The efficiency of membrane anaerobic system (MAS) in treating sugarcane mill effluent (SCME)

Z H Yasmeen, N H Abdurahman*, M S Hybat and R M Yunus
Faculty of Chemical and Process Engineering Technology, College of Engineering Technology, Universiti Malaysia Pahang, 26300 Kuantan, Pahang, Malaysia.

*E-mail: nour2000_99@yahoo.com

Abstract. In recent times, the environmental issues have been on an alarming rate mostly for public authorities, societies, and industrial establishments. Sugarcane mill effluent (SCME) which contain high miscellaneous pollutants such as the chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solid (TSS) and the volatile suspended solid (VSS). However, the conventional method has the merit of COD reduction from SCME, but is limited in capturing the methane gas produced. In this study the membrane anaerobic system (MAS) was used as a cost-effective replacement method for treating SCME. In this study, six steady states were reached as part of the kinetic study with concentration ranging from 6312 to 14043 mg/l for the mixed liquor suspended solids (MLSS) and 4790 to 12887 mg/l for mixed liquor volatile suspended solids (MLVSS). The three kinetic equations (Monod, Contois and Chen and Hashimoto) were used to explain the kinetics of SCME treatment at organic loading rates ranging from 0.5 to 13 kg COD/m$^3$/day. The removal efficiency of COD was from 94.2% to 93.9% and produced methane gas (CH$_4$) 75.4%. The scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (SEM/EDX), and Fourier transforms infrared spectroscopy (FTIR) were subsequently used to quantitatively and qualitatively determine the content of the biomass before and after treatment.

1. Introduction
Industrial wastewater treatment is one of the great worldwide challenging environmental issues. Due to a large amount of water used in a sugarcane milling operation, there are many contaminants in the sugar cane mill effluent. This water contains high BOD and COD level and hence cannot be discharged directly as it has standard disposable limit according to the Department of Environmental (DOE). The COD and BOD level for untreated SCME is around 16000 to 1500 mg/L respectively which shows that it has higher decay of microorganisms and particles (organic and inorganic material) thereby constituting pollution to the water body, if not treated properly [1,3]. The pollutant capacity could be the main source of environmental pollution with a direct effect on human health if they are not treated perfectly[4]. There are many types of wastewater such as POME, sugarcane, and slaughter mill effluents. The anaerobic digestion was found by researchers to be the most appropriate for effluents treatment which contains a high organic carbon concentration [1,5]. In engineering, the anaerobic digestion of methanogenic involves an organic matter decay which include anaerobic microorganism’s with different types [6,7]. One of the basic requirements in anaerobic digestion is the absence of oxygen molecules to decompose the biomass which includes the organic and inorganic materials [7-8]. The intermediate component should be converted into basic products, such as methane (CH$_4$) and carbon dioxide (CO$_2$) which involves the biological transformation of the organic substrate. This transformation
happens under the anaerobic requirement initiated by the hydrolysis, acidogenesis, acetogenesis, and methanogenesis [8-9]. However, the anaerobic digestion process has a major role for the decomposition of organic matter to produce methane gas in the electricity generation and save fossil energy [10-11]. These processes belong to the conventional SCEM treatment method which takes a very long period of time and large area for treatment. Anaerobic bioreactors with the high rate, have been used in the laboratory-scaled wastewater treatment like in the up-flow anaerobic sludge blanket (UASB) reactor [7]. Recently, AD has become a good source of treatment of wastewater effluent treatment in the world [12]. AD technology is employed in renewable energy recapture of biogas and in the treatment of a huge diversity of waste from industrial process, wastewater treatment plants, agriculture, and household [13]. In this study the membrane anaerobic system was used to treat SCME. Economically, the use of MAS has the capacity to overcome high chemical oxygen demand and easily capture the methane gas. In addition, estimation of the dynamic process parameters shall be carried out using three kinetic models (Monod, Contois, Chen and Hashimoto) for growth the specific substrate [14] as presented in table 1.

### Table 1. Mathematical Substrate utilization rates for kinetic model

| Kinetic Model          | Equation 1                                                                 | Equation 2                                                                 |
|------------------------|---------------------------------------------------------------------------|----------------------------------------------------------------------------|
| Monod                  | \( U = \frac{kS}{k_s + S} \)                                              | \( \frac{1}{U} = \frac{K_s}{K} \left( 1 - \frac{1}{S} \right) + \frac{1}{k} \) |
| Contois                | \( U = \frac{U_{max} \times S}{Y(B \times X + S)} \)                     | \( \frac{1}{U} = \frac{a \times X}{\mu_{max} \times S} + \frac{Y(1 + a)}{\mu_{max}} \) |
| Chen & Hashimoto       | \( U = \frac{\mu_{max} \times S}{Y K S_o + (1 - K) S Y} \)                | \( \frac{1}{U} = \frac{Y K S_o}{\mu_{max} S} + \frac{Y(1 - K)}{\mu_{max}} \) |

2. Materials and Methods

2.1. Configuration of MAS

The anaerobic digester with volume capacity of 200 L was used for the treatment of the crude sugar cane wastewater. The design is included the feeder conservation tank (to pass the food to microorganisms), a pressure gauge (to control the pressure that ranges from 1-2 bar). The MAS consists of a cross-flow ultra-filtration membrane (CUF), the centrifugal pump, and an anaerobic reactor. The MAS ultrafiltration membrane is characterized with a cut-off (MWCO) of 200,000 molecular weight, a 1.25 cm tube diameter, 0.1 µm pore size, and 30 cm tube length. The membrane house area was 0.024 m². The membrane highest pressure was 55 bars at 60 °C, the pH range started from 4.5 to 0 7.5. The reactor was made from PVC and the internal diameter is measured at 45 cm shown in figure 1.
2.2. Analytical Testing
The parameters analyzed were TSS, BOD, COD, VSS. The HACH colorimetric digestion method (Method 8000, HACH Company, and Loveland, CO, USA) was used for COD measurement. On the other hand, the influence of mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) was carried out by drying the sample at 105 and 550 ± 50 °C. To determine the CH₄, the Gas chromatography was employed with 200 cm × 0.3 cm stainless steel column which is packed with 30–60 mesh active carbon, and thermal conductivity detector.

2.3. Sugarcane (SC) Wastewater
Raw samples of the sugarcane wastewater were obtained from in Central Sugars Refinery located in Selangor, Malaysia. The sugarcane wastewater was characterized with higher COD and BOD, fishy, a fermented odour and with a dark brownish colour which disappears after treatment into a light brown colour. The total suspended solids are made up of carbohydrates, Ca, K, Mg, and organic matter [15]. To therefore evaluate the quality characteristics of the water after SCME treatment, the sample was subjected to some physicochemical characterization such as SEM, EDX, FTIR Which invariably explored the removal mechanism [16].

3. Results and Discussion

3.1. The operation of Bioreactor
The performance of MAS was estimated under six steady states at different CPD concentration as presented in Table 2. These range from 7541 to 23822 mg/L and the organism feeding (OLR) from 0.5 to 13 kg COD/m³/day. To achieve good result, condition must be provided for operating and control parameters which must be within ± 10% of the average value. Pulled the gas from the top of reactor used a syringe at the end of an elastic tube to easily collect the gas. Then, added sodium hydroxide solution (NaOH) to biogas produced CO₂ and CH₄ only in order to absorb CO₂. The biogas was produced as the organic material degrades by methanogens bacteria in the absence of oxygen. Skorek and
Włodarczyk [16] reported that the biogas contains about 50-75% methane (CH₄), 25–45% carbon dioxide (CO₂) and fewer amounts of the other gases. Then, add sodium hydroxide solution (NaOH) to biogas produced CO₂ and CH₄ only in order to absorb CO₂.

| Steady state (SS) | 1    | 2    | 3    | 4    | 5    | 6    |
|-------------------|------|------|------|------|------|------|
| COD feed, mg/L    | 7541 | 10377| 15200| 18631| 20431| 23822|
| COD permeate, mg/L| 440  | 661  | 897  | 903  | 1200 | 1455 |
| Gas production (L/day) | 200.5 | 230  | 280  | 320  | 340  | 381  |
| Total gas yield, L/g COD/day | 0.31  | 0.38 | 0.42 | 0.51 | 0.56 | 0.63 |
| % Methane         | 66.4 | 69.4 | 68.4 | 70   | 73.6 | 75.4 |
| CH₄ yield, l/g COD/day | 0.21  | 0.26 | 0.29 | 0.357| 0.41 | 0.48 |
| MLSS, mg/L        | 6312 | 8236 | 10532| 12964| 13639| 14043|
| MLVSS, mg/L       | 4790 | 7087 | 9922 | 10465| 11753| 12887|
| % VSS             | 6.4  | 86.04| 94.21| 80.72| 86.17| 91.77|
| HRT, day          | 150.8| 103.77|30.4 | 23.3 | 18.57364|18.32462|
| SRT, day          | 300  | 250  | 180  | 30   | 20.6 | 11   |
| OLR, kg COD/m³/day| 0.5  | 1    | 5    | 8    | 11   | 13   |
| SSUR, kg COD/kg VSS/day | 0.225 | 0.659 | 4.663 | 7.953 | 12.164 | 15.735 |
| SUR, kg COD/m³/day | 0.047 | 0.093 | 0.470 | 0.760 | 1.035 | 1.221 |
| COD removal (MAS) | 94.2 | 93.6 | 94.1 | 95.1 | 94.1 | 93.9 |

### 3.2 Performance of the Membrane Anaerobic System (MAS) Performance

The data achieved from the evaluated MAS performance is presented in Table 3. The application of MAS process was under different COD influent concentrations, as well as HRTs. From Eq. 2, the coefficients models were obtained using a linear relationship as shown in Table 1. The average of the model’s coefficients is summarized in Table 3. Furthermore, the important value of the coefficients models was brief in the same table.

| Model         | Equation                                      | R²(%) |
|---------------|-----------------------------------------------|-------|
| Monod         | $U^{-1} = 2025S^{-1} + 3.61$                  | 99.8  |
|               | $K_s = 498$                                   |       |
|               | $K = 0.350$                                   |       |
|               | $\mu_{Max} = 0.259$                           |       |
| Contois       | $U^{-1} = 0.306X + 2.78$                      | 99.3  |
|               | $B = 0.111$                                   |       |
|               | $\mu_{Max} = 0.344$                           |       |
|               | $a = 0.115$                                   |       |
|               | $\mu_{Max} = 0.384$                           |       |
|               | $K = 0.519$                                   |       |
| Chen & Hashimoto | $U^{-1} = 0.0190S^{-1} + 3.77$             | 99.8  |
|               | $K = 0.006$                                   |       |
|               | $a = 0.006$                                   |       |
|               | $\mu_{Max} = 0.277$                           |       |
|               | $K = 0.374$                                   |       |

The MAS showed the best performance due to the capacity of the membrane ultrafiltration that cleans the surface where the molecules are collected and bacteria from SCME. One of the important parameters
to produce methanogenesis bacteria is pH. This was found to be steady to the optimal points ranging from 6.7–7.8 for the reaction’s anaerobic digesters when the experimental achieved the steady-state conditions, it found that the influent COD concentrations of 7541 –23822 mg/L. At the six steady states The VSS decreased to became 65.08 due to the presence of high suspended solids in the sugarcane wastewater mill effluent which can lead to the reduction in the value obtained. The highest value of VSS reached 70.05% in the reactor. The results have shown the long solid retention time, SRT of MAS facilitated the decay of the suspended solids and their subsequent conversion to methane (CH₄), these findings reported by [7]. At this stage, the performance of MAS achieved 99.8% removal efficiency. Increasing the OLRs that indicated to increase SUR and SSUR. This suggests that there is a multiplication in the population of bacteria within the MAS [26]. Hence, the increase in the concentration of the substrate might have led to the significant increment in the specific substrate utilization rates, and SSURs. This is an indication that the increasing amount of COD influent supplied to the reactor was accounted for by the amount of COD consumed by the bacteria populations [3]. The results obtained was applied in the famous three modules shown in Figure 2 to 4. MAS can be applied and treat SCME efficiently. The Monod and Chen & Hashimoto model verified an excellent relationship (R² > 99%) for the treatment of sugarcane wastewater using an anaerobic membrane system as explained in Figure. 2,3,4.

![Figure 2. The Monod model](image)

![Figure 3. The Contois model](image)
The Monod and Chen and Hashimoto models performed better, implying that the digester performance should consider OLR. These two models suggested that the predicted permeate COD concentration \( (S) \) as a function of influent COD concentration \( (S_o) \). In the Contois model, however, \( S \) is independent of \( S_o \). The best fit of these three models (\( R^2 > 99\% \)) in this study showed that the MAS process has an ability of handling sustained organic loads between 0.5 and 13 kg m\(^{-3}\)/d.

3.3 The relationship between COD and HRT
The SCME exhibited higher COD until 25000 mg/l. For that need treatment before discharge to the river. This is estimated in the expression of COD as depicted in Figure 5. This illustrated that the COD removal efficiency increased as HRT increased from 18.32 to 150.82 days at ambit of 94%-93%. Otherwise, COD% decreased for lower HRT of 103.77 the COD was 93.6% this was due to the washout phase as showed in Table 2. Moreover, in the reactor process, while the biomass concentration increased, the washout phase was expected to happen. This may be indicated too high OLR with low HRT. The increase OLR create the VFA which in turn leads to a reduced COD concentration. The ultrafiltration (UF) membrane influx rates, usually exhibit a strong effect on the hydraulic retention times and also could determine the amount volume of the influent (SCME), fed into the reactor.
3.4 Characterization of biomass

3.4.1 Scanning electron microscope (SEM)
The SEM was characterized by providing very high resolution for image more than the previous analyses. This technique could be connected with the X-ray emission which lead to an electron beam of high energy microanalysis to identify the elemental distribution of biomass structure (anaerobic processes) and morphology [17-18]. It also studied the efficiency of the treatment before and after the biological treatment and the existence of some bacteria that might be responsible for producing biogas [19].

![Figure 6. Scanning Electron Microscope (SEM), (a) Before treatment 500 XK (b) After treatment 500KX.](image)

Biomass formation was observed using SEM, under specific conditions after the four reactions process which is responsible for the aggregation of bacteria on the surface of the substrate and produces CH₄ [20] in figure 6 (a) Observation on the surface of the substrate with SEM almost covered with the methanogenesis bacteria. The bubbles gas and the gaps between the particles indicated the presence of methanogenesis bacteria in the substrate of AD. The microorganism appeared noodle-like and they linked to each other in a network shown in figure 6 (a) [21]. This provided information about the various stages of anaerobic digestion biomass development, demonstrating the non-homogeneous distribution of biomass in figure 6 (a) before treatment [19]. The surface morphology after treatment (b) appeared less rough and corrugated and the distance between the particle increase and this shows the presence of high organic material captured inside the membrane. Furthermore, some microorganism are expected to have died during it arrived to steady state in the surface of biomass [22].

3.4.2 Energy dispersive X-ray (EDX) analysis
Energy-Dispersive X-ray spectroscopy (EDX) analysis proved to be one of the characterization methods, which the breakdown of organic compounds in the wastewater. EDX spectrum explains the morphology of SCME before and after the treatment, changing in the structure progression as a result of biochemical digestion of organic admixture inside the anaerobic reactor [23-24]. The EDX spectrum also revealed degradation of some organic material as well as a breakdown and damage of biological material in the membrane. It can be seen from the EDX data he chemical content composition of the adsorbent used is shown in figure 7. before treatment. Figure 8. After treated some elements decrease and the other one disappeared due to digestion during the anaerobic process, shown that in table 3.
Figure 7. EDX spectra of influent of SCME after operation for 14 days.

Figure 8. EDX spectra of permeate of SCME after operation for five hours

| Element | Weight (%) Before | Weight (%) After |
|---------|------------------|-----------------|
| Carbon  | 21.699           | –               |
| Oxygen  | 27.771           | 38.209          |
| Sodium  | 9.321            | 24.404          |
| Magnesium | 0.177           | 0.370           |
| Aluminum| 0.143            | –               |
| Chlorine| 11.199           | 23.098          |
| Calcium | 2.276            | –               |
| Iron    | 10.382           | –               |
| Copper  | 3.807            | –               |
| Zinc    | 3.825            | –               |
3.4.3 Fourier Transform Infrared Spectroscopy (FTIR) Analysis
The FTIR spectroscopy mechanism was used to elucidate the surface functional groups and to obtain an inherent interaction of the groups with other parts of the molecule found in both untreated and treated SCME samples. The FTIR spectra of the SCME were recorded on an instrument (Nicolet IS5 FTIR) in the range of 400–4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\) [23]. The sugarcane mill effluent bands are illustrated in Figure 9. For carboxylate (COO\(^{-}\)) and hydroxyl (OH\(^{-}\)) groups a strong adsorption band was observed from 3500 cm\(^{-1}\) to 3000 cm\(^{-1}\), with a peak maximum at 3302 cm\(^{-1}\). This can be assigned to bonded OH groups [24]. The bands 2100-2245 cm\(^{-1}\) which represents the \(\text{C}≡\text{C}\) stretch in alkynes group. The peak of 1642 cm\(^{-1}\) indicates OH group in water. Broadband in the range between 1585 and 1600 can be assigned to \(\text{C}–\text{C}\) stretch (in-ring) aromatics [25]. Also, the bands from 1040 cm\(^{-1}\) to 1250 cm\(^{-1}\) represent carboxylic acids group. After treatment some functional group disappear that indicate to organic material and small particles sedimentation on the membrane and digested during the four anaerobic processes inside the reactor [26].

![FTIR spectra with labels A and B](image)

**Figure 9.** FTIR spectra of sugarcane wastewater mill effluent (wavenumber 4000 to 400 cm\(^{-1}\)): (A) Before treatment. (B) after treatment

4. Conclusion
The membrane anaerobic system (MAS) seemed to be an improved biological treatment reactor system, for the treatment of raw SCME. The reactor volumes are considered to be smaller than the conventional digester required volumes. This in a very short period of time has the capacity to achieved high COD removal efficiency up to 95.1%. The gas production, and the methane concentration in the gas, was satisfactory amount and, therefore, both could be considered. The amount of methane gas produced is an additional energy source appropriate for use at the sugarcane mill effluent. In MAS, the preliminary data on anaerobic digestion at 36\(^°\)C showed the potential of the proposed technology, which substantially reduce the SCME wastewater pollution load. A significant quantity of energy (methane 75.4%) could be recovered by the MAS process, which could be used for electricity generation and fuel purposes. The infrared spectrometric, Fourier transform analyses indicated an improvement of the sugarcane wastewater mill effluent after treatment due to the decrease in the absorbance bands of carboxylate (COO\(^{-}\)) and hydroxyl (OH\(^{-}\)) groups. The morphological observation by scanning electron microscopy (SEM) for SCME before and after treatment, proved to be having bubbles from methanogenesis bacteria which in turn leads to the production of CH\(_4\). MAS showed that the proposed technology has a potential to substantially decrease the pollution load of SCME wastewater.
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Nomenclature

COD  chemical oxygen demand (mg/L)
OLR  organic loading rate (kg/m³/d)
CUF  cross flow ultra-filtration membrane
SS  steady state
SUR  substrate utilization rate (kg/m³/d)
TSS  total suspended solid (mg/L)
MLSS  mixed liquid suspended solid (mg/L)
HRT  hydraulic retention time (day)
SRT  solids retention time (day)
SSUR Specific substrate utilization rate (kg COD/kg VSS/d)
MAS  Membrane anaerobic System
MLVSS mixed liquid volatile suspended Solid (mg/L)
VSS  volatile suspended solids (mg/L)
MWCO molecular weight Cut-Off
BLR  biological loading rate
U  specific substrate utilization rate (SSUR) (g COD/G VSS/d)
S  effluent substrate concentration (mg/L)
So  influent substrate concentration (mg/L)
X  micro-organism concentration (mg/L)
μmax Maximum specific growth rate (day⁻¹)
K  Maximum substrate utilization rate (COD/g/VSS.day)
Ks  Half velocity coefficient (mg COD/L)
X  Micro-organism concentration (mg/L)
b  specific microorganism decay rate (day⁻¹)
Y  growth yield coefficient (gm VSS/gm COD)

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