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THE USE OF SEAWATER AS A SOURCE OF MAGNESIUM CHLORIDE ($MgCl_2$) IN MAGNESIUM AMMONIUM PHOSPHATE (MAP) TREATMENT METHOD

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ABSTRACT

POME is a thick brownish liquid that contains high solids, oil and grease (O&G), chemical oxygen demand (COD) and Biochemical Oxygen Demand (BOD) content. When POME discharged untreated into watercourses, it will adversely affect the aquatic life and domestic water supply. POME is commonly treated using conventional systems, however, these systems failed to utilize the nutrient contained within POME. The use of several magnesium and phosphate based chemicals or magnesium ammonium phosphate (MAP) precipitation method have been shown to provide an effective treatment of wastewater containing substantial amount of nutrients. MAP precipitation method extract precious nutrient in the form MAP crystals. MAP display excellent fertilizer quality when compared to commercially available fertilizers. The extraction of MAP although rapid, however, is rather costly as it involves several different chemicals. Alternatives to magnesium based chemicals such as seawater may be used to reduce operational cost. This study focuses on treatment of POME from Sime Darby Jabor Palm Oil Mill using MAP precipitation method. $MgCl_2$ and Na_2HPO_4 are mixed with raw POME. Seawater was also used as substitute as $MgCl_2$. The results indicated that, MAP precipitation method can be used to treat POME and at the same time produced of high quality fertilizer. About 70% to 80% Mg and COD concentrations were removed. A maximum of 23 g of MAP were extracted for each 250 ml of POME used. However, the water contents of the precipitates were very high, particularly when extracted using seawater thus, further drying and dewatering are required.

ABSTRAK

POME adalah cecair coklat pekat yang mengandungi kandungan pepejal yang tinggi, O&G, COD dan BOD. Apabila dilepaskan ke dalam sungai tanpa rawatan, ia boleh memberi kesan buruk kepada hidupan air dan saluran air domestik. POME kebiasaanya dirawat dengan menggunakan sistem konvensional, bagaimanapun sistem ini gagal menghasilkan nutrien yang terkandung dalam POME. Penggunaan beberapa magnesium dan bahan kimia berasaskan fosfat atau kaedah mendakkan MAP telah menunjukkan bahawa rawatan yang berkesan untuk sisa buangan menghasilkan sejumlah besar nutrien. Kaedah pemendakan MAP akan menghasilkan nutrien berbentuk kristal. MAP menghasilkan kualiti baja yang sangat baik berbanding dengan baja yang didapati secara komersial. Pengekstrakan MAP walaupun pesat, bagaimanapun adalah agak mahal kerana ia melibatkan beberapa bahan kimia yang berbeza. Alternatif lain kepada bahan kimia berasaskan magnesium seperti air laut boleh digunakan untuk mengurangkan kos operasi. Kajian ini memberi tumpuan kepada rawatan POME daripada Kilang Minyak Sawit Sime Darby Jabor dengan menggunakan kaedah pemendakan MAP. $MgCl_2$ dan Na_2HPO_4 dilarutkan dengan POME mentah. Air laut juga digunakan sebagai pengganti kepada $MgCl_2$. Keputusan menunjukkan bahawa, kaedah pemendakan MAP boleh digunakan untuk merawat POME dan pada masa yang sama akan menghasilkan baja yang berkualiti tinggi. Kira-kira 70% hingga 80% kepekatan Mg dan COD dikeluarkan. Maksimum MAP dihasilkan bagi setiap 250 ml POME digunakan adalah 23 g. Walau bagaimanapun, kandungan air daripada mendakan MAP adalah sangat tinggi terutamanya apabila diekstrak menggunakan air laut, oleh itu rawatan lain seperti pengeringan dan pembuangan air diperlukan.

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LIST OF SYMBOLS

%	Percentage
°C	Degree Celcius
°	Degree
g	Gram
L	Liter
ml	Millimeter
mg/L	Milligram per liter
rpm	Revolution per minutes

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometer
BOD	Biochemical Oxygen Demand
Ca	Calcium
$CaCO_3$	Calcium Carbonate
$Ca(OH)_2$	Calcium Hydroxide
COD	Chemical Oxygen Demand
CPO	Crude Palm Oil
CH_4	Methane
CO_2	Carbon Dioxide
DOE	Department of Environment
EFB	Empty Fruit Bunches
FFB	Fresh Fruit Bunch
GHG	Greenhouse Gases
HR	High Range
K	Potassium
Li	Lithium
MAP	Magnesium Ammonium Phosphate
MPOB	Malaysia Palm Oil Board
Mg^{2+}	Magnesium
$MgCl_2$	Magnesium Chloride
$Mg(OH)_2$	Magnesium Hydroxide
N	Nitrogen
Na	Sodium

NaOH	Sodium Hydroxide
Na_2HPO_4	Di-Sodium Hydrogen Phosphate
NH_4^+	Ammonium
O&G	Oil and Grease
P	Phosphorus
PO_4^{3-}	Phosphate
POME	Palm Oil Mills Effluent
TN	Total Nitrogen
TS	Total Solids
TSS	Total Suspended Solid
TVS	Total Volatile Solids
WWTP	Wastewater Treatment Plants

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Malaysia is identified one of the major contributor of oil in South East Asia. Palm oil is one of the world's most rapidly expanding equatorial crops. Malaysia and Indonesia is the largest producing countries that produce palm oil and is rich with numerous endemic, forest-dwelling species. Malaysia has a tropical climate and is prosperous in natural resources. Oil palm currently occupies the largest acreage of farmed land in Malaysia (Arif *et al,*. 2001). According to Malaysian Palm Oil Board, (M.P.O.B, 2006) the global production of palm oil with the plantation area has been increased and Figure 1.1 shows that Malaysia contributes 41% of the world production.

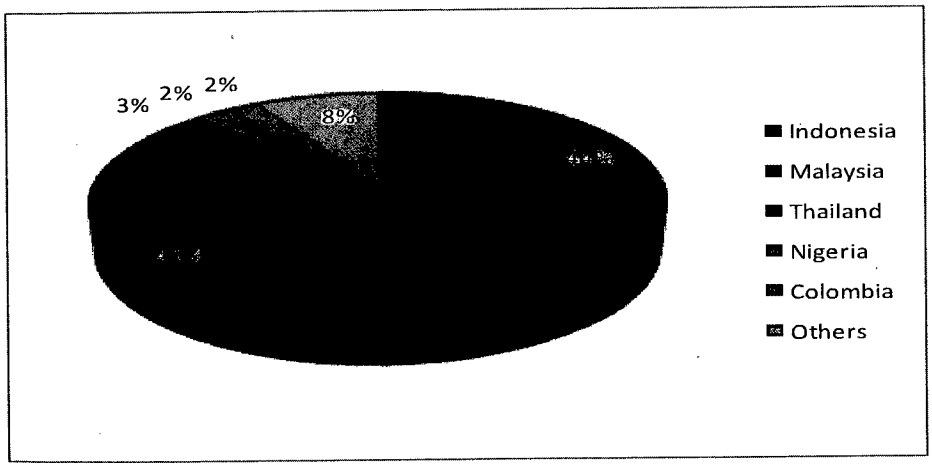

Figure 1.1 : World palm oil productions 2008

Couple with the production of palm oil, the country also produces the largest palm oil based pollution load into the river due to the production of huge quantities of by-products from the oil extraction process (Varripan and Yen, 2008). About 30 million tonnes of palm oil mills effluent (POME) and 26.7 million tonnes of solid biomass were generated in 2004 (Rupani, 2010). (Ma, 2000) states that POME containing high amount of total solids (TS), oil and grease (O&G), chemical oxygen demand (COD) and also biochemical oxygen demand (BOD) with pH 4.7. Since these compounds are injurious to the environment, it becomes necessary that these effluents water should be purified or treated before discharged into the environment (Igwe and Onyegbado, 2007). Therefore, it is important and necessary to treat POME using efficient treatment to avoid environmental pollution. Currently, there are several types of POME treatment methods that available such as anaerobic and aerobic digestion and also ponding system (Rupani *et al.,* 2010). Although these systems were found to be more effective, but it failed to utilize the nutrient contained within POME.

POME has been identified as a source of nutrient and may be converted into fertilizer for agricultural use. Composting technology and vermicomposting techniques using earthworms are usually employed in the conversion of POME into commercial grade fertilizers. These techniques however, require significant amount of time and other additional additives such as urea to boost the quality of fertilizer produced. As substantial amount of POME is generated each day, composting and vermicomposting technologies may not be the ultimate solution.

Magnesium ammonium phosphate (MAP) has been shown from previous research that nutrient can be achieved at high quality of fertilizer. Previous study shows that MAP precipitation was recovered as the method or technique in treatment of wastewater. It has been studied and practiced in different types of wastewater such as digester supernatant in wastewater treatment plants, tannery effluent in leather industries, wastewater from coke plants and nitrogen work and also sludge liquor (Li *et al.*, 1999). In this method, several chemicals were mixed into the wastewater and high quality of fertilizer was produced. Other than that, these methods only take a short time and at the same time were reduce the

concentration of contaminants within the wastewater and also were reduce the cost. The use of MAP precipitation method to treat POME and extracting fertilizer has not been carried out to date.

In this study, MAP precipitation method was used to treat and extract valuable nutrient in the form of fertilizer from POME. This study also was substitute the seawater as a source of Magnesium Chloride solution for the MAP precipitation method.

1.2 PROBLEM STATEMENT

The use of several magnesium and phosphate based chemicals or Magnesium Ammonium Phosphate (MAP) precipitation method have been shown to provide an effective treatment of wastewater containing substantial amount of nutrients. MAP precipitation method extract precious nutrient in the form MAP crystals. MAP display excellent fertilizer quality when compared to commercially available fertilizers. The extraction of MAP although rapid, however, is rather costly as it involves several different chemicals. Alternatives to magnesium based chemicals such as seawater may be used to reduce operational cost. Treatment of POME by means of MAP precipitation method and the effectiveness of seawater to substitute magnesium based chemicals has not been carried out.

1.3 OBJECTIVE OF STUDY

During this research, some of the important objectives been considered to ensure the success of the research. The objectives are as follows:

1. To determine the effectiveness of MAP precipitation method in treating of raw POME.
2. To investigate whether seawater can be used as a source of Magnesium Chloride ($MgCl_2$) in MAP treatment method.
3. To determine the amount of seawater needed equivalent to $MgCl_2$ in MAP treatment method.
4. To determine the amount of fertilizer extracted using $MgCl_2$ solution and seawater.

1.4 SCOPE OF STUDY

To achieve the objectives of this research, there are four main research fields to be carried on:

1. Raw POME from Sime Darby Palm Oil Mill Jabor are considered in this study.
2. Laboratory tests are conducted which is to identify the effectiveness of seawater as a substitute to $MgCl_2$ solution and as a source of Magnesium (Mg) ions in MAP precipitation method. Comparisons are made between combination of $MgCl_2$ solution and seawater.
3. The purpose of the study is to treat the POME and also to identify the amount of fertilizer extracted using MAP
4. Two water quality parameter are considered, namely COD and Mg concentration prior to and after treatment.

1.5 THESIS OVERVIEW

Chapter 2 presents, an overview about Malaysia Palm Oil Industry, generation of waste by palm oil mill followed by treatment of POME .POME as a nutrient source, MAP precipitation, and seawater as a source of Magnesium ion is also covered in this chapter.

Chapter 3 discussed the detail about the collection of raw POME used in the study followed by the characteristic of raw POME. The detail of the experimental procedure and the water quality parameter then elaborated in this chapter

Chapter 4 present, the main part of this thesis that will be analyzed all the result obtained. In the first section, properties of raw POME are analyzed in detailed followed by the second section that elaborates the result of the water quality after the POME been treated. Then, the details for the characteristics of fertilizer that obtain from the MAP extraction are discussed.

Chapter 5 was concluded the overall of the findings from the current studies based on the objective. For the recommendations, it will relate for the future studies from the understanding and information generated in the present study. These recommendations are given due to their significance and important to be further investigated and explored by future research work.

CHAPTER 2

LITERATURE REVIEW

2.1 MALAYSIAN PALM OIL INDUSTRY

The Malaysian palm oil industry has grown rapidly over the years and become the world's largest producer and exporter of palm oil and its products. The growth of the palm oil industry in Malaysia has been phenomenal over the last 4 decades. Approximately 14.96 million tonnes of crude palm oil (CPO) was produced in every year 2005 which increased by 4.7% from 13.98 million tonnes in the year 2004 (MPOB, 2006). According to (Sulaiman *et al.* 2011) the total oil palm planted area in Malaysia increased by 2.8% to 4.17 million hectares in 2006. Oil palm cultivation and processing like other agricultural and industrial activities, raises environmental issues.

Other than that, POME also contains about 4000-6000 mg/L of oil and grease, approximately 2000 mg/L of residue oil is present in an emulsified form in the supernatant of POME. The suspended solids is about 4-5% in the POME are mainly cellulosic material from the fruits. Emulsified oil droplets are experienced spontaneous coalescence into larger flocs, thus making oil separation by gravity is difficult and time consuming process.

2.2 WASTE GENERATION FROM PALM OIL MILL

Beside the main product of the CPO, the mills also generate many by-products and liquid wastes which may give a significant impact on the environment if they are not dealt with properly. Due to this fact, the palm oil industry faces the challenge of balancing the environmental protection, sustainable development and its economic viability. The main wastes generated from palm oil mill are in the form of air emission, solid waste and liquid effluent.

2.2.1 Air Emission

Generally, palm oil mills are self-sufficient in terms of energy requirements due to the availability of adequate quantities of shell and fibre materials that are used as a solid fuel in the stream boiler. The two major problems associated with air emission are biogas released by POME in the ponds during anaerobic digestion and boiler ash. The biogas is a mixture of mainly methane and carbon dioxide (CO_2). Methane (CH_4), a greenhouse gas (GHG) is 20 times more harmful than CO_2 on climate change. The composition of boiler ash is a mix of clinkers and ash. Boiler ash is used as fertilizer for cropland application or for application on the road network in the plantation. Some of the palm oil mills use the boiler ash as a floor-cleansing agent. There are two principle sources of the air pollution in the mills which is incinerator and the boiler that are caused by incomplete combustion of the solid waste materials (Thani *et al.*, 1999). The emission of GHG which is CH_4 and CO_2 from these systems to the atmosphere has been recently reported as a more source of air pollution generated from the palm oil mills (Ahmad *et al.*, 2005).

2.2.2 Solid Waste

Solid wastes comprise mainly of Empty Fruit Bunches (EFB), shells and mesocarp fibers. Initially EFBs were incinerated and plantation based palm oil mills returned the ashes to the field as fertilizer. The solid wastes materials are generated in the palm oil extraction process are presented as follows:

1. EFB - 23 % of Fresh Fruit Bunch (FFB)
2. Potash – 0.5 % of FFB
3. Palm kernel – 6 % of FFB
4. Fibre – 13.5 % and 6
5. Shell – 5.5 % of FFB

Based on previous study, (Thani *et al.*, 1999) the EFB may be incinerated to produce potash which is applied in the plantation as fertilizer by mulching. This is a cost saving measure as it reduces the dependence on fertilizers as fertilizers are mainly imported to Malaysia. The shell and fibre materials are used as boiler fuel. The palm kernels are usually sold to palm kernel oil producers for the extraction of the palm kernel oil.

2.2.3 Liquid Effluent

The production of palm oil results in the generation of large quantities of polluted wastewater commonly referred to as POME. A significant quantity of water needed in the palm oil mill extraction (Tan *et al.*, 2006). Typically, 1 tonne of crude palm oil production requires 5.0-7.5 tonnes of water over 50% of which ends up as POME (Ma, 2000). At any conventional palm oil mill processes, it has been estimated each tonnes of crude palm oil produced approximately 2.5m^3 to 3.5$m^3$of POME are generated.

POME comprises a combination of the wastewaters which are principally generated and discharged from the following major processing operations (DOE, 1999):

1. Sterilization of FFB-sterilizer condensate is about 36% of total POME
2. Clarification of the extracted crude palm oil-clarification wastewater is about 60% of total POME
3. Hydrocyclone separation of cracked mixture of kernel and shell-hydrocyclone wastewater is about 4% of total POME

It contains various suspended components including cell walls, organelles, short fibres, a spectrum of carbohydrates ranging from hemicelluloses 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 (Ma, 2000).

2.3 PALM OIL MILL EFFLUENT (POME)

Raw POME is a thick brownish in colour liquid which is highly concentrated colloidal slurry with pH between 4.0-5.0, brownish colloidal suspension that containing high concentration of organic matter. Palm oil is a form of edible vegetable oil obtained from the fruit of the oil palm tree. POME contains plant nutrients and an organic matter that are excellent substitutes for organic fertilizer. Characteristics of palm oil mill effluent depend on the quality of the raw material and palm oil production processes in palm oil mills.

The chemical characterizations of POME that include BOD, COD,TS, O&G and other chemical properties are shown in Table 2.3.

Table 2.1 : Chemical properties of raw POME (Alrawi *et al*, 2002)

Property	Range	Property	Range
pH	4.15 - 4.45	Total Nitrogen (TN)	300 - 410
BOD	21500 - 24500	Total Suspended Solid (TSS)	15660 – 23560
COD	45500 - 65000	Total Solid (TS)	33790 – 37230
O&G	1077 - 7582	Total Volatile Solids (TVS)	27300 – 30150

* Unit for all parameters is mg/L except pH

Freshly POME usually discharged at temperature between 80°C-90°C and possesses a very high BOD, which is 100 times as polluting as domestic sewage (Ahmad *et al.*, 2003). The volume of the combined POME discharged depends to a large extent on the milling operations (Ma, 2000). As no chemicals were added during the oil extraction process, POME is considered as non-toxic, but it is identified as a major source of aquatic pollution by depleting dissolved oxygen when discharge untreated into the water bodies (Khalid and Wan Mustafa, 1992). However, it also contains appreciable amounts of Nitrogen (N), Phosphorus (P), Potassium (K), Calcium (Ca) and Mg which is vital nutrient elements for plant growth (Rupani *et al.*, 2010).

2.4 POME TREATMENTS

Nowadays, there are various treatment process have been studied to treat the POME. POME is a high strength wastewater and would result in high organic load even at a low influent flow rate like providing a low up-flow velocity. Wastewater composition depends mainly on the season, raw matter quality and the particular operations being conducted at any given time. Generally palm oil mill wastewater is low in pH because of the organic acids produced in the fermentation process, ranging about 4 until 5. In general, the process of POME can be categorized into a dry and a wet process.

POME compositions are include O&G, COD, BOD, TS, TSS, TVS, TN and ammonia (NH_4^+) (Man and Keat, 2010). POME is produced from the extraction of palm oil from the FFB that will go through several process. The process that will be involved include sterilization, stripping, digestion, pressing, clarification, purification, and vacuum drying. Palm oil mill process will be produces a large quantity of wastes. The effluents from palm oil mill may lead to considerable environmental problems, if the discharged untreated. Therefore, POME should be treated or purified by follow the standard before it discharge into the watercourse to minimize the environmental problem. The treatments of POME that currently used are anaerobic and aerobic treatment system and ponding system. Table 2.2 shows the Discharge Standards for POME from Malaysian Palm Oil Board

Table 2.2 : Palm Oil Mill Effluent Discharge Standards (MPOB, 2012).

Parameter	Std A	Std B	Std C	Std D	Std E	Std F
pH	5-9	5-9	5-9	5-9	5-9	5-9
Biological Oxygen Demand (BOD)	5000	2000	1000	500	250	100
Chemical Oxygen Demand (COD)	10000	4000	2000	1000	-	-
Total Solids	4000	2500	2000	1500	-	-
Suspended Solids	1200	800	600	400	400	400
Oil and Grease	150	100	75	50	50	50
Ammonia Nitrogen	25	15	15	10	150	100
Total Nitrogen	200	100	75	50	-	-

* All parameters in mg/L except pH

2.4.1 Anaerobic Treatment System

In Malaysia, the most common way for extracting palm oil is usually using the wet process. It has been established that the anaerobic process is in many ways ideal for wastewater treatment. Anaerobic process is a biological treatment process that occurs in the

absence of oxygen that has more advantage than other treatments because it is less energy demands, minimum sludge formation and also no unpleasant odor and production of methane due to efficient break down of organic substances by anaerobic digestion bacteria (Rupani *et al.,* 2010).

Anaerobic digestion is the most suitable method for the treatment of effluents that containing high concentration of organic carbon such as POME. Anaerobic treatment of wastewater is a complex biological process involving several groups of microorganisms (Cha and Noike, 1997). Efficient treatment system is the closed anaerobic digester tank that becomes more popular at present. According to (Perez *et al.,* 2001) anaerobic process is a most suitable treatment method due to the high organic characteristic of POME. Usually anaerobic stabilization ponds are widely used for treatment of wastewater from palm oil production because it has low capital and operating cost.

2.4.2 Aerobic Treatment System

Aerobic treatment process is another biological treatment that occurs in the presence of oxygen. Aerobic digestion actually refers to the use of aerobic bioreactors to stabilize particulate organic matter arising from biological treatment (predominantly biomass) and primary clarification (predominantly biodegradable organic matter) of wastewaters. Biodegradable particulate organic matter is hydrolyzed and converted into biodegradable soluble organic matter, releasing nutrients such as phosphate and ammonia-N. The biodegradable soluble organic matter is then converted into CO_2, water, active biomass through the action of heterotrophic bacteria (Leslie, *et al*, 1999).

There are several significant advantages for aerobic treatment method and is almost certainly assured of increase usage in the future. The advantages of anaerobic process are as listed below (Singh, 1996):

i. Less energy requirement as no aeration is needed
ii. Energy generation in the form of methane gas

iii. Less biomass (sludge) generation
iv. Less nutrients (nitrogen and phosphorus) requirement
v. Application of higher organic loading rate
vi. Space saving because application of higher loading rate requires smaller small reactor thereby saving the land requirement

2.4.3 Ponding System

Therefore, the most conventional method for treating POME is using ponding system (Ma and Ong, 1985; Khalid and Wan Mustafa, 1992). The ponding system has been applied in Malaysia for POME treatment and they are classified as a waste stabilization pond since 1982 (Onyia *et al.,* 2001). The raw effluent is treated using a ponding system comprising of three phases, which is anaerobic, facultative, and algae processes. More than 85% of palm oil mills are use ponding systems due to their low costs and easy operating systems (Perez *et al.,* 2001). However, ponding system need a large treatment area and normally operated at a normal rate. The treatment system have particular disadvantages such as a long hydraulic retention time of 45–60 days, bad odour, difficulty in maintaining the liquor distribution to ensure smooth performance over huge areas and difficulty in collecting biogas which can have detrimental effects on the environment. The size and configuration of the ponds, the processes are relatively difficult to control and monitor.

2.5 POME AS A NUTRIENT SOURCE

POME contained very high nutrient content, thus extracting this precious nutrient would benefit the Industry (Shaji and Kamaraj, 2002). The nutrients that usually contain in plant are N, P, and K. The current practice that usually used is composting technology and vermicomposting technique.