ENHANCED ANAEROBIC DEGRADATION OF PALM OIL MILL EFFLUENT USING BUTYRATE, CaO-CKD AND DENITRIFYING SULFIDE REMOVAL

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ABSTRACT

During this research three experiments were performed. In the first experiment Palm oil Mill Effluent (POME) with concentrated butyrate was treated in a 4.5 L upflow anaerobic sludge blanket reactor (UASBR), run over a range of influent concentrations (16.5-46.0 g-COD L^{-1}), chemical oxygen demand (COD) loading rates (1.5-11.5 g COD$L^{-1}d^{-1}$) and 11-4 days hydraulic retention time (HRT) at 37 °C by maintaining pH between 6.5-7.5. The process consistently removed 97-99% of COD at loading rates up to 1.5-4.8 g COD $L^{-1}d^{-1}$ by varying HRT (11-7.2 days). The conversion of acetate to methane appeared to be rate limiting step. Maximum biogas (20.17 L$L^{-1}d^{-1}$) and methane production (16.2 L$L^{-1}d^{-1}$) were obtained at COD loading rate of 4.80 g$L^{-1}d^{-1}$ and HRT of 7.2 days. The biogas and methane production were higher in the presence of butyrate compared to control. The methane content of the biogas was in the range of 70-80% throughout the study while in control it was 60-65%. Finding of this study clearly indicates the succesful treatment of POME with butyrate in UASBR. In the second experiment, calcium oxide-cement kiln dust (CaO-CKD) was used to enhance the granulation process. The granulation process in POME using CaO-CKD provided an attractive and cost effective treatment option. In this study the efficiency of CaO-CKD at doses of 1.5 to 20 gL^{-1} was tested in batch experiments and found that 10 g of CaO/L caused the greatest degradation of VFA, butyrate and acetate. An upflow anaerobic sludge blanket (UASB) reactor was operated continuously at 35 ºC for 150 days to investigate the effect of CaO-CKD on sludge granulation and methanogenesis during start-up. The treatment of POME emphasized the influence of varying organic loading rates (OLR). Up to 94.9% of COD was removed when the reactor was fed with the 15.5 to 65.5 g-COD gL^{-1} at an OLR of 4.5-12.5 Kg-COD$m^{-3}d^{-1}$, suggesting the feasibility of using CaO in an UASB process to treat POME. The ratio of volatile solids/total solids (VS/TS) and volatile fatty acids in the anaerobic sludge in the UASB reactor decreased significantly after long-term operation due to the precipitation of calcium carbonate in the granules. Granulation and methanogenesis decreased with an increase in the influent CaO-CKD concentration. In the third experiment, the inhibitory effects of 134.82-771.9 mg$L^{-1}d^{-1}$ of sulfide loading rate (SLR) and 58.79-337.56 mg$L^{-1}d^{-1}$ of nitrate loading rate (NLR) on methanogenesis were investigated in a mixed methanogenic culture using butyrate as carbon source. A novel strategy was adopted to cultivate mature granules using anaerobic sludge of palm oil mill effluent (POME) as seed sludge, incubated in DSR medium to acclimate the denitrifiers. Biological denitrification was used to eliminate carbon, nitrogen and sulfur in an anaerobic granular bed reactor (AGBR) of 4.5 L by varying hydraulic retention time from 35.6-6.2 days. The maximum nitrate and sulfide removal efficiencies were observed up to SLR and NLR of 188.42 mg$L^{-1}d^{-1}$ and 82.39 mg$L^{-1}d^{-1}$ respectively. Maximum VFA removal of 82% was obtained on SLR and NLR of 230 mg$L^{-1}d^{-1}$ and 100.62 mg$L^{-1}d^{-1}$.

ABSTRAK

Dalam ini tiga eksperimen telah dijalankan. Dalam eksperimen pertama sisa efluen kelapa sawit berkandungan butyrate telah dirawat di dalam reaktor berisipadu 4.5 L yang menggunakan reaktor laluan ke atas tanpa oksigen (UASB), mempunyai julat influen COD (keperluan oksigen kimia) di antara 16.5 ke 46.0 gL^{-1}, kadar kemasukan COD di antara 1.5-11.5 gCOD $L^{-1}d^{-1}$ dan nilai tahanan hidraulik di antara 11-4 hari pada suhu 37 ^{o}C serta pH kawalan di antara 6.5 ke 7.5. Proses rawatan menggunakan UASB mampu mengurangkan 97%-99% COD pada kadar kemasukan 1.5-4.8 gCOD $L^{-1}d^{-1}$ dengan variasi masa tahanan antara 7.2 ke 11.2 hari. Jumlah maksimum gas bio terhasil adalah 20.17 $LL^{-1}d^{-1}$ dan gas metana adalah 16.2 $LL^{-1}d^{-1}$ pada kadar kemasukan COD 4.80 g $L^{-1}d^{-1}$dan masa tahanan (HRT) 7.2 hari. Penghasilan gas bio dan mentana adalah lebih tinggi dalam kehadiran butyrate berbanding sampel kawalan. Jumlah mentana di dalam gas bio adalah di antara 70% ke 80% sementara sampel kawalan adalah 60% ke 65%. Hasil kajian ini jelas menunjukkan kejayaan rawatan POME menggunakan butyrate dalam UASBR. Dalam kajian yang kedua, kalsium oksida-tanur habuk simen (CaO-CKD) telah digunakan untuk meningkatkan proses granulasi. Proses granulasi dalam sisa efluen kelapa sawit menggunakan CaO-CKD menunjukkan rawatan pilihan yang menarik dan lebih murah. Dalam kajian ini keberkesanan CaO-CKD pada kadar di antara 1.5 gL^{-1} ke 20 gL^{-1} telah diuji dalam eksperimen berasingan dan didapati bahawa 10 g CaO/L mampu menghasilkan degradasi VFA, butyrate dan acetat. Reactor laluan ke atas tanpa oksigen telah beroperasi secara berterusan pada suhu 35 ^{o}C selama 150 hari dalam usaha untuk mengkaji kesan CaO-CKD ke atas granulasi kumbahan dan proses metanogenesis. Rawatan POME ini menumpukan kepada pengaruh variasi OLR(kadar muatan organik) yang mana didapati 94.9% COD telah dikurangkan semasa reaktor diberi kemasukan COD di antara 15.5 to 65.5 g-COD gL^{-1} pada kadaran OLR 4.5-12.5 Kg-$CODm^{-3}d^{-1}$. Ini jelas menunjukkan keberkesanan penggunaan CaO pada UASB dalam merawat POME. Kadar pepejal mudah ruap kepadah jumlah pepejal (VS/TS) dan VFA dalam reaktor UASB dedapati menurun secara signifikan pada operasi jangka panjang. Ini disebabkan oleh pemendapan kalsium karbonat dalam granul. Proses granulasi dan metanogenesis berkurangan dengan pertambahan influen yang mempunyai CaO-CKD. Dalam eksperimen ketiga, kesan perencatan sulfide 134.82-771.9 $mgL^{-1}d^{-1}$ (SLR) dan kadar kemasukan nitrat 58.79-337.569 $mgL^{-1}d^{-1}$ (NLR) ke atas metanogenesis di kaji di dalam kultur campuran metanogenik menggunakan butyrate sebagai sumber carbon. Granul yang matang dikultur menggunakan kumbahan POME tanpa oksigen sebagai benih kumbahan. Bahan ini di inkubator dalam media DSR bertujuan menyesuaikan bahan bakteria pengurang nitrat. Pengurangan nitrat secara biologi digunakan untuk menggurangkan kandungan karbon, nitrogen dan sulfur di dalam reaktor granular tanpa oksigen (AGBR) melalui variasi masa tahan hidraulik antara 35.6 ke 6.2 hari. Keberkesanan pengurangan nitrat dan sulfida dilihat berlaku kepada SLR dan NLR sehingga 188.42 $mgL^{-1}d^{-1}$ dan 82.39 $mgL^{-1}d^{-1}$.

TABLES OF CONTENTS

CHAPTER 2 LITERATURE REVIEWS (16-63)

CHAPTER 3 MATERIALS AND METHODS (64-99)

CHAPTER 4 RESULTS AND DISCUSSTION (100-155)

CHAPTER 5 CONCLUSION AND RECOMMENDATIONS (156-160)

LIST OF TABLES

LIST OF PLATES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AD	Anaerobic degradation
AFBR	Anaerobic fluidized bed reactor
AGBR	Anaerobic granular bed reactor
Al_2O_3	Alumina
BOD	Biochemical oxygen demand
BuLR	Butyrate loading rate
$CaCl_2$	Calcium chloride
CaO	Calcium Oxide
$CaCO_3$	Calcium carbonate
$Ca(OH)_2$	Calcium hydroxide
CH_3COOH	Acetic acid
CH_4	Methane
CKD	Cement kiln dust
CO_2	Carbon dioxide
$CoCl_2.6H_2O$	Cobalt (II) chloride hexahydrate
COD	Chemical oxygen demand
CPO	Crude palm oil
CSTR	Continuous stirrer tank reactor
$CuCl_2.2H_2O$	Copper (II) chloride dehydrate
DNRA	Dissimilatory nitrate reduction to ammonium
DOE	Department of Environment
DSR	Denitrifying sulfide removal
EFB	Empty fruit bunch

EQA	Environmental Quality Act
F/M	Food to micro-organism ratio
$FeCl_2.4H_2O$	Iron(II) chloride tetrahydrate
Fe_2O_3	Ferric oxide
FFA	Free Fatty Acids
FFB	Fresh fruit bunch
FFR	Fix film reactor
Ha	Hectare
H_2S	Hydrogen sulfide
H_2SO_4	Sulfuric acid
H_3BO_3	Boric acid
GHG	Green house gas
GSL	Gas-solid-liquid
HRT	Hydraulic retention time
$KMnO_4$	Potassium Permanganate
KH_2PO_4	Potassium dihydrogen phosphate
KSLH	Kilang Sawit Lepar Hiller
K_2O	Potassium oxide
LCFAs	Long chain fatty acids
MPOB	Malaysia palm oil board
$MgCl_2$	Magnesium chloride
MgO	Magnesium oxide
MPa	Mega Pascal
MW	Megawatt
$MnCl_2.4H_2O$	Manganese(II) Chloride Tetrahydrate

N_2	Nitrogen
$NaHCO_3$	Sodium bicarbonate
$Na_2MoO_4.2H_2O$	Sodium molybdate dihydrate
NaOH	Sodium Hydroxide
NH_4Cl	Ammonium chloride
NLR	Nitrate loading rate
NO_3^-	Nitrate
NO_2^-	Nitrite
NGOs	Non-governmental organizations
$NiCl_2.6H_2O$	Nickel (II) chloride, hexahydrate
NO	Nitric oxide
NO_2	Nitrogen dioxide
NOx	Nitrogen oxide
OLR	Organic loading rate
P	Phosphorous
Pa	Pascal
POME	Palm oil mill effluent
PO_4^{3-}	Phosphate
PVC	Polyvinyl chloride
Q	Flow rate
RE	Renewable energy
SCOD	Soluble chemical oxygen demand
SD	Standard deviation
SE	Standard error

SCOD	Soluble chemical oxygen demand
SiO_2	Silicon dioxide
SO_3	Sulfur trioxide
SLR	Sulfide loading rate
SRT	Sludge retention time
SS	Suspended solids
TKN	Total Kjeldahl nitrogen
TN	Total nitrogen
TP	Total phosphorous
TS	Total solids
TSS	Total suspended solids
UASFF	Upflow anaerobic sludge fixed film reactor
UASBR	Upflow anaerobic sludge blanket reactor
USDA	United States Department of Agriculture
VFA	Volatile fatty acid
VS	Volatile solids
VSS	Volatile suspended solids
$ZnCl_2$	Zinc chloride

LIST OF APPENDICES (197-221)

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

This chapter includes a brief description of Palm oil industry in Malaysia, Palm oil mill effluent (POME) and Cement kin dust (CKD). The last part of this chapter describes effluent discharge standards along with the problem statement, objectives and the scope of study.

1.1.1 Research Background

1.1.2 Palm Oil Industry in Malaysia

Over the last 30 years, Malaysian palm oil industry has grown rapidly to become the world's second largest producer of palm oil (Lam and Lee, 2011). The total productions of CPO in 2008 and 2009 are 17,734,441 and 16,044,874 tonnes, respectively (MPOB, 2008a, 2009). The high production of crude palm oil prompts the palm oil industry to become an important contributor to Malaysia's GDP. In year 2008, the total export of palm oil and derived products raked RM 64,808 million (USD 20,268 million), or 9.8% of the total national revenue (Yusof and Yew, 2009). Simultaneously, from merely 54,000 ha in the early 1960s, the oil palm plantation area has gradually increased to 1.8, 3.5, 3.8, 4.2 and 4.3 million hectares in 1990, 2001, 2003, 2005 and 2007, representing 56% of the total agricultural land and 11.75% of the country’s total land area. As of 2009, there were 416 palm oil mills operating in Malaysia, 249 mills from Peninsular Malaysia and 167 from Sabah and Sarawak. There were 120 mills with total capacity 29,893, 200 tonnes FFB per year located in Sabah alone. Total of 17,564,937 Metric Tons (MT) crude palm oil produced in year 2009 and 31.03% of total CPO was produced in Sabah (MPOB, 2009). Such a high percentage was mainly attributed to the largest oil palm planted state amounting for 1.36 million hectares or 29% of the total planted area in the country (Wahid, 2010). The oil palm planted area in 2011 increased 3% y/y to 5mn hectares due to increase in planted area in Sabah and Sarawak. CPO production in 2011 increased 11.3% y/y to reach a record-high of 18.9mn. Today, Malaysia and Indonesia account for about 87 percent of world production (Figure 1.1). POME generation rates in different seasons, given by Habib et al. (1997) have been shown in Appendix A1.

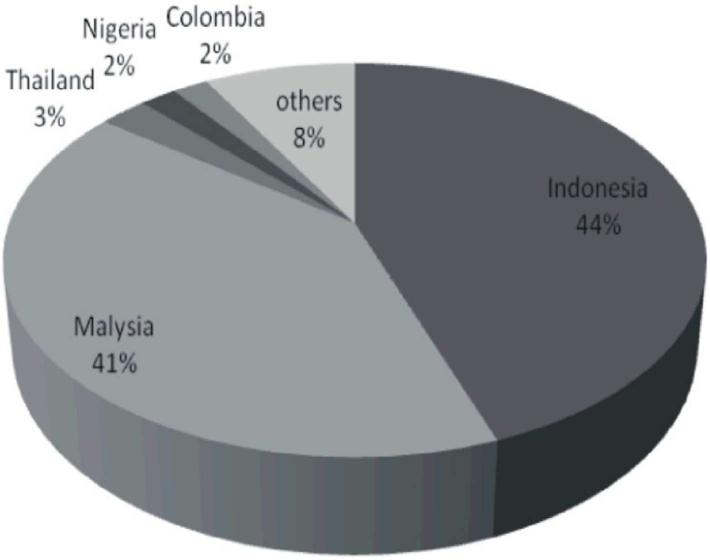

Figure 1.1: World palm oil production 2008 (MPOB)

1.1.3 Palm Oil Mill Effluent

In the palm oil milling process large amounts of steam and hot water are used (Zinatizadeh et al. 2006; Rupani et al. 2010), which in turn generate a large volume of wastewater. This large quantity of polluted wastewater is commonly referred to as palm oil mill effluent (POME). Effluents from palm oil mills and processing plants have been identified as the major cause of the rapid deterioration of the biosphere and the environment in the past and in recent times (Plate 1.1). POME is generated mainly from the oil extraction, washing, and cleaning processes (sterilizer, hydrocyclone and centrifuge effluent in the mill palm). Characteristics of POME during palm oil mill processing time are shown in Appendix A2. Discharge of un-treated effluent into water streams may cause considerable environmental problems (Lam and Lee, 2011), due to the its high value of BOD (25,000 mg L^{-1}), COD (75 g L^{-1}), oil and grease (8.5 g L^{-1}), total solids (45 g L^{-1}), and suspended solids (21 g L^{-1}) (Ma, 1995, 2000).

Based on palm oil production in 2005 (14.8 million tonnes), an average of about 53 million m^3 POME is being produced per year in Malaysia (Lorestani, 2006). Thus, it was estimated that in year 2009, 43.8 million m^3 (11,600 million gallon) of POME was generated from Malaysian palm oil mills base on the total crude palm oil production of 17.56 million tonnes (Malaysian Palm Oil Board, 2010).

The palm oil mill industry in Malaysia has thus been identified as that which discharges the largest pollution load into water bodies and the environment throughout the country (Wu et al. 2010). This adverse environmental effect from the palm oil industry cannot be ignored. Thus, there is an urgent need to find an efficient and practical approach to preserve the environment while maintaining the economy in good condition.

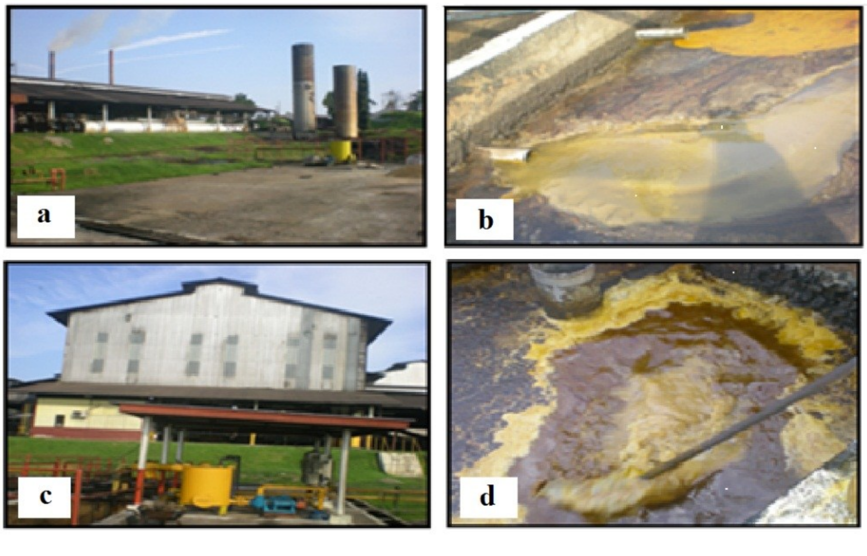

Plate 1.1. Palm oil mills (a, b) and Palm oil mill effluent (c, d).

1.2 ENVIRONMENTAL REGULATIONS OF POME DISCHARGE

1.2.1 POME rules in Malaysia

The Department of Environment (DOE, 1999) of the government of Malaysia issued POME (management and handling) rules in the year 2000. The highlighting agenda of EQA was to set acceptable standards for the emission and discharge or deposits of pollutants into the environment rather than prevention, with an exception given to the necessities on environmental impact measurements. The environmental restrictions in palm oil industry were decided to be a necessary licensed approach that would permit close control of individual factories. On the basis of prevailing environmental circumstances, environmental restrictions also provide a mechanism for permitting variable effluent standards. . The environmental quality regulations for the crude palm oil industry were the first set of regulations promulgated under the Environmental Quality Act (EQA), 1977 for control of industrial pollution source (Thani et al. 1999), enforced by the Department of Environment, (DOE). Therefore, palm oil mill owners have to obtain the license for factories operation that includes ensuring acceptable condition of effluent discharge, proper waste disposal and air emission control throughout the operation (Environmental Quality Act 1974, 2005).

The proper management, treatment, and disposal of POME must be ensured and existing facilities must be upgraded for the acceptable discharge to rivers and streams. As per the provision, DOE has been assigned to monitor the implementation of these rules, and the MPOB will be required to submit annual reports regarding the status of POME in their areas to the DOE. These rules are applicable to MPOB in Malaysia, which is responsible for POME management. In addition, there are EQA by different industries such as the FELDA. These EQA also deal with environmental pollution caused by improper disposal of POME.

The Malaysian Government proposed and legalized standards for POME discharge into water courses. Since then, palm oil mills are required to treat their POME