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Mesophilic and thermophilic biomethane production by co-digesting pretreated petrochemical wastewater with beef and dairy cattle manure

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ABSTRACT

The use of pretreated petrochemical wastewater as provender wastewater for anaerobic degradation was explored in a continuous stirred tank reactor with dairy and beef cattle manure, under both mesophilic and thermophilic states. The co-digestion of the wastewaters contributed 50% enhancement in methane production, followed by a $98 \pm 0.5\%$ reduction in chemical oxygen demand at 10 days hydraulic retention time. No VFA aggregation was identified. In comparison with the digestion of PWW alone, methane yield increased by 50–60% under mesophilic conditions and 50–65% under thermophilic conditions due to co-digestion.

1. Introduction

Anaerobic co-digestion, a sustainable green technology, is extensively adapted to various waste treatments [1–3], particularly of animal manure. Manure is an outstanding co-substrate because it possesses eminent buffering capacity and a broad range of nutrients essential for optimal microbial growth [4]. The establishment of co-digestion of plant materials and manure was initially studied by Hills and Roberts in 1981 [5] and Hashimoto in 1983 [6]. They found that the combined effect could ameliorate the C:N ratio of the wastewater, thus reducing the hazard of ammonia inhibition of the degradation process [7]. Those optimistic synergistic effects have been used to increase methane yields [8]. Hence, at an apt C:N ratio and steady pH and balance of nutrients, enhanced methane production might be achieved from co-digestion with manure [9]. Consequently, food waste [10], potato tubers and their industrial byproducts [11], and energy crops and crop residues have already been successfully treated by co-digestion with manure [12].

Anaerobic digestion (AD) presents an outstanding opportunity for both energy conversion and pollution control. The commencement of high-rate reactors in which active biomass and liquid retention is performed is one of the basic factors contributing to the success of AD [13,14]. AD is accomplished via three basic mechanisms; namely hydrolysis, acidogenesis and methanogenesis [15,16]. It is notable that hydrolysis is considered to be a rate-defining stage in AD; particularly due to recalcitrant substrates. Fatty acids in wastewater have an inhibitory impact on many microorganisms, which makes biological degradation difficult [17,18]. It has been revealed that pretreatment might play a role in improving biochemical degradation efficiency [19]. Many pretreatments [20,21] aspire to solubilize or hydrolyze the substrate to improve degradability in biological reactors. These consist of physical size reduction, thermal hydrolysis, ultrasonic treatment, chemical treatment using acid or alkali, and ozonation and oxidation by H_2O_2. H_2O_2 is a versatile, vigorous oxidative agent that reacts via a hydroxyl radical mechanism with an oxidizing potential of 2.6 V, which reduces chemical oxygen demand (COD), produces H_2O and CO_2, and enhances biodegradability of organic compounds.

However, during AD, there is the potential of nutrient recycling and generation of renewable energy [22,23]. Moreover, reducing organic loading of wastewater by AD yields fuel gas comprising 55–70% methane [15]. The number of active microorganisms inside reactor and changes in operational and environmental conditions within the reactor indicate its efficiency [24]. The integral transformation of organic matter to methane is caused by acidogenic and methanogenic bacteria. The

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Nomenclature

AD	Anaerobic digestion
PWW	Petrochemical waste water
BCM	Beef cattle manure
DCM	Dairy cattle manure
CSTR	Continuous stirred tank reactor

use of numerous organic and chemical supplements under various operating conditions can enhance biogas production. Anaerobic co-digestion has been investigated in contemporary research. Co-digestion of pretreated corn stalks with manure in four different proportions (manure: corn stalks: 1:1, 1:2, 1:3 and 1:4) to generate biogas has been described by Li et al. [25] and a proportion of 1/3 was found suitable for biogas generation. The current studies include anaerobic co-digestion of breweries and its residue by lab-scale UASB reactor [26]. Others have included co-digestion of fruit and vegetable waste with abattoir wastewater and treating them in an anaerobic sequencing batch reactor at mesophilic and thermophilic temperatures [27]. By using two stages of anaerobic acidogenic and methanogenic reactors, Dareioti et al. [28] have co-digested a mixture of olive mill wastewater, liquid cow manure, and cheese whey. Currently, research has been aimed at anaerobic treatment of petroleum wastewater (PWW) by up-flow fixed film reactor. Both the removal efficiency of organic matter, especially COD, and methane production can be enhanced simultaneously by adopting a co-digestion process.

Nevertheless, despite these benefits, AD is not practiced widely in petrochemical wastewater (PWW) treatment due to its slow reactions, leading to prolonged hydraulic retention time (HRT) and indigent process stability. Even if there were widespread application of AD, the methane yield would be minor and related with elevated nitrogen and lignocellulose content [29]. Hence, co-digestion of pretreated PWW with beef cattle manure (BCM) and dairy cattle manure (DCM) could offer an efficient solution, with marked reduction in VFA accumulation and improved reactor stability. In this study, we focused on the effect of various mixing proportions on the methane yield efficiency and the stability of the continuous stirred tank reactor (CSTR) at different environments.

2. Materials and methods

2.1. Sample collection and characterization

A 100-L sample of PWW was collected in plastic containers from the effluent receiving stream of the petroleum refinery at Tarranganu, Malaysia. Approximately 100 kg partially digested BCM and DCM were collected from evacuation of cow fatteners on a mid-sized farm in Gambang, Malaysia. The PWW, BCM and DCM were placed in compact ice containers and transferred in 2 h. After that, all was placed into 2-kg covered bags and preserved at −20 °C until use. Effluent pH was fixed at 6.5, by 5 N NaOH solution. Alkalinity of the same was maintained at 1500–1700 mg/L $CaCO_3$ by $NaHCO_3$. The COD: N: P ratio of 250:5:1 was achieved by adding nitrogen (NH_4Cl) and phosphorous (KH_2PO_4) as supporting nutrients. Table 1 explains the composition and characterization of PWW, BMC, DCM and inoculum.

Table 2
Effect of DCM & BCM mixing ratio on methane production.

Mixing ratio	C/N ratio	pH	Mean methane yield (ml/g)
0:100	17/1	7.5 ± 0.20	50
25:75	20/1	7.3 ± 0.20	75
50:50	29/1	7.2 ± 0.20	90
75:25	33/1	7.17 ± 0.20	56
100:0	40/1	6.99 ± 0.20	24.5

2.2. Pretreatment (oxidation by H_2O_2)

Four wastewater samples of equal volume (150 mL) were placed in conical flasks. Thereafter, each of the three volumes of wastewater was treated with 50 mL standard volume of 30% H_2O_2 solution and 1.0 mM Fe^{3+}. To find the optimal dose of H_2O_2 solution for better degradation, the percentage of H_2O_2 added was gradually increased (i.e. 0.5% to 1% and 1.5%). The liquid content of effluent with H_2O_2 was agitated for 30 min with a mechanical device. The residual H_2O_2 was scavenged by catalase activity. The optimal H_2O_2 dosing (1%) was predetermined by a preliminary study that aimed to attain eminent biodegradability. Application of 2.5-h oxidation by H_2O_2 achieved approximately 49% enhancement in biodegradability from 0.53 ± 0.10 to 0.79 ± 0.06 accompanied by 35% COD reduction.

2.3. Pretreatment of manure

Thermal pretreatment of manure is effective at increasing methane production by 20% and reducing fibrous particle sizes [30]. Hence, solids of manure were heated to 100–145 °C before AD, to improve methane yield and volatile solids degradation stated by Mladenovska et al. [31].

2.4. Batch test studies

Plastic bottles with a capacity of 1.5 l were selected as digesters. This was a modified form of the compact system digester that

Table 1
Chemical and elemental compositions of PWW, DCM, BCM and active inoculum *values are the mean ± S.D. of the 3 observations.

Parameters	PWW	DCM	BCM	Inoculum	
				Mesophilic	Thermophilic
Acetic (mg/1)	1060 ± 20	125 ± 15	58 ± 10	50 ± 6	30 ± 6
Propionic (mg/1)	0	36 ± 5	33 ± 5	28 ± 3	40 ± 5
Isobutyric (mg/1)	0	40 ± 5	105 ± 4	22 ± 4	26 ± 3
Butyric (mg/1)	0	53 ± 5	115 ± 7	22 ± 5	20 ± 2
Total VFA (mg/1)	2210 ± 20	324 ± 6	375 ± 5	3200 ± 20	3000 ± 20
TKN (mg/1)	46 ± 5	2487 ± 6	5870 ± 150	1044 ± 90	835 ± 34
pH	6.12 ± 0.2	7.10 ± 0.23	7.43 ± 0.4	7.15 ± 0.03	6.98 ± 0.10
TS (g/g)	0.30 ± 0.05	0.145 ± 0.05	0.107 ± 0.06	0.026 ± 0.01	0.024 ± 0.01
VS (g/g)	0.46 ± 0.02	0.115 ± 0.02	0.085 ± 0.04	0.021 ± 0.01	0.020 ± 0.01
COD (mg/1)	15,000 ± 30	21,000 ± 20	16,000 ± 20	6840 ± 20	7700 ± 20
TOC (mg/1)	4950 ± 50	55,969 ± 1000	64,320 ± 1050	3900 ± 50	4100 ± 40
C/N ratio	107/1	22.5/1	10.9/1	–	–