN TREATMENT OF PALM OIL MILL EFFLUENT (POME)

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ABSTRACT

The process of oil extraction from palm oil industry resulted in the generation of liquid waste commonly known as palm oil mill effluent (POME). POME is a viscous brown liquid containinghigh concentrations of fine suspended solids, oil and grease andother contaminants. Several treatment technologies have been used for POME treatment, since the direct discharge of POME adversely affects the environment. Majority of palm oil mill uses conventional biological treatment of aerobic, anaerobic or facultative ponds which needs large area and long treatment periods. The conventional treatment system is quite inefficient andleads to environmental issues. The use of chemical precipitation method such as magnesium ammonium phosphate (MAP) precipitation has been studied and was found to be effective in treating landfill leachate. The key feature of this recovery technique is the combined removal of ammonium (NH_4^+), phosphate (PO_4^{3-}) and magnesium (Mg^{2+}) from supersaturated solutions. The by-product of this method is magnesium ammonium phosphate hexahydrate (MgNH₄PO₄·6H₂O), which is commonly known as struvite. Extracting nutrient using MAP precipitation method may be beneficial in treatment of POME. However, MAP precipitation alone would not be sufficient to remove contaminants concentration regulatory discharged limits. In this study, MAP precipitation method was used to treat raw POME obtained from Sime Darby, Jabor palm oil mill. Additionally, filtration using activated carbon (AC) and glass carbon (GC) was also used further treatthe POME. Results indicated that, after treatment process, the lowest, turbidity 21,433 NTU, COD is 66,300 mg/L, TOC is 26,600 mg/L and oil and grease is 8,269 mg/L of treated POME were achieved. Although both methods reduced the contaminant concentration to desired limits, the final COD and TOC concentration is much greater than allowable standard limits. It was also observed that for all water quality parameters considered, GC filter performed slightly better than of AC filter.

ABSTRAK

Proses pengekstrakan minyak daripada industri minyak sawit menyebabkan penjanaan sisa cecair dikenali sebagai kilang minyak sawit (POME). POME adalah cecair likat coklat yang mengandungi kepekatan tinggi pepejal terampai, minyak dan gris dan bahan cemar lain. Beberapa teknologi rawatan telah digunakan untuk rawatan POME, kerana pelepasan langsung POME menjejaskan alam sekitar. Kebanyakan kilang kelapa sawit menggunakan rawatan biologi konvensional aerobik, anaerobik atau fakultatif kolam yang memerlukan kawasan yang besar dan tempoh rawatan yang panjang. Sistem rawatan konvensional agak tidak cekap dan membawa kepada isu-isu alam sekitar. Penggunaan kaedah pemendakan kimia seperti magnesium ammonium fosfat (MAP) mendakan telah dikaji dan didapati berkesan dalam merawat tapak pelupusan sampah. Ciri utama teknik pemulihan ini adalah penyingkiran gabungan ammonium (NH4⁺), fosfat (PO4³⁻) dan magnesium (Mg²⁺) daripada penyelesaian supertepu. Dengan produk kaedah ini adalah magnesium ammonium fosfat hexahydrate (MgNH₄PO₄ • 6H₂O), yang dikenali sebagai struvite. Pengekstrakan nutrisi menggunakan kaedah pemendakan MAP mendakan boleh memberi manfaat dalam rawatan POME.Walaubagaimanapun, MAP mendakan sahaja tidak akan mencukupi untuk membuang bahan cemar kepekatan had peraturan dilepaskan. Dalam kajian ini, kaedah pemendakan MAP telah digunakan untuk merawat POME mentah yang diperolehi daripada kilang minyak sawit Sime Darby, Jabor. Selain itu, penapisan menggunakan karbon diaktifkan (AC) dan kaca karbon (GC) juga digunakan merawat POME. Keputusan menunjukkan bahawa, selepas proses rawatan, yang paling rendah, kekeruhan 21433 NTU, COD adalah 66,300 mg / L, TOC adalah 26,600 mg / L dan minyak dan gris adalah 8.269 mg / L POME dirawat telah dicapai. Walaupun kedua-dua kaedah mengurangkan kepekatan bahan cemar kepada had yang dikehendaki, COD akhir dan kepekatan TOC adalah lebih besar daripada had standard dibenarkan. Ia juga diperhatikan bahawa untuk semua parameter kualiti air dianggap, penapis GC dilakukan sedikit lebih baik daripada penapis AC.

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LIST OF SYMBOLS AND TERMINOLOGY

AC	Activated Carbon		
BOD	Biological Oxygen Demand		
COD	Chemical Oxygen Demand		
СРО	Crude Palm Oil		
EFB	Empty Fruit Bunch		
FFB	Fresh Fruit Bunch		
GC	Glass Carbon		
KKS	Kilang Kelapa Sawit		
GDP	Gross Domestic Product		
Mg/L	Milligram per litre		
MAP	Magnesium Ammonium Phosphate		
NTU	Nephelometric Turbidity Units		
РКС	Palm Kernel Cake		
POME	Palm Oil Mill Effluent		
POMS	Palm oil mill sludges		
UF	Ultrafiltration		

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Palm oil production is the main source income of Malaysia (Abu Hassan and Puteh, 2007). The total plantation area of oil palm in Malaysia was 4,487,957 ha in 2008 (Rajeev *et al.*, 2010). Moreover, Malaysia is blessed with favourable weather conditions which prevail throughout the year which is advantageous for palm oil cultivation (Yusoff, 2006). Thus, it is not surprising that the highest yields have been obtained from palms grown in this region, which is far from its natural habitat. Palm oil-processing mills are the most prominent vegetable oil industry which discharges large volumes of oily and colloidal wastewater (Ahmad *et al.*, 2006). In the year 2004, more than 40 million tonnes of Palm Oil Mill Effluent (POME) was generated from 372 mills in Malaysia (Yacob *et al.*, 2006). POME is a thick brownish liquid that contains high solids, oil and grease, Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) values and it's considered the most harmful waste for the environment if discharged untreated (Rupani *et al.*, 2010).

The improvement of processing technology will no doubt lead to further increase in world's palm oil supply. However, the rapid development of the industry had serious consequences on the natural environment, which mainly related to water pollution due to a large discharge of untreated or partially treated POME into watercourses (Abu Hassan and Puteh, 2007). The environmental issues are increasingly becoming more important in Malaysia and the world over. The palm oil industry is aware of the environmental pollution

and is striving towards quality and environmental conservation through 'sustainable development and cleaner technology' approach (Yusoff, 2006). Thus, to remain competitive, the oil palm industry must be prepared for the new challenges ahead.

Several treatment technologies have been used for POME treatment, since the direct discharge of POME adversely affects the environment. Due to the presence of high total solids in POME, attempts have been made to convert this waste into valuable products such as feed stock and organic fertilizer (Rupani *et al.*, 2010). Majority of palm oil mill uses conventional biological treatment of aerobic, anaerobic or facultative ponds which needs large area and long treatment periods (Ahmad *et al.*, 2003). They noted that, conventional treatment system is quite inefficient and leads to environmental issues. The use of chemical precipitation method such as magnesium ammonium phosphate (MAP) precipitation has been studied and finds out to be effective in treating landfill leachate (Sugiyama *et al.*, 2005). According to Yetilmezsoy and Zengin (2008), the application of recovered MAP sludge as a valuable slow release fertilizer for the used in agriculture

In this study, MAP precipitation is used to treat raw POME. Additionally, activated carbon (AC) and glass carbon (GC) are used to further reduce the remaining contaminant concentration.

1.2 PROBLEM STATEMENT

POME would cause severe deterioration to receiving water bodies if left untreated due to high concentration of contaminants. Extracting nutrient using MAP precipitation method may be beneficial in treatment of POME. However, MAP precipitation alone would not be sufficient to remove contaminants concentration regulatory discharged limits. Additional treatment such as filtration using AC and GC may assist in further treats raw POME.

1.3 OBJECTIVE OF STUDY

The study outlines the following objectives:

- 1.3.1 to study the applicability of MAP precipitation method in removal turbidity, COD,TOC, oil and grease from POME.
- 1.3.2 to determine the effectiveness of activated carbon and glass carbon as polishing media.

1.4 SCOPE OF STUDY

Raw POME taken from Sime Darby Jabor Palm Oil Mill was considered in this study. Laboratory test was conducted in treating raw POME. Two treatment methods were considered namely, MAP precipitation and filtration method using AC and GC. To identify the effectiveness of these treatment methods, three water quality parameters are measured and monitored. These parameters include COD, Total Organic Carbon (TOC), turbidity and oil and grease.

1.5 THESIS OVERVIEW

This thesis consists of 5 consecutive chapters.

Chapter 2 presents the literature review explained about the palm oil industry, production of palm oil and waste generation in the palm oil mill. This chapter also discussed about the previous method of POME treatment, MAP precipitation and pre-treatment process which is related to this study. The further treatment of POME by using activated carbon and glass carbon also explained in this chapter.

Chapter 3 explains methodology of this study. This chapter described about the flow of the work that have been conducted. Besides that, this chapter also discuss the material and chemicals used in this study. Flow chart is used in order to organize work arrangements from start to completion to facilitate the work. The detail experimental procedure is explained in this chapter according to the test of each parameter. Then, it is also include with the process of MAP precipitation and polishing by using activated carbon and glass carbon.

Chapter 4 discuss the result and analyze the data obtain. The determination of water quality parameter is based on turbidity, COD, TOC and Oil and Grease. The result obtained will be compared between the pre-treated of MAP precipitation with the further treatment by using the activated carbon and glass carbon.

Chapter 5 conclude the study based on the result obtained. The most effective type of filtration media in polishing pre-treated POME is determined in this chapter. Recommendations related to this study also include in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter highlights the general information of palm oil industry in Malaysia, production of palm oil, process of MAP precipitation, characteristics of raw POME and the changes characteristics after being treated by using polishing media. This chapter also explained the different method had been used in treatment of POME before using the MAP precipitation method. Besides that, this chapter provides the comparison result by the researchers with various methods.

2.2 PALM OIL INDUSTRY

Global demand for edible oils is increasing in the last few decades, which resulted in a tremendous increase in the area of oil crop cultivation, particularly of soybean and oil palm (Yacob, 2008). Today, Malaysia is the world's largest producer and exporter of palm oil, replacing Nigeria as the chief producer since 1971 (Yusoff, 2006) where Malaysia is blessed with favourable weather conditions which prevail throughout the year which is advantageous for palm oil cultivation. Thus, it is not surprising that the highest yields have been obtained from palms grown in this region, which is far from its natural habitat. In the year 2003 there were more than 3.79 million hectares of land under palm oil cultivation, occupying more than one third of the total cultivated area and 11% of the total land area of Malaysia (Yusoff and Hansen, 2007). The high production of crude palm oil prompts the palm oil industry to become an important contributor to Malaysia's Gross Domestic Product (GDP) (Wu *et al.*, 2010). Export earnings from palm oil, palm kernel oil and relating products in 1998 amounted to almost US\$5.6 billion, equivalent to 5.6% of the GDP (Yusoff, 2006). Furthermore, the palm oil industry provides a source of livelihood to rural families in government land schemes and private smallholders, as well as employment opportunities to agricultural workers in estates (Wu *et al.*, 2010 : Lam and Lee, 2011).

2.3 PRODUCTION OF PALM OIL

According to Idris *et al.* (2010), there are two main products produced by the oil palm fruit namely crude palm oil (CPO) and crude palm kernel oil (CPKO). CPO is obtained from the mesocarp and CPKO is obtained from the endosperm (kernel). Figure 2.1 shows the conventional palm oil extraction and sources of waste generation.



Figure 2.1: Conventional palm oil extraction process and sources of waste generation (Thani *et al.*, 1999).

Fresh Fruit bunches (FFB) are transported to the palm oil mills, several unit operations are involved in order to extract palm oil. Each FFB consists of hundreds of fruits, each of which containing a nut surrounded by a bright orange pericarp which contains the palm oil (Rupani *et al.*, 2010). These FFBs are sterilized with steam at a pressure of 3 bars and a temperature of 140 °C for 75-90 min. The objectives of this process are to prevent further formation of free fatty acids due to enzyme action, facilitate

stripping and prepare the fruit mesocarp for subsequent processing. The steam condensate coming out of the sterilizer constitutes as one of major sources of liquid effluent (Thani *et al.*, 1999).

The process to extract the oil requires significantly large quantities of water for steam sterilizing the palm fruit bunches and clarifying the extracted oil (Rupani *et al.*, 2010). The crude palm oil (CPO) from the screw presses consists of a mixture of palm oil (35-45 %), water (45-55 %) and fibrous materials in varying proportion. It is then pumped to a horizontal or vertical clarification tank for oil separation. In this unit, the clarified oil is continuously skimmed-off from the top of the clarification tank. It is then passed through a high speed centrifuge and a vacuum dryer before sending it to the storage tanks. Production of palm oil produces a lot of waste.

2.4 GENERATION OF WASTE FROM PALM OIL MILL

The oil palm industry produces a wide variety of wastes in large quantities. From the oil extraction and processing there are also liquid wastes arise. While from the solid wastes are the leaves, trunk, decanter cake, empty fruit bunches, seed shells and fibre from the mesocarp. The main product produced by the production of palm oil mill is crude palm oil (CPO). Besides that, the mills also generate many by-products as well as liquid wastes which might deteriorate the surrounding environment. Based on the study of Ahmad *et al.* (2003), for every tone of the CPO produced, about 3.5m³ of POME is generated, which indicates that with some 500 palm oil mills, more than 17.5 million tones of CPO is produced annually. It is estimated that about 55 million m³ of POME is generated from the palm oil industry.

2.4.1 Gaseous Emission

Palm oil mills are generally self-sufficient in terms of energy requirements due to the availability of adequate quantities of fibre and shell materials that are used as solid fuel in the stream boiler. The boiler and incinerator that are the principle sources of air pollution in the mills which caused by incomplete combustion of the solid waste materials (waste fibre, shell materials and EFB) (Thani *et al.*, 1999). The emission of greenhouse gases (GHG) (CH₄ and CO₂) from these systems to the atmosphere has been recently reported as a source of air pollution from the palm oil mills (Yacob *et al.*, 2005) with regard to that the main practice of treating POME is by using ponding or open digesting tank systems (Ma *et al.*, 1999).

2.4.2 Solid Waste

POME also contains substantial quantities of solids, both suspended solids and total dissolved solid in the range of 18,000 mg/L and 40,000 mg/L (Rupani *et al.*, 2010). Basically, these solids are commonly named palm oil mill sludges (POMS).The most common among these by products is the empty fruit bunch, palm oil mill sludge (POMS), palm kernel cake (PKC) and decanter cake. Besides that, palm kernel oil (white palm oil) is obtained from the seed known as kernel or endosperm. When oil has been extracted from the kernel, what remains is known as 'palm kernel cake' (PKC).This is rich in carbohydrate (48%) and protein (19%) and is used as cattle feed (Onwueme and Sinha 1991). Palm kernel cake can be processed into animal feed and chicken feed (Rupani *et al.*, 2010). They also states that the protein content of PKC can be increased, improving its marketable value.

2.4.3 Liquid Effluent

In the palm oil industry, the process of oil extraction results in generation of liquid waste commonly named POME (Rupani et *al.*, 2010). POME is generated mainly from oil extraction, washing and cleaning processes in the mill and these contains cellulose material, fat, oil and grease etc. (Agamuthu, 1995). Furthermore, 1 tonne of crude palm oil production requires 5-7.5 tonnes of water; over 50 % of which ends up as POME (Ma, 1999a). The POME comprises a combination of wastewater from three main sources clarification 60%, sterilization 36% and hydrocyclone 4% units (Ma, 2000). It contains various suspended components

including cell walls, organelles, short fibres, a spectrum of carbohydrates ranging from hemicellulose to simple sugars, a range of nitrogenous compounds from proteins to amino acids, free organic acids and an assembly of minor organic and mineral constituents (Ugoji, 1997).

2.5 PALM OIL MILL EFFLUENT (POME)

POME is generated from three major sources, namely sterilizer condensate, hydro cyclone waste and separator sludge (Borja and Banks, 1994). Characteristics of POME depend on the quality of the raw material and palm oil production processes in palm oil mills (Rupani et al., 2010). Based on the study of Ahmad et al. (2006), POME is a colloidal suspension containing 95-96% water, 0.6-0.7% oil and grease and 4-5% total solids. POME is a viscous brown liquid with fine suspended solids at pH ranging between 4 and 5 (Najafpour et al., 2006). The palm contains a high nutrient which mainly depends on the yield potential determined by the genetic make-up of the planting material and yield limit set by climatic factor such as water, effective sunshine and temperature (Rupani et al., 2010). POME is rich in organic carbon with a biochemical oxygen demand (BOD) higher than 20 g/L and nitrogen content around 0.2 g/L as ammonia nitrogen and 0.5 g/L total nitrogen (Ma et al., 2001). POME is suitable to be used as a carbon source because it consists of high organic acids (Alias and Tan, 2005: Md Din et al., 2006a). The discharge of untreated POME though creates adverse impact to the environment, the notion of nurturing POME and its derivatives as valuable resources should not be dismissed. This is because POME contains high concentrations of protein, carbohydrate, nitrogenous compounds, lipids and minerals that may be converted into useful materials using microbial processes (Agamuthu, 1985). There is an urgent need to find a compromising way that will enable the balance between the environmental protection and sustainable reuse of the nutrient sources found in the POME Wu et al. (2007). Table 2.1 shows the typical characteristics of POME.

Parameter	Concentration (mg/l)	Element	Concentration (mg/l)
Oil and grease	4000-6000	Phosphorus	180
Biochemical oxygen demand	* 25000	Potassium	2270
Chemical oxygen demand	50000	Calcium	439
Total solids	40500	Boron	7.6
Suspended solids	18000	Iron	46.5
Total volatile solids	34000	Manganese	2.0
Ammonicals nitrogen	35	Copper	0.89
Total nitrogen	750	Magnesium	615
		Zinc	2.3

Table 2.1 Characteristics of palm oil mill effluent (after Ahmad et al., 2006)

2.6 PALM OIL MILL EFFLUENT TREATMENT

POME is a highly polluting wastewater that pollutes the environment if discharged directly due to its high COD and BOD concentration (Poh and Chong, 2009). The treatment of, POME is an important issue for the minimization of water pollution Bhatia *et al.* (2007). The discharged of untreated POME into public watercourses with contain of fairly high acidic will give harm to the public. Furthermore, POME contributes 83% of the industrial organic pollution load in Malaysia (Vigneswaran *et al.*, 1999). Pre-treatment of POME was carried out in order to remove the suspended solids and residual oil using flocculation, solvent extraction, adsorption and membrane separation process (Abdul Latif et *al.*, 2003). The presence of unrecovered palm oil in the raw or partially treated has extremely high content of degradable organic matter.

2.6.1 Ponding System

Several innovative treatment technologies have been developed and applied by palm oil mills to treat POME where conventional biological treatments of anaerobic or facultative digestion are the most commonly used (Quah *et al.* 1982). However, this biological treatment system needs proper maintenance and monitoring as the processes rely solely on micro-organisms to break down the pollutants. The micro-organisms are very sensitive to changes in the environment and thus great care has to be taken to ensure that a conducive environment is maintained for the micro-organisms in which to thrive Wu *et al.* (2007). It also generates vast amount of biogas (Rupani *et al.*, 2010). This biogas contains methane, carbon dioxide and trace amounts of hydrogen sulphide which these gases are corrosive and odorous. The treated wastewater cannot be reused in the plant, and it is being discharged into the environment. Figure 2.2 shows the ponding system in treating of POME.



Figure 2.2 Ponding system

2.6.2 Aerobic Treatment System

The anaerobic liquor is aerated to further reduce the BOD content in the extended aerobic system. In addition to providing oxygen, the floating aerators also ensure complete mixing is achieved and the pod contents are always in suspension (Ahmad and Chan, 2009). In this process, levels of beneficial micro-organisms are increased which in turn hasten the conversion of pollutants into carbon dioxide, water and energy. The aerobic suspension is allowed to settle in a settling tank to ensure production of a fairly clean supernatant. The main advantages of extended aerobics systems are its high BOD removal efficiency and low solid yield.

2.6.3 Membrane Technology

POME contains trace amount of mineral sand heavy metals Ahmad *et al.* (2006). A proper treatment method to remove the organic matter minerals and heavy metals is required. Membrane technology has become a recognized separation method that is well suited for there cycling and reuse of wastewater. The main advantages of membranes technology are compact process and plant, separation based on size exclusion, invariable quality of produced water, constant production and water quality independent of feed water quality, easy automation and absence of bacterial regrowth and residual toxicity (Xia *et al.*, 2004). Recently, ultrafiltration (UF) has been successfully used as a separation method in various industrial processes especially in the production of pure water, food and pharmaceutical industries. However, major drawbacks of using membrane includes fouling, and decline in permeate flux (Ahmad *et al.*, 2006). Based on Idris *et al.* (2010), this flux decline leads to an increase in the membrane cleaning and replacement costs.

2.7 POME AS NUTRIENT SOURCE

2.7.1 Vermicomposting

Composting or natural conversion of biodegradable waste into high quality fertilizer with the help of earthworms is known as vermicomposting. Vermicomposting is the process in which earthworms are used to convert organic materials into humus-like material known as vermin compost or earthworm compost Rupani *et al.* (2010). Then, through vermicomposting process physical, chemical and biological reactions take place, resulting changes in the organic matter. The resultant product vermicast is much more fragmented, porous and microbially active (Edwards, 1988).The latter product which is vermin compost is considered as homogenous, has reduced levels of contaminants and tends to hold more nutrients. Based on the study of Rupani *et al.* (2010), during the vermicomposting process, important plant nutrients such as nitrogen, phosphorus, potassium, and others present in the waste are converted into much soluble and available to plants. They have reported that the nutrient composition of vermicomposting may increase the plant nutrients as compared to the simple composting. In order to make use of earthworms successful in vermicomposting, its survival, growth and fecundity in different wastes should be known (Garg *et al.*, 2006).

There are many methods that had been used in treating of POME. Based on each method of treatment pome, there are advantages and disadvantages. In this present study MAP precipitation is introduced as a method for treating POME. Then, the effectiveness of MAP and filtration method by using the polishing media in treating of POME is the further study of present study. The current treatment system, which is based mainly on biological treatments of anaerobic and aerobic systems, is quite in efficient and this unfortunately leads to the environmental pollution issues (Wu *et al.*, 2007).