

PALM OIL MILL EFFLUENT TREATMENTS AND BIOMETHANE  
PRODUCTION USING RICE HUSK ASH AND  
PALM KERNEL ASH

NURHAMIEZA MD HUZIR

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Faculty of Engineering  
Universiti Teknologi Malaysia

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## **DEDICATION**

*This thesis is dedicated to my family who gave me everlasting love and encouragement. Thank you for being my pillar of strength throughout this journey.*

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## ABSTRACT

Palm oil mill effluent (POME) is one of the major wastes in palm oil industry. Prior to the disposal, POME should be pretreated as it can reduce soil fertility and contribute to human health hazards. Until now, many approaches have been investigated to improve waste management of POME. Traditionally, sedimentation process is used for removal of suspended solids trapped in the water. However, one-step treatment only is unable to remove high amount of solids in shorter time. The use of coagulation-flocculation (CF) prior to sedimentation process helps to form proper flocs, thickened the volatile solid (VS) in the sludge and facilitate the sedimentation process. Based on previous work, numerous natural coagulants had been used in POME treatment such as chitosan, *Moringa oleifera* seed, rice starch and other novel biocoagulants. In this study, the potential of rice husk ash (RHA) and palm kernel ash (PKA) were assessed as natural coagulant. A comparison study between natural coagulants and aluminium sulphate (alum) were conducted using jar test. The optimum dosage, pH and settling time of each coagulant were investigated based on responses of chemical oxygen demand (COD) and total solid (TS). Response surface methodology was used to predict the removal efficiencies and optimum conditions for each sample. Results showed that, alum was capable to remove COD up to  $52.36 \pm 1.49\%$  and  $84.94 \pm 0.12\%$  of TS using 6.50 g of alum, pH 6.0 and 41.69 min of settling time. At optimum condition,  $52.38 \pm 0.85\%$  of COD and  $83.88 \pm 1.03\%$  of TS were removed using 6.00 g RHA, pH 3.6 and 57.00 min of settling time. Meanwhile, PKA was capable to remove  $50.50 \pm 0.97\%$  of COD and  $80.64 \pm 0.64\%$  of TS by using 7.14 g of PKA, pH 5.97 and 40.65 min of sedimentation time. The results showed that RHA and PKA had attained similar removal efficiencies of COD and TS as alum. The flocs produced from CF process were further tested for biogas production in 150 mL serum bottle. The test was done by using biomethane potential (BMP) assay to determine the effect of each coagulants used towards amount of biogas produced. BMP assay for RHA produced maximum amount of biogas (480.25 mL/gVS) within 36 days. The methane potential was 244.03 mL/gVS and the methane content in the serum from overall biogas produced was 66.71%. To predict the performance of biogas produced, first order kinetic model was selected as it is prevalently used to evaluate anaerobic digestion process from various substrates. The results obtained from kinetic study revealed that RHA possessed the highest kinetic constant,  $k = 0.0403$ . From this work, it is proven that RHA was better than PKA and it is capable to replace alum in POME treatment as well as good enhancer for biogas productions.

## ABSTRAK

Sisa efluen kilang kelapa sawit (POME) adalah salah satu sisa utama dalam industri kelapa sawit. Sebelum pembuangan, POME perlu dirawat terlebih dahulu kerana ia dapat mengurangkan kesuburan tanah dan mengancam kesihatan manusia. Sehingga kini, pelbagai pendekatan telah dibuat untuk menambahbaik pengurusan sisa POME. Secara tradisional, proses pemendapan digunakan untuk menghilangkan pepejal terampai yang terperangkap di dalam air. Walau bagaimanapun, satu langkah rawatan sahaja tidak mampu menghapuskan pepejal yang banyak dalam masa yang singkat. Penggunaan pengentalan-pemberbukuan (CF) sebelum proses pemendapan membantu membentuk bukuan yang sesuai, menebalkan pepejal meruap (VS) di dalam enapcemar dan memudahkan proses pemendapan. Berdasarkan kajian lepas, terdapat pelbagai bahan pengentas semulajadi yang telah digunakan untuk merawat POME seperti kitosan, biji *Moringa oleifera*, kanji beras dan bio-bahan pengentas baharu yang lain. Dalam kajian ini, penggunaan abu sekam padi (RHA) dan abu isirung sawit (PKA) dinilai sebagai bahan pengentas semula jadi. Perbandingan antara bahan pengentas semulajadi dan aluminium sulfat (alum) dijalankan menggunakan ujian balang. Dos, pH dan masa mendapan yang optimum bagi setiap bahan pengentas dikaji berdasarkan permintaan oksigen kimia (COD) dan jumlah pepejal (TS). Kaedah sambutan permukaan digunakan bagi meramal kecekapan penyingkiran dan keadaan optimum bagi setiap sampel. Hasil kajian mendapati bahawa alum mampu mengurangkan COD sehingga  $52.36 \pm 1.49\%$  dan  $84.94 \pm 0.12\%$  TS dengan menggunakan 6.50 g alum, pH 6.0 dan 41.69 min tempoh mendapan. Pada keadaan optimum, sebanyak  $52.38 \pm 0.85\%$  COD dan  $83.88 \pm 1.03\%$  TS telah dikurangkan dengan menggunakan 6.00 g RHA, pH 3.6 dan 57.00 min tempoh mendapan. Sementara itu, PKA mampu mengurangkan  $50.50 \pm 0.97\%$  COD dan  $80.64 \pm 0.64\%$  TS dengan menggunakan 7.14 g PKA, pH 5.97 dan 40.65 min masa pemendapan. Keputusan kajian mendapati RHA dan PKA mampu mencapai kadar kecekapan penyingkiran COD dan TS yang menyamai alum. Bukuhan yang dihasilkan daripada proses CF digunakan untuk ujian selanjutnya bagi pengeluaran biogas dengan menggunakan botol serum 150 mL. Ujian ini dilakukan dengan menggunakan ujian potensi biometana (BMP) untuk menentukan kesan setiap bahan pengentas terhadap jumlah biogas yang dihasilkan. Daripada ujian BMP, RHA mengeluarkan jumlah maksimum biogas (480.25 mL/gVS) dalam tempoh 36 hari. Potensi metana adalah 244.03 mL/gVS dan kandungan metana dalam serum daripada keseluruhan penghasilan biogas adalah sebanyak 66.71%. Untuk meramalkan prestasi biogas yang dihasilkan, model kinetik tertib pertama dipilih kerana ianya sering digunakan untuk menilai proses pencernaan anaerobik dari pelbagai substrat. Hasil yang diperoleh daripada kajian kinetik mendapati bahawa RHA mempunyai pemalar kinetik tertinggi,  $k = 0.0403$ . Dari kerja ini, terbukti bahawa RHA lebih baik daripada PKA dan mampu menggantikan alum dalam rawatan POME serta penambah baik untuk penghasilan biogas.

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## LIST OF ABBREVIATIONS

AD	-	Anaerobic digestion
Al	-	Aluminium
Ag <sub>2</sub> SO <sub>4</sub>	-	Silver sulphate
ANOVA	-	Analysis of variance
APHA	-	American Public Health Association
BOD	-	Biochemical oxygen demand
BBD	-	Box-Behnken design
BMP	-	Biomethane potential
Ca	-	Calcium
CaCl <sub>2</sub> ·2H <sub>2</sub> O	-	Calcium chloride dihydrate
cm	-	Centimeter
CF	-	Coagulation-flocculation
CH <sub>4</sub>	-	Methane
CoCl <sub>2</sub> ·6H <sub>2</sub> O	-	Cobalt (II) chloride hexahydrate
CO <sub>2</sub>	-	Carbon dioxide
COD	-	Chemical oxygen demand
CPO	-	Crude palm oil
CuCl <sub>2</sub> ·2H <sub>2</sub> O	-	Copper (II) chloride dihydrate
DOE	-	Department of Environment
EDTA	-	Ethylenediaminetetraacetic acid
EFB	-	Empty fruit bunches
EEA	-	Environmental Quality Act
F/I	-	Food to inoculum
Fe	-	Iron
FeCl <sub>3</sub> ·4H <sub>2</sub> O	-	Iron (III) chloride hexahydrate
FTIR	-	Fourier Transformed Infra-red
G	-	Gram
g/mL	-	Gram per mililitre
g/L	-	Gram per litre
GHG	-	Greenhouse gas

H <sub>2</sub>	-	Hydrogen
H <sub>2</sub> SO <sub>4</sub>	-	Sulfuric acid
HBO <sub>3</sub>	-	Boric acid
HCl	-	Hydrochloric acid
HgSO <sub>4</sub>	-	Mercuric sulfate
HRT	-	Hydraulic retention time
K	-	Potassium
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	-	Potassium dichromate
K <sub>2</sub> HPO <sub>4</sub> ·3H <sub>2</sub> O	-	Potassium-hydrogen phosphate trihydrate
L	-	Litre
M	-	Molar
mg/L	-	Milligram per litre
Mg	-	Magnesium
MgSO <sub>4</sub> ·7H <sub>2</sub> O	-	Magnesium sulfate heptahydrate
Min	-	Minute
mL	-	Milliliter
mL/g	-	Milliliter per gram
mL/L	-	Milliliter per litre
MnCl <sub>2</sub> ·4H <sub>2</sub> O	-	Manganese (II) chloride tetrahydrate
Na	-	Sodium
Na <sub>2</sub> SeO <sub>3</sub> ·5H <sub>2</sub> O	-	Sodium selenite pentahydrate
NaH <sub>2</sub> PO <sub>4</sub> ·2H <sub>2</sub> O	-	Sodium dihydrogen phosphate
NaOH	-	Sodium hydroxide
NH <sub>4</sub> Cl	-	Ammonium chloride
(NH <sub>4</sub> ) <sub>6</sub> Mo <sub>7</sub> O <sub>2</sub> ·4H <sub>2</sub> O	-	Ammonium molybdate tetrahydrate
NiCl <sub>2</sub> ·6H <sub>2</sub> O	-	Nickel (II) chloride hexahydrate
OLR	-	Organic loading rate
OPF	-	Oil palm frond
OPT	-	Oil palm trunk
P	-	Phosphorus
PAC	-	Polyaluminum chloride
PKC	-	Palm kernel cake
PKA	-	Palm kernel ash

PKO	-	Palm kernel oil
POME	-	Palm oil mill effluent
RGA	-	Residual gas analyzer
RHA	-	Rice husk ash
Rpm	-	Revolutions per minute
RSM	-	Response surface methodology
S	-	Sulfur
Si	-	Silicon
SRT	-	Solid retention time
SS	-	Suspended solid
TS	-	Total solids
TSS	-	Total suspended solids
VFA	-	Volatile fatty acid
VS	-	Volatile solid
ZnCl <sub>2</sub>	-	Zinc chloride











## **1.5 Significance of Study**

The use of natural coagulants which are RHA and PKA eventually help to reduce the generation of local waste from their mills. Utilizing the natural coagulants in POME treatment makes the digestate sludge of POME applicable and safe to soil. This is because the excess sludge can be recovered as biofertilizer with many nutritional values compared to POME treated with chemical coagulants. Application of biocoagulants in wastewater treatment indicates a significant progress in sustainable environmental technology. Furthermore, this study also introduced the natural coagulants and determined the effect of coagulants addition towards biogas production.

Even though POME is a waste that escalates the environmental problem, it capable to be exploited for biogas productions. Biogas composed of gaseous mixture commonly methane and carbon dioxide. It is a renewable source of energy that can be used as fuels to generate heat and electricity. Since nowadays researchers are looking for sustainable energy to replace the current depletion of fossil fuels, the demand for utilization of POME and conversion to biogas become a concern. Thus, integration of CF pretreatment with biogas production of POME could be used as an effective system which minimize disposal of RHA and PKA and use it as useful resources to reduce POME pollutants and increase the biogas productions.

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