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Evaluation of the bio-kinetics of cement kiln dust in an upflow anaerobic sludge blanket reactor for treatment of palm oil mill effluent as a function of hydraulic retention time

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ABSTRACT

In this paper we operated an upflow anaerobic sludge blanket reactor (UASBR) continuously at 35 °C in order to observe the effects of varying the hydraulic retention time (HRT) from 3.5 to 34.5 d and varying the organic loading rate (OLR) from 1.5 to 46 kg COD m^{-3} d^{-1}. The pH of the digester improved, which we varied from 1.5 to 14.5 g L^{-1} CaO-CKD, a range pH 7.5. A high COD degradation rate of 97% and mixed liquor suspended solids (MLVSS) of 99,000 mg L^{-1} were achieved at an HRT of 24.5 d. The maximum methane yield was 0.346 l CH_4/g $COD_{removed}$. A CO_2 reduction of 87% was obtained at an OLR of 26.5 (r = 0.99). The optimum conditions for digestion of the palm oil mill effluent were determined by studying the bio-kinetics of granulation. The growth yield (Y_G) was 1.45 g VSS/g $COD_{removed}$ day; the specific biomass decay (b) was 0.056; the specific biomass growth rate (μ_{max}) was 0.988 d^{-1}; the saturation constant (K_s) was 460; and the critical retention time (Θ_c) was 2.464 d^{-1}. With a feed flow rate (Q_F) of 1.65 l/d, the upflow velocity (V_{up}) was 0.6 m/h, and for a Q_F of 2.45 l/d, V_{up} was 0.75 m/h.

1. Introduction

Palm oil mill effluent (POME) is a thick, brownish liquid that has a biochemical oxygen demand (BOD) and chemical oxygen demand (COD) of 26.3 and 65.9 g L^{-1}, respectively. The pH of POME usually ranges from 4 to 5 [1]. The pH is important for the anaerobic digestion of POME, because methane-producing bacteria require a neutral to slightly alkaline environment to produce the maximum amount of methane. Most microbes grow best in a pH between 6.2 and 7.8, while values lower than 4 and higher than 9.5 are not tolerated [2,3]. Cement kiln dust (CKD) is used as a substitute for lime to neutralize the acidity of wastewater streams [4]. CKD contains high levels of $CaCO_3$ and CaO of fine particle size [5,6]. In practice, neutralizing acidic wastewater precipitates the dissolved metals as hydroxides and carbonates, which can then be removed. Studies that evaluated CKD as a neutralizing agent in POME treatment found that lime concentrations between 25 and 27.5 g L^{-1} produce a pH of approximately 12.0 [7].

POME anaerobic digestion is an excellent way to produce energy and control pollution [8]. In Malaysia, UASBR has been used to overcome the problems of conventional pond treatment: slow degradation, the long hydraulic retention times (HRT) needed to degrade volatile fatty acids (VFA), and poor process stability [9]. UASBR is efficient and cheap at high organic loading rates (OLR) using CKD and produces usable biogas while sequestering carbon dioxide [9]. The efficiency of UASBR depends on granulation of the sludge, which can be optimized by changing wastewater characteristics such as OLR, HRT, and pH [10,11].

Abbreviations: UASBR, upflow anaerobic sludge blanket reactor; Alk, alkalinity; b, specific biomass decay; BOD, biochemical oxygen demand (mg L^{-1}); D, dilution rate, 1/HRT (day^{-1}); CaO-CKD, calcium oxide-cement kiln dust; CKD, cement kiln dust; POME, palm oil mill effluent; HRT, hydraulic retention time (day); L, liter; NH_3-N, ammonia nitrogen (mg L^{-1}); O&G, oil and grease (mg L^{-1}); OLR, organic loading rate (kg/m^3/d); Q, flow rate (l/day); S, substrate concentration in the reactor (mg L^{-1}); S1, influent substrate concentration (mg L^{-1}); S2, effluent substrate concentration (mg L^{-1}); SCOD, soluble chemical oxygen demand (mg L^{-1}); SRT, solid retention time (d); SS, suspended solid (mg L^{-1}); t, time (day); MLVSS, mixed liquor volatile suspended sludge (mg L^{-1}); SVI, sludge volume index (mL/L); COD, chemical oxygen demand (mg L^{-1}); TN, total nitrogen (mg L^{-1}); TS, total solids (mg L^{-1}); TVS, total volatile solids (mg L^{-1}); UASFF, up-flow anaerobic sludge fixed film; V, volume reactor (L); VFA, volatile fatty acid (mg L^{-1}); TVFA:Alk, total volatile fatty acid:alkalinity; VSS, volatile suspended solids (mg L^{-1}); SSV, sludge settling velocity (m/h); SMA, specific methanogenic activity (mg CH_4 COD/mg VSS. d); X, biomass concentration in the reactor (mg L^{-1}); Y_G, growth yield (g VSS/g $COD_{removed}$ day); b, specific biomass decay (day^{-1}); r_X, specific substrate utilization rate (day^{-1}); r_v, substrate utilization rate per volume (L^{-1} day^{-1}); $r_{x,max}$, maximum specific substrate utilization (day^{-1}); K_s, saturation constant for substrate (g COD/L); Θ_c, critical retention time (day); μ_{max}, specific biomass growth rate (day^{-1}); V_{up}, upflow velocity (m/h); Q_F, feed flow rate (l/d).

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The quality and stability of the sludge directly affects the behaviour of the entire treatment system. One analysis showed an 85% reduction in pollution by using a two-stage anaerobic digestion system with no cell recycling and a total HRT of 31 d [11,12]. Extensive literature is available on the role of multivalent cations on granulation. Some metal ions, such as Ca^{2+}, Fe^{2+}, Al^{3+}, Mg^{2+}, CaO, and $Ca(OH)_2$, enhance granulation and play an important role in microbial aggregation [8,13]. CaO-CKD may be better and less expensive than Ca^{2+}, Al^{+3}, and Fe^{2+} for enhancing sludge granulation and methanogenesis in UASBRs [8,14,15]. The granularity, granulation, granule size distribution, sludge characteristics, and bio-kinetic parameters are key factors that determine the settling of total solids (TS) and granule velocity in UASBRs [16–18]. This paper analyses CKD as a substrate to neutralize and granulate POME in a laboratory-scale UASBR fed with CaO-CKD. To accomplish this, we studied how granule characteristics varied at various OLRs and HRTs as well as evaluated granule bio-kinetics and the mass fraction of methanogens (f) with different fed substrates.

2. Materials and methods

2.1. Sample collection

A dry-kiln CKD sample was collected from YTL Pahang Cement located at 30 km east of Kuantan, Malaysia. This sample was washed with water and filtered to obtain a fairly homogenous particle size. Table 1 summarizes our characterization of the CKD sample used in this study for POME treatment.

Raw POME was collected from a local oil-palm mill (Felda Oil Palm Industries, CPSC Oil Palm Plantation, Kuantan, Malaysia). Table 2 summarizes the characteristics of the POME sample used in this study. The POME was stored and prepared according to Ahmad et al. [8].

2.2. Formation of seed sludge

After the preliminary treatment, we seeded the POME to activate the microbes, it was necessary to use activated sludge to allow for proper monitoring of pH variations when adding CaO-CKD. The nutrient medium was prepared with the following macro- and micronutrients (all units in g L^{-1}): NH_4Cl, 174; KH_2PO_4, 28.3; $(NH_4)_2SO_4$, 28.3; $MgCl_2$, 25; KCl, 45; yeast extract, 3; $FeCl_2{\cdot}6H_2O$; H_3BO_3, 0.05; $ZnCl_2$, 0.05; $CuCl_2{\cdot}2H_2O$, 0.038. After adding these nutrients, the samples were kept at room temperature for 20 days. The total volatile solids concentration of the seeded sludge was 10 g L^{-1}. To ensure microbial activity, we added 5 mL of sludge to 50 mL diluted POME with a COD of 5000 mg L^{-1} in a 150 mL fermenter serum bottle. The gas produced from the fermenter was analysed after one day and was found to contain high amounts of methane (data not included), which supported the presence of anaerobic activity in the seed sludge. Gas samples were obtained through an inverted funnel placed above baffles near the top of the reactor. Biogas composition was determined using a gas chromatograph (GC-8A, Shimadzu, Kyoto) with a thermal conductivity detector equipped with a steel column packed with WG-100 (GL Sciences, Tokyo) at 50 °C. Volatile fatty acids (VFA) were determined with a gas chromatography (W-NK-O.SA, Shinagawa), equipped with a 2 m × 4 mm glass column packed with Suplocopor (100–120 mesh) coated with 10% Fluorad FC 431. The temperatures of the column, injection port and flame ionisation detector, were 130, 220 and 240 °C, respectively.

Table 1
Characterization of CKD samples.

Parameter	Dry-kiln CKD (% by weight)	Dry-kiln CKD (% by weight)[b]
pH	13.6[a]	–
CaO	51	44.9
SiO_2	11.6	9.64
Al_2O_3	6.1	3.39
Fe_2O_3	3.3	1.10
MgO	1.1	1.29
K_2O	1.69	2.4
SO_3	5.4	6.74
Particle size	<25 μm	1–40

[a] Unitless parameter.
[b] Adaska and Taubert (2008).

Table 2
Physio-chemical characteristics POME.

Parameter[a]	Raw POME	EIA standards
Temp.[b]	55.5	45
pH	4.5	5.0–9.0
BOD	36	50
COD	62	100
VSS	20	400
TS	45	
TVS	26.3	
TP	9.50	
TOC	25	
O and G	15	50
NH_3-N	0.9	150
TKN	8.9	
TN[c]	9.45	200
VFA	19	
SO_4	0.5	
Zn	0.002	
Br	0.004	
Fe	0.005	
Mn	0.001	

[a] All parameters are in g L^{-1} except pH.
[b] As Temp.
[c] As total nitrogen.

2.3. Lime slacking

Prior to our experiment, we performed lime slacking with different ratios of CKD as described by Ahmad et al. [8]. After lime slacking, bench-scale experiments were carried out with five 500 mL flasks of POME by using five ratios of calcium hydroxide to examine the neutralizing effects of CKD. Slacked solutions with 12.5 g L^{-1} CaO-CKD were found suitable for maintaining a pH range of 6.9–7.9. The reaction was slow, but it successfully maintained the pH of the POME substrate in the reactor. The amount of calcium oxide in the cement extract was determined from the volume of the $KMnO_4$ solution used, according to Ahmad et al. [8].

2.4. Experimental setup and reactor operation

The experiment was performed in a previously constructed UASBR, continuously operated at 35 °C. We heated the reactor by circulating hot water through a surrounding jacket. The feed was introduced from the bottom of the reactor by a peristaltic pump with a flow rate of 0.52 l d^{-1} at various HRTs of 3.5–34.5 d. A gas–solid–liquid (GSL) separator was installed at the top of the reactor to capture the biogas. To prevent CaO-CKD from settling in the reactor, we modified the previous UASBR for these experiments with a 5 rpm stirrer. The experimental setup of the UASB reactor is shown in Fig. 1. The UASBR was inoculated with 350 mL seed sludge. We acclimatized the sludge to the POME by bench feeding diluted sludge (5 g COD/L) for five days. The average of the volatile suspended solids (VSS) of the sludge after bench feeding for 5 days was 11.3 g L^{-1}. Continuous feeding began with an initial organic loading rate (OLR) of 4.5 kg COD m^{-3} d^{-1} and a