Role of Bio-filtration in Petrochemical Wastewater treatment using CSTR

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Abstract— Continuous stirred tank reactors (CSTR) operated at 35"C, were efficaciously used for the anaerobic digestion of a petrochemical effluent. Bio-filtration of petrochemical wastewater was carried out and the results were evaluated in terms of basic water quality parameters. The effects of organic loadings, solid retention time were also investigated. COD reductions of 93-98% were found at an optimum retention time of 2.3 days and a loading rate of 4.7 kg COD/m3/d. The amount of biogas produced was 0.88 $m^3/m^3/d$ (STP) with a methane content of 90-96%. Volatile fatty acid removal was also achieved up to 97% after performing bio-filtration process. Therefore, the current work revils that bio-filtration of petrochemical wastewater using CSTR might be an effective solution to the prevailing treatment limitation.

Index Terms—Anaerobic digestion, Petrochemical wastewater, CSTR, Methane

I. INTRODUCTION

In today's industrial civilization, it has become increasingly important to prevent the pollution of our limited water resources by providing adequate treatment of effluents from industrial sources [1]. Anaerobic waste treatment is one of the major biological waste treatment processes in use, and has been employed for many years in municipal sewage treatment units [2]. The search for greater efficiency and better economy as well as the interest in methane as a renewable energy source, has led to the study of new types of anaerobic reactors [3]. In recent years considerable attention has been focused on a new range of reactors for the treatment of high strength industrial waste water [4]. One of the most successful of this range is the continuous stirred tank reactors [5]. The continuous stirred tank reactor (CSTR) is equivalent to a closed-tank digester equipped with mixture facility [6]. Over and above basic reactor design, the filling of most anaerobic digesters are mixed to assure competent transfer of organic material for the active microbial biomass, to discharge gas bubbles trapped in the medium and to prevent sedimentation of denser particulate material [7].

In Malaysia a unique high strength petrochemical effluent is produced by the crude petroleum refining process. This high strength effluent contains approximately 93-95 g/L volatile fatty acids. Large amounts of these fatty acids are produced per annum and have to be disposed of by other means. This paper reports on the use of continuous stirred tank reactors for the anaerobic treatment of high strength petrochemical effluent.

II. MATERIALS AND METHODS

a) Sample collection and characterization

A100 L of PWW sample was collected in plastic containers at the point of discharge in to the main stream and from the receiving stream. Then, transported to the laboratory and preserved at 4˚C for further study were physicochemical analysis and treatment. Effluent pH was maintained at 6.5, using 5N NaOH solution. Alkalinity was maintained between 1400-1800 mg CaCO3/l by NaHCO3. Complementary nutrients like nitrogen (NH4Cl) and phosphorous (KH2PO4) were employed to maintain a COD: N: P ratio of 250:5:1. Table1 explains composition and characteristics of PWW. With a view to eliminate trash materials, the prepared sludge was initially passed through a screen.

Table 1 Composition and Characteristics of PWW

Parameters	CPW
pH	6.5-8.5
BOD	8-32
COD	15-60
TOC	6-9
Total solids	0.02-0.30

Acetic acid	46.60
Phenol	0.36
Total Nitrogen	0.05-0.212
Total Phosphate	0.102-0.227
Volatile fatty acids	93-95

***Except pH and Acetic acid, all parameters in gL-1**

CSTR Construction and Operation.

Details of the continuous stirred tank reactor (CSTR) are given in Figure 1. The reactors consisted of 1 m glass columns, each with a working volume of 3.5 liter. The operational temperature was 35°C [8]. Inside each reactor an inert cylindrical, polyethylene bacterial carrier was placed. The surface area of the support material was 3,500 cm2. The substrate was continuously pumped in at the top of the reactor at the required rate while the reactor effluent was removed from the bottom. The reactor liquid level volume was electronically controlled [9]. Gas exited at the top of the reactor and volumes were determined by a means of a brine displacement system. At the start-up, the reactors were filled with sludge from a local municipal plant and slowly fed with a diluted fatty acid solution, which corresponded to the fatty acid composition of the factory effluent. With the start of gas production, the dilution was gradually reduced until the fatty acid solution corresponded to 50% of the effluent fatty acid concentration. Approximately 8 weeks were required, at a hydraulic retention time of 4.0 days, to obtain a 90% COD removal.

Analytical Methods

The COD was measured by direct digestion method, using HACH apparatus LR (3–150 COD), HR (20–1500 mg/L COD), and HR plus (20–15,000 mg/L COD and above). Total organic carbon was measured by direct method of low, medium, and high range tests (N tube reagent set), using HACH DBR 200 TOC program in HACH apparatus. Day-to-day gas yield was determined, by a revocable device, having liquid displacement technology. Biogas configuration was determined by a Perkin Elmer gas chromatograph having a thermal conductivity detector. A GC column packed with supelco 100/120 mesh was employed to distinct CH_4 and CO_2. Helium was employed as carrier gas maintaining flow rate 30 mL/ min. The columns sustained at 50˚C. Volatile fatty acids (VFAs) were analyzed using that similar GC, having a flame ionization detector connected to a supelco capillary column. Helium was employed as carrier gas maintaining flow rate 50 mL/ min. Injector and detector temperatures were 200 and 220˚C, individually. The kiln temperature was fixed at 150˚C for 3 min and subsequently amplified to 175˚C. The recognition limit for VFA investigation was 5.0 mg/L [10].

Statistical Analysis

Data analysis was performed with Microsoft EXCEL 2010. Regression coefficient (R^2) was calculated to analyze the effect of OLR on COD removal efficiency, biogas, and methane.

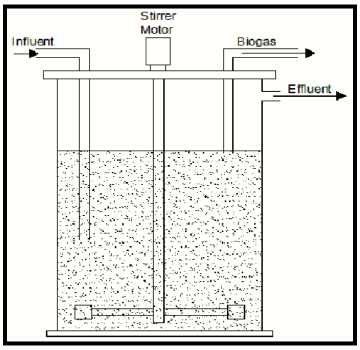

Figure 1: CSTR experimental setup

III. RESULT AND DISCUSSION

Chemical Oxygen Demand, Hydraulic retention time, Organic loading rate and Methane

After adjusting the pH of the petrochemical effluent, a red-brown precipitate formed. This was ascribed to the precipitation of iron and other trace metals. With continuous agitation on a magnetic stirrer this was used as substrate to feed a preconditioned reactor. The proficiency of this reactor was found to deteriorate with time and stabilized at a COD reduction of approximately 39% (Table 2). This low performance was ascribed to the precipitation of the minerals which possibly caused a growth limitation for the microbial population. A second reactor was fed with effluent that had been filtered through a Whatman no. 1 filter to remove the precipitate and to which a mineral solution had been added, to prevent any growth limitations to the microbial population. This reactor operated satisfactorily and for a period of 120 days a COD reduction of more than 98% was found (Table 2). These results show that the petrochemical effluent can be effectively treated by the anaerobic digestion process using a continuous stirred tank reactor

(CSTR). The data, shown in Table 2, was obtained at the hydraulic retention time (HRT) with the highest COD reduction. With the shortening of the HRT beyond this point a sharp decrease in COD reduction and corresponding increase in volatile fatty acids, especially propionic acid, was found. Thus the HRT with the highest COD reduction was considered as the optimum for the system under the described conditions. It is possible that with a bigger microbial surface area or different film supports, shorter HRT's could be obtained as shown by Movahedyan et al (2007)[11]. The results also showed that the microbial population, especially the methanogens, was successfully retained on the support material. The reactor effluent COD was found to consist of mainly soluble COD with the difference in soluble and total COD being less than 2.0%. The methane content of the gas produced by this type of reactor was very high compared with the results of others [12]. The collected gas contained approximately 90-96% methane. Since the petrochemical effluent was initially neutralized, the fatty acids were thus in the salt form. During the digestion process the acetate ions are assimilated by the microbial population and the sodium ions are set free into the surrounding medium where sodium hydroxide is regenerated. The pH of the reactor effluent was found to be around 7.1. This could be the result of the regenerated sodium hydroxide. The carbon dioxide formed in the reactor, and not used by the methanogens, will react to form sodium carbonate [13]. The excess carbon dioxide is thus removed from the reactor and mostly only methane is set free explaining the high methane to carbon dioxide ratio [14]. That's how this experiment reviles a clear concept of producing much more biogas with the help of co-digestion technology. However, bio-filtration with continuous stirred tank reactor (CSTR) appears to be effective treating petrochemical wastewater.

Table 2: CSTR performance via filtration

Parameter	Effluent	
	Unfiltered	Filtered
Hydraulic retention time (days)	4	2
Loading rate (kg COD/m^3/d)	3.17	4.7
COD removal (%)	39	98
Biogas production rate (m^3/m^3/d)	0.13	0.90
Methane content (%)	57%	92%
Volatile fatty acid removal (%)	40%	97%
pH reactor effluent	6±0.3	7.1±0.2

B. Petroleum Hydrocarbon, Microbial cell production & MLSS:

Fig 2 explains that total petroleum hydrocarbon concentration was gradually decreased with the increase of SRT. Under these testing conditions, the MLSS Values. Moreover, as SRT values exceed beyond 10 days, relatively small incremental changes formed for both petroleum hydrocarbons and MLSS concentrations. During AD, it is a must to measure the quantity of sludge produced per day due to its effect on process stability and disposal facilities. In order to prevent excess accumulation of microbial cell in the system, the quantity of sludge produced/ day must be wasted [15-16]. As AD incorporates cell recycle, the additional importance of cell decay and sludge production at increasing SRT can be seen by examining SRT with respect to MLSS and microbial cell production, as illustrated by Fig. 3. This plot illustrates the net synthesis in the system broadly, the mass of cells formed less those lost by decay. The highest daily production of 110 g/d was found at 3 d SRT. It reflects the necessary time frame and accumulative production at which a great deal of the dissolved petroleum substrate has been degraded and transformed to cells while decay is not yet a major factor . Nevertheless, sludge production started to turn down steadily through the remaining SRT values with the extended SRT values. A shift from cell synthesis to cell decay due to the increasing SRT values and the attainment of complete stabilization of the petroleum hydrocarbons might be suggested by the declination of the curve. The regression values (R^2) of fig 2 and 3 were determined 0.96 and 0.97 which implies that the results have obvious consistency.

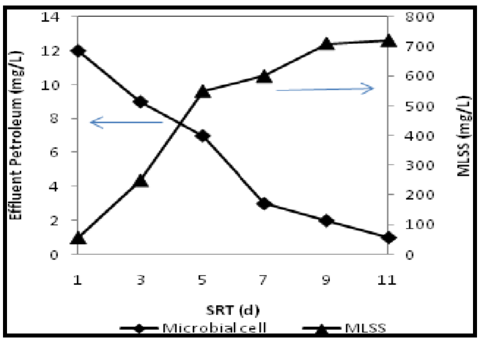

Figure 2: Effluent petroleum concentration vs. solid retention time for co-digestion process

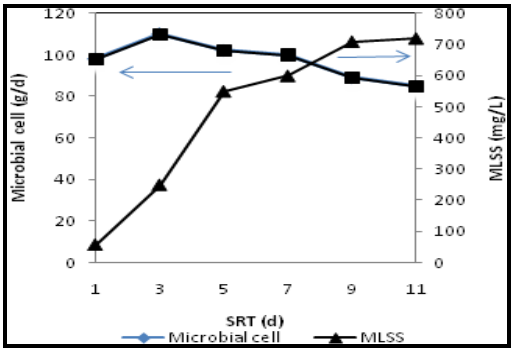

Figure 3: Effluent microbial cell concentration vs. solid retention time for co-digestion process.

IV. CONCLUSION

1. The results show that effluent from a petrochemical industry is amendable to treatment by an anaerobic digestion process. The HRT's could probably be shortened by the increase in microbial surface area.

2. The precipitation of iron and trace metals caused a growth limitation for the microbial population. This limitation could be removed by filtering the effluent and adding a mineral solution.

3. The methane content was high (90-96%) due to the self-scrubbing effect of this type of reactor.

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