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Anaerobic Digestion of Paper Mill Wastewater

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Abstract: In general, paper mill wastewater contains complex organic substances which could not be treated completely using conventional treatment processes, e.g. aerobic processes. As a result, anaerobic technology is a promising alternative for paper mill wastewater treatment due to its ability to degrade hard organic compounds. In the present study, treatment of paper mill wastewater using a stage anaerobic reactor was investigated. The more specific objectives of this study were to confirm whether paper mill wastewater can be tolerated by methanogenic sludge and to assess the stability of reactor for measured parameters (e.g. COD removal, and methane composition). Results showed up to 98% COD removal efficiency in the anaerobic reactor when the reactor was operated at an OLR of 1.560 kg COD/m^3.d. Anaerobic digestion can provide high treatment efficiency for recalcitrant substrates, which generates robust microorganism (acidogenesis and methanogenesis), for the degradation of recalcitrant compounds such as in the paper mill wastewater.

Key words: Anaerobic digestion; Paper mill wastewater; Recalcitrant compound.

INTRODUCTION

The anaerobic digestion process involves biological conversions in a step-wise fashion, of organic material to various end products including methane (CH_4) and carbon dioxide (CO_2). The process offers several advantages and disadvantages over other treatment method [1]. A well managed anaerobic digestion system has the ability to produce maximum methane production, and will not discharge any gases to the atmosphere. This system will also provide a source of energy with no net increase in atmospheric carbon which contributes to climate change. Energy generated through the anaerobic digestion process can help reduce the demand for fossil fuels.

The pulp and paper industry is one of the most important industries in Malaysia. The sector is a very water-intensive and can consume as high as 60 m^3 of freshwater per tonne of paper produced [2]. Paper mill wastewater contains complex organic matter and if these compounds are not removed by one-site treatment they will be discharged to sewage treatment plants (STPs) and could disturb the biological process and the microbial ecology in the STP and the receiving surface waters. Results from literature on the anaerobic treatment of paper mill wastewater clearly demonstrate that anaerobic treatment is not commonly used as a mean for treating paper mill wastewater [3].

Generally, the generation of wastewater and the characteristics of pulp and paper mill effluent depend upon the type of manufacturing process adopted. Hence, the treatments of the wastewaters from different mills become complicated because no two paper mills discharge identical effluents.

Pulp and paper mill wastewater has also been considered as one of the most polluting agro-industrial residues. The primary source of fibres used in pulp and paper mill is wood. Major constituents in woods are cellulose, hemicellulose, lignin and extractives that are hard to biodegrade. Pulp and paper mill wastewater is produced from wood preparation, pulping process, pulp washing, screening, washing, bleaching, and paper machine and coating operations [3].

The wastewater generated from pulping process is called black liquor. Black liquor is the most polluting stream in pulp and paper mill. Black liquor is dark in color with high pH, biochemical oxygen demand (BOD), chemical oxygen demand (COD) and suspended solid.

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Generally, black liquor is burnt in conventional boilers to recover the pulping chemicals and generate biomass energy. Black liquor gasification is a promising alternative for recovery of energy and chemicals from black liquor in the pulp and paper industry because the organic fraction of black liquor comes from biomass and the degradable products that are dissolved in alkaline pulping liquor [4]. In addition, wastewater from pulp and paper mills constitutes a major source of aquatic pollution since it contains extractives (resin acids), chlorinated organics (measured as adsorbable organic halides, AOX), suspended solids, metals, fatty acids, tannins, lignin and its derivatives [5]. Lignin and its derivatives can form highly toxic and recalcitrant compounds and are responsible for the high BOD and COD. Alkylphenol polyethoxylates (APEOs) or nonylphenolic compounds can also be found in the pulp and paper mills effluent [6].

Various pulping wastewater treatment had been studied. The anaerobic digestion of black liquor generated from cereal straw using soda pulping achieved 55% COD removal at the optimum organic loading rate (OLR) of 8.0 kg COD/m^3.day [7]. The biogas production and the methane yield were 11 m^3/d and 71%, respectively. Anaerobic-aerobic treatment with up-front effluent recirculation was studied by Kortekaas [8] to treat hemp stem wood black liquor. This treatment yielded 72% and 97% COD and BOD removal respectively at OLR of 3.6 g COD/L.d. Anaerobic treatment of black liquor obtained from a mixture of biogases, rice and wheat straw yielded 71% COD reduction and 80% methane with addition of 1% w/v glucose while in the absence of glucose only 33% COD reduction was achieved [9].

An average COD removal efficiency of 80% was achieved in up-flow anaerobic sludge blanket (UASB) system treating black liquor from Kraft pulp plant [10]. COD removal of 73±10% was achieved in an aerobic sequencing batch reactor operated at 45°C for the degradation of bleached kraft pulp mill effluent [11]. Additionally, in the filtration of black liquor with straw as raw material, approximately 80% and 90% lignin retention was achieved with microfiltration and ultrafiltration membranes system respectively [12].

In this study, the objectives were to investigate treatment of paper mill wastewater in a novel anaerobic reactor system. The more specific objectives were to confirm paper mill wastewater can be tolerated by methanogenic sludge, assess the stability of reactor for measured parameters (e.g. COD removal and methane composition).

MATERIALS AND METHODS

Anaerobic Reactor: An up-flow anaerobic reactor having four identical systems, each comprising four compartments (stages), were constructed for the present study. Each stage of the reactor had a 3-phase separator baffle, which was placed below the effluent ports, to prevent floating granules from washing out with the effluent. Each stage was equipped with sampling ports that allowed biological solids and liquid samples to be withdrawn from the sludge bed. The influent wastewater entered through a down comer tube and allowed feed to flow upward through the sludge bed. Effluent from each stage of the reactor flowed by the gravity to the next, as each stage was placed on a stepped platform.

Seed sludge: The anaerobic reactor was seeded with anaerobic digested sewage sludge (IWK, Bunus Treatment Plant, Kuala Lumpur). This was sieved pass 2.0 mm mesh, giving solid contents of 53,750 mg TSS/L and 41,500 mg VSS/L. Each stage of reactor was added with 7.5 L of the sieved sludge. The remaining volume of the reactor was then filled with tap water. After seeding, the head plates were attached and the headspace above each reactor was flushed with nitrogen gas to displace residual air in the system before introducing the feed. The reactor was allowed to stabilize at 37ºC for 24 hours in 7 d without further modification.

Reactor operation: In general, this study was carried out in three (3) major steps; a) Start-up of reactor, b) Acclimatization to paper mill wastewater at OLR 0.256 –0.512 kg COD/m^3.d) at constant HRT of 3.9 d and, c) Effect of OLR from 0.640–1.560 kg COD/m^3.d by adjusting HRT from 3.9–1.6 d. The start-up was established with a synthetic (glucose) wastewater and Table 1 shows the operating conditions during the treatment process. Glucose was used since it is readily degradable, soluble carbohydrate and does not limit the rate of anaerobic biodegradation [13]. Nutrient deficiency was corrected using macronutrients N100 (Table 2, from Bio-Systems Corporation Asia Pacific Sdn Bhd). Once the reactor had reached steady state

Table 1: Reactor operating conditions during treatment process.

Synthetic wastewater (%)*	Paper Mill wastewater (%)*	OLR (kg COD/m^3.d)	HRT (d)	Feed COD (mg/L)	Day
100	0	0.256	3.9	1000	1
90	10	0.384	3.9	1500	17
70	30	0.512	3.9	2000	23
50	50	0.512	3.9	2000	29
40-10	60-90	0.512	3.9	2000	35
0	100	0.640	3.9	2500	42
0	100	1.080	2.3	2500	113
0	100	1.560	1.6	2500	120

*proportion based on COD

(90% COD removal), the feed to the reactor was supplemented incrementally with paper mill wastewater (10–90% as COD) to allow the methanogenic bacteria to acclimate to any potential inhibitory effects from its recalcitrant content.

Sampling and analysis: Supernatant liquor, gas and sludge samples were taken separately from each stage for analysis purposes. In addition, gas composition rate was determined separately for each stage. Routine analysis such COD, SS, VSS and pH were carried out in accordance with Standard Method [14]. Reactor gas composition (CO_2 and CH_4) was determined using Gas Analyzer (GeoTech 2000).

RESULTS AND DISCUSSION

COD Removal: Fig. 1 shows temporal changes in the total COD removal and fractional contribution by each stage of the reactor treating paper mill wastewater. Initial fluctuations were attributed to technical problems with the peristaltic feed pump. From day 42, the reactor was fed with 100% paper mill wastewater at an OLR of 0.640 kg COD/m^3.d and HRT of 3.9 d. During the acclimatization period (from OLR 0.256 to 0.512 kg COD/m^3.d), the COD removal efficiency of the reactor system was around 88%. This indicated that there were no substantial reductions in the COD removal efficiency when the paper mill wastewater was present up to 90% of the feed. In addition, these results also indicated that there was not any substantial inhibitory effect to the methanogens when paper mill wastewater was introduced in the reactor system. At reactor OLR of 0.640 kg COD/m^3.d the soluble COD reduction was around 82–97%. The reactor shows continuous improvement in terms of COD removal when OLR was increased further to 1.560 kg COD/m^3.d. The average COD reduction efficiency was around 95% during this period. It is evident that stages 2, 3 and 4 showed a relatively minor contribution (less than 10%) to total COD removal (Fig. 1), and around 60–90% COD reduction took place in Stage 1 of the reactor. The above results on COD removal are comparable with other studies on treatment of paper mill wastewater using anaerobic reactor; single-stage up-flow anaerobic sludge bed (UASB) reactors and multi-stage anaerobic reactors is about 45–65% [15, 16] and 65–75% [17], respectively.

pH Levels: The pH levels during the acclimatization period showed some fluctuation, especially at OLR 0.512 kg COD/m^3.d (Fig. 2) where lowest pH was observed in the effluent of the reactor (pH 5.3, Stage 1). These sudden reduction of pH were probably due to the rapid production of VFAs (data not taken) resulting from increased acidogenic activity. However, this fluctuation was not permanent, as the pH recovered above 7.0 when the reactor operated with 100% paper mill wastewater at OLR 0.64 kg COD/m^3.d , indicating that acidogenesis and methanogenesis had recovered balanced levels. Thereafter, the pH levels were generally stable (pH 6.8 7.8) in all stages of the reactor when the OLR was increased gradually to 1.56 kg COD/m^3.d, indicating stable performance during the study of effect of OLR.

Table 2: Characteristics of macronutrient N100

Nutriens	Composition	Nutrients	Composition
Crude Protein (min)	5%	Manganese	0.09%
Crude Fat (min)	2%	Roiboflavin	8.00 mg
Crude Fibre (max)	8%	Selenium	0.00002%
N.free Extract	45%	Zinc	0.005%
Calcium	2%	Vitamin A	50,000 IU
Phosphorus	1%	Vitamin D	3,000 IU
Magnesium	0.50%	Vitamin E	150 IU
Sulfur	2%	Vitamin K	1.00 mg
Potassium	2%	Vitamin B12	0.04 mg
Salt	2%	Ascorbic Acid	1500.00 mg
Iron	0.08%	Biotin	0.30 mg
Iodine	0.03%	Choline	50.00 mg
Boron	0.018%	Folic Acid	0.30 mg
Cobalt	0.0008%	Niacin	25.00 mg
Copper	0.0005%	Panthothenic Acid	0.20 mg
Flourine	0.015%	Thiamin	3.00 mg

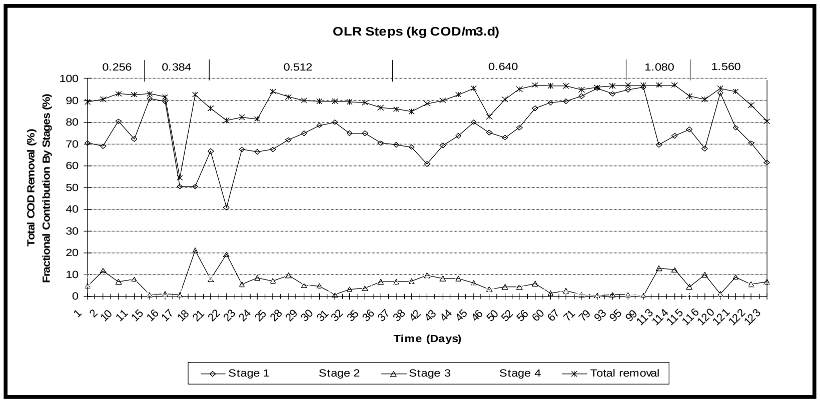

Fig. 1: Total COD reduction (%) of the anaerobic reactor and fractional contribution (%) to the total COD reduction by each stage at different OLR.

The pH reduction profile followed the order of Stage 1 > Stage 2 > Stage 3 > Stage 4 which reflected the actual OLR of each stage (OLR Stage 1 > Stage 2 > Stage 3 > Stage 4) on account of the sequential degradation of the influent COD load as it passed through the reactor system. In addition, from the pH data it can be assumed that the metabolic processes differed between Stages 1 to 4 of the reactor system and this would cause each stage to favour a unique population of microorganisms. Previous research has shown a correlation between high hydraulic dead spaces and increased channelling [18], and these factors may control the amount of biomass that is in direct contact with the substrate at any time. A short contact time between the substrate and biomass has been shown to favour acidogens which have faster growth kinetics and adapt better to reduced pH than the methanogens [19].

Biogas Composition: The effect of organic loading rate on biogas composition can be used as a direct indicator of the vitality of the anaerobic digester. Biogas production was monitored in all stages throughout the operation of the reactor, particularly for the assessment of methanogenic activity. Fig. 3 illustrates the methane composition produced in each stage of the reactor system during the treatment of paper mill wastewater at OLR 0.64–1.56 kg COD/m^3.d. The highest methane composition was produced in Stage 2 of the reactor (62%; OLR 1.560 kg COD/m^3.d). From the biogas composition data, it can be concluded that, even high COD removal efficiency was observed during this periods, the methane composition profile does not reflect the actual methane composition. This is probably due the problem of the gas measurement device. In actual fact, the methane composition should reflect the performance of the reactor system.

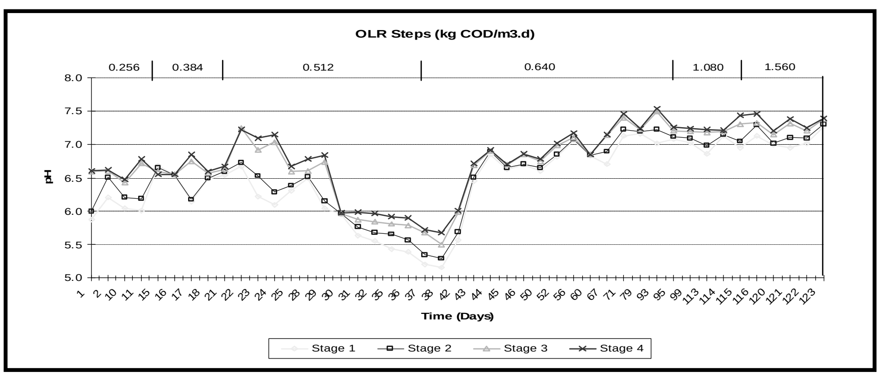

Fig. 2: pH profile in each stage of the reactor at different OLR.

Solid Washout: The sludge washout from the reactor system was measured frequently during the period of experiment (Fig. 4). The volatile suspended solids (VSS) washout from the reactor fluctuated from around 50 mg/L (when the OLR was below 0.512 kg COD/m^3.d) to 100 mg/L (at maximum OLRs) after which point washout values dropped sharply when the OLR was 1.08 kg COD/m^3.d. The low levels of VSS were washed out from the reactor confirming the three phase separator baffle prevented solids washout with typical levels of 50-100 mg/L for all OLRs.

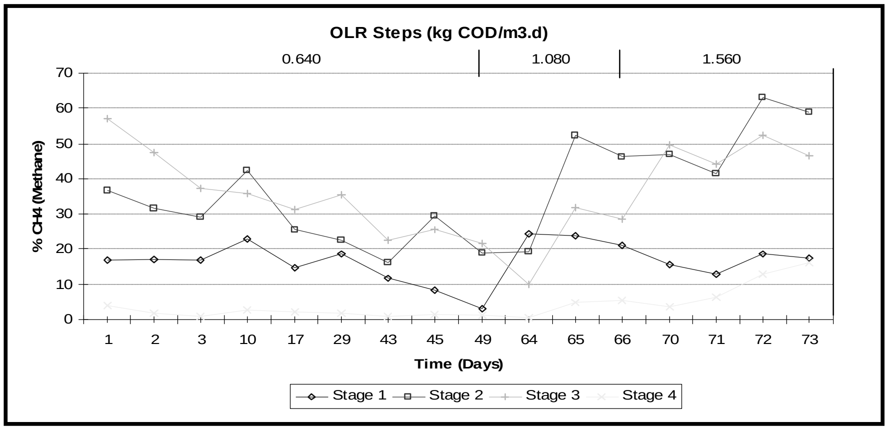

Fig. 3: Proportion of CH_4 (%) in the biogas in each stage of the reactor at different OLR.

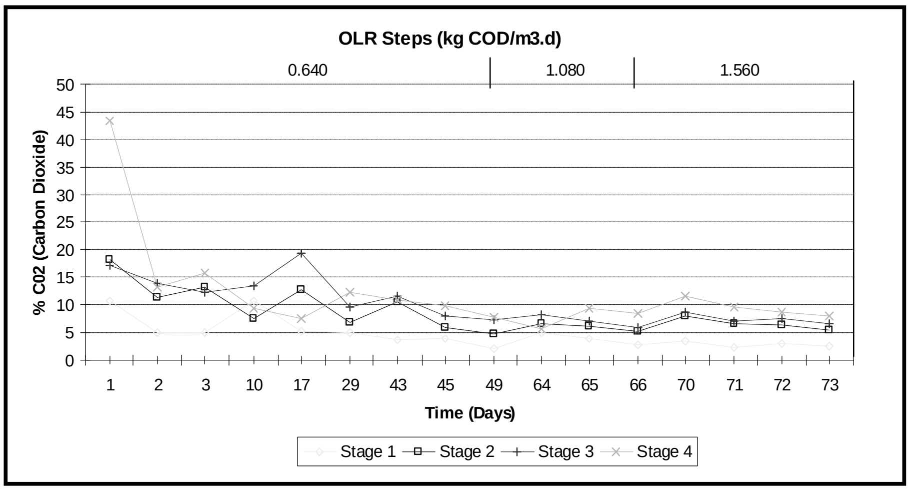

Fig. 4: Sludge washout from the reactor at different OLR.

CONCLUSION

Paper mill wastewater has been successfully treated using a novel anaerobic stage reactor and at a reactor OLR of 1.560 kg COD/m^3.d (HRT of 1.6 d). An average COD reduction of 95% was observed in the reactor system, confirming tolerance of methanogenic microorganisms to the recalcitrant paper mill wastewater. Stage reactors can provide high treatment efficiency for recalcitrant substrates because phase separation, which generates separate environments for acidogenesis and methanogenesis, also promotes favorable conditions for microbial populations which are involved in the degradation of recalcitrant compounds. Further study should be carried out at higher OLR and shorter HRT in order to investigate the potential application of the reactor.

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