Treatment Feasibility of NSSC Pulping Effluent using UASB Reactor

Arshad Ali, Hashim Nisar Hashmi, Inthikhab Ahmad Querashi, and Athar Saeed

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Abstract: The safe disposal of black liquor generating from Neutral Sulfide Semi-Chemical pulping section of the paper mills is one of the challenging issue in the developing countries. A treatment feasibility study was conducted on a laboratory scale UASB (Upflow Anaerobic Sludge Blanket) reactor running on continuous flow basis for about 30 weeks at neutral pH and at constant temperature of 33°C. It is observed that about 35% of black-liquor COD could be reduced at a hydraulic retention time of 38 hours and at an organic loading rate of 2.75 kg-COD/m^3-day. The average gas production and methane gas conversion at optimum conditions was observed to be 0.17 m^3/kg-COD$_{rem}$-day and 0.88 L-CH$_4$/g-COD$_{rem}$-day, respectively. The overall methane composition was noticed to be 61% of the biogas. This study suggests that the post-treatment of NSSC pulping effluent is required to meet the safe effluent disposal standards.

Key words: NSSC pulping, UASB, anaerobic digestion, lignin-COD, Pakistan

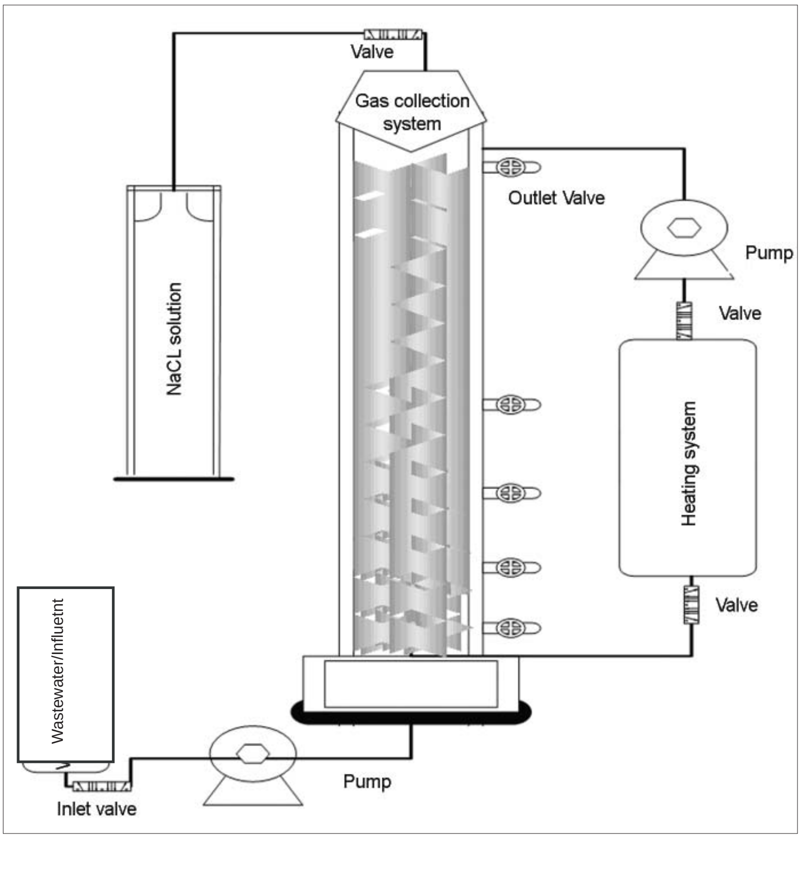
Nomenclature: COD=chemical oxygen demand, CH4=METHANE, HRT=hydraulic retention time, NSSC=neutral sulfide semi-chemical, OLR=organic loading rate, VSS=volatile suspended solids, UASB=upflow anaerobic sludge blanket.

Introduction

In Pakistan there are more than 60 pulp and paper mills with nearly annual production of 400,000 tonnes. The production is mainly based on local grass, wheat straw, waste paper, etc. The pulping process being employed in Pakistan is Neutral Sulfide Semi-Chemical (NSSC) pulping. Majority of the mills do not have wastewater treatment facility and discharge the effluent into the receiving streams without any treatment, thus posing a great threat to the eco-system (EPTI, Pak-EPA 1999).

The pulping effluent, called black-liquor, is the major source of environmental pollution. Black liquor when combined with the chlorinated compounds gives rise to the formation of absorbable organic halides (AOX) that are formed as a result of the reaction between the residual lignin in black liquor with chlorine and chlorine compounds. The AOX compounds are hydrophobic, recalcitrant and persistent. They are highly toxic, some of them are found to be carcinogenic and mutagenic (Savant 2005). Therefore, the treatment of black liquor is essential, since it is a serious environmental problem, especially for the developing countries like Pakistan where most of the industrial wastes are disposed without proper treatment.

Although, the physio-chemical methods like chemical recovery plants or the de-lignification process give promising results in terms of the black liquor treatment, because of their cost these process are not viable for developing countries. In developing countries more emphasis should be given to biological treatment processes (Bhatti 1995). Biological treatment processes are mainly of two types, aerobic processes or anaerobic processes. Since the aerobic treatment process is not very efficient in terms of treating the black liquor (Woodard 1964), more attention is being paid to the anaerobic process. The anaerobic process represents a cost-effective approach for the removal of various kinds of pollutants, and is widely acknowledged for the treatment of domestic and industrial effluents. This is based on knowledge gained during the operation of several anaerobic treatment units



worldwide, including the treatment of pulp and paper mills effluent. Very little knowledge is available, however, on the treatability performance of Upflow Anaerobic Sludge Blanket (UASB) reactor for Neutral Sulfide Semi-Chemical (NSSC) pulping effluent (Schellinkhout 1993, Fatima 1999). Therefore, the treatment feasibility of pulping effluent using UASB reactor needs further investigation. Hence, this study was designed to evaluate the treatability performance of the UASB reactor using actual wastes of the Neutral Sulfide Semi-Chemical (NSSC) pulping section of a pulp and paper mill. The main objective was to study the lignin-COD removal and bio-gas potential of NSSC pulping effluent at varying HRT and OLR.

Material and Methdology

Experimental UASB Reactor

Due to the advantages and high application potential of UASB reactor for the developing countries, it was decided to employ UASB reactor for this study. A UASB reactor made up of acryl resin material with a total effective volume of 7.84 liters was employed in this study. The internal diameter of the reactor was 11 centimeter and the thickness of the water jacket was 1.5 centimeter. The reactor had a water jacket to maintain a constant temperature of 32±2^{o}C. The reactor was also equipped with a gas solid separator (GSS) and a mixer, as shown in the figure (previous page).

Substrate and Nutrients

Actual pulping effluent and methanol were used as the sole carbon source in the feed (influent). Nitrogen and phosphorous were added in the form of $(NH_4)_2SO_4$ and KH_2PO_4 in accordance with the COD:N:P ratio of 650:7:1 (Henze 1983). Trace nutrients were added at a concentration of 1.0 milliliter/liter after making a stock solution of nutrients in the following concentration, as shown in the Table 1 (Bhatti 1995).

Trace Nutrient	Concentration (mg/l)
$FeCl_3.6H_2O$	4.9
$CoCl_2.6H_2O$	0.3
$ZnSO_4$	0.35
$CaCl_2.2H_2O$	0.35
$CuSO_4$	0.09

Table 1. Trace Nutrient Concentrations

Operating Conditions of the Reactor

- *Temperature* was controlled at about 32±2^{o}C, similar to that of the actual effluent for the pulping section of the mills.
- *pH* was maintained neutral in the reactor, by adding $NaHCO_3$ to the feed solution.
- *Loading rate* – the reactor was started-up step-wise by gradually increasing the organic loading rate from 0.51 kg-COD/m^{3}day to 6.7 kg-COD/m^{3}day in order to avoid organic loading shocks to the system.
- *Hydraulic retention time* was gradually decreased during operation

Monitoring and Analysis

pH, temperature, influent and effluent COD, gas production and methane composition were monitored regularly 2 to 3 times weekly. Gas was collected over tap water saturated with NaCl. All analyses were carried out according to the Standard Methods (Clescerl et al, 1998).

Results and Discussion

Treatability Study of the UASB Reactor

pH is the most important and principle operating parameter of anaerobic digestion. The optimum pH of 5.5 to 6.0 for the processes of anaerobic digestion in UASB reactor is reported bu Lettinga (1980), but since the methanolic bacteria are highly restricted to the neutral pH for their optimum growth (Bhatti 1995), therefore, in this study the pH of the reactor was kept around neutral by adding an external buffer in the form of $NaHCO_3$ addition to the feed solution. Thus, the average pH of the reactor throughout the study observed was about 7.04±0.31. The lowest pH value of 6.4 and highest pH value of 7.5 was observed during 9th week and 21st week, respectively. The figure 1.0 shows the time course of pH during operational period.

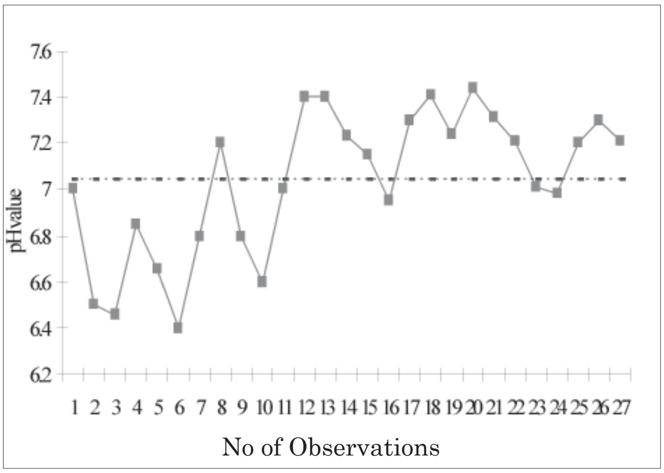


Figure 1.0: Time course of pH during the study period

The COD removal efficiency of the UASB reactor greatly depends upon the hydraulic retention time (HRT) and organic loading rate (OLR); i.e., the longer retention time seems to be more favorable than the shorter retention time, similarly lesser organic loading rate seems to be more encouraging than the higher organic loading rate in terms of treatability performance of the UASB reactor. Time courses of HRT versus COD removal and OLR versus COD removal are shown in the Figures 2.0 and 3.0, respectively.

It was observed that for every step there was an increase in COD removal efficiency of the reactor after establishing a steady state conditions under a given OLR. And in every step of increasing OLR, it was observed that there was an abrupt decrease in the COD removal efficiency that might be

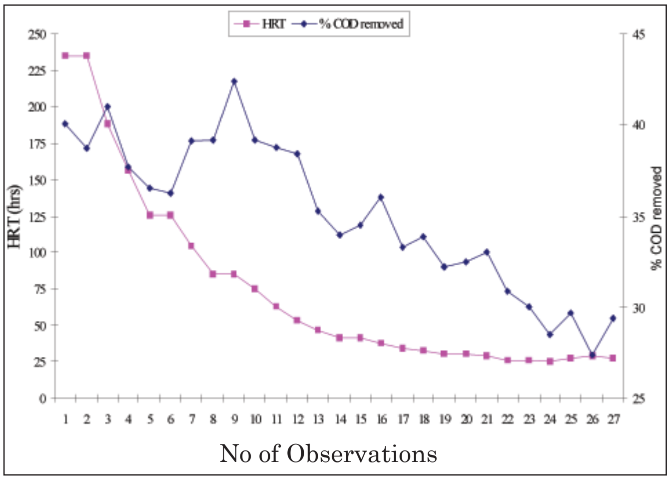


Figure 2.0 : Time course of Hydrulic Retention Time VS COD Removal efficieny

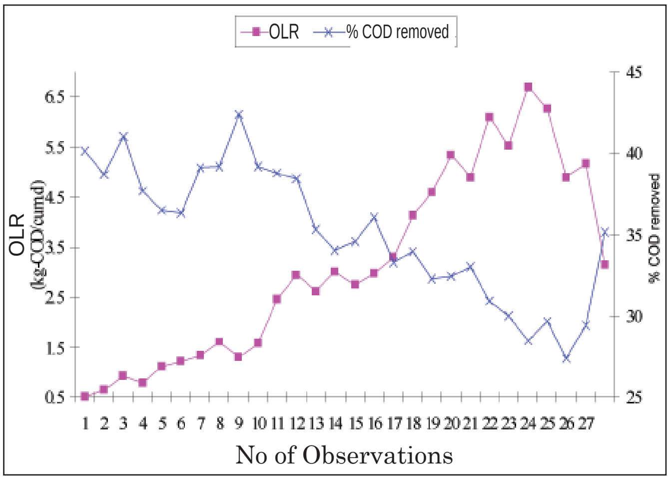
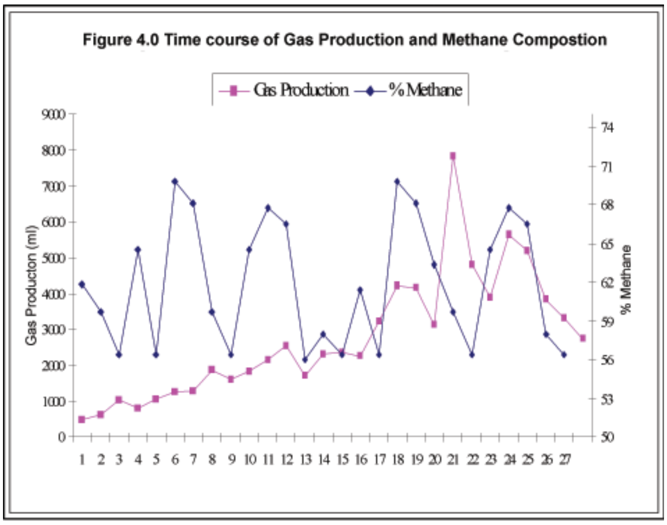


Figure 3.0 : Organic Loading Rate versus COD removal efficiency

due to the accumulation of organic acids within the system and impacts of heavy organic shocks. The maximum COD removal efficiency of 43% was observed during the 12th week where the OLR was about 1.3 kg-COD/m^3-day and the HRT was about 86 hours. Similarly, the lowest value of COD removal of 25% was observed during 27th week where the OLR and HRT was about 4.89 kg-COD/m^3-day and 29 hours, respectively.

A COD reduction of 65-70% COD was observed by Latola (1985) working on paper mills effluent in a multistage reactor. In 1993, Dangong and Qiting reported 50-60% COD reduction of alkaline black liquor in a lab-scale UASB reactor and the treatment of thermo-mechanical pulping in a lab-scale UASB reactor at 55°C notices that 55% COD reduction could be achieved (Rintala 1991). Similarly, 68% of COD reduction for soda pulping effluent was observed by Littinga in 1980. But in this study it is observed that for the optimum design of UASB reactor treating actual NSSC pulping effluent an OLR of 4.5 kg-COD/m^3-day and HRT of 20 hours gives only 32% of COD removal efficiency. This indicate that the treatment of lignin-COD



No of Observations

of NSSC pulping could not be degraded easily in a UASB reactor alone, and hence a post-treatment is required for the safe disposal of such type of industrial effluent. This low treatability performance of UASB reactor for the black liquor COD might be due to the absorption of lignin-COD in the wastewater on the sludge biomass, and due to the recalcitrant material present in it.

Gas Production

Small bubbles were observed from the start of the study. The gas was collected in a smaller system saturated with NaCl solution. The average gas collected was observed to be 2757 mL/day, [0.17 L-CH_4/g-COD_{rem}.day] as shown in the figure 4.0. It was noticed that the rate of biogas generation was very low at the beginning; i.e., 500 mL/day during 5th week, which later on showed an improving trend, and during the 22nd week a maximum biogas production of 7843 mL/day was observed.

The lowest gas production during initial weeks indicates that the population of methanogenic bacteria had not grown appreciably and that facultative microbes may be competing for the substrate with the methane producing organisms.

Methane content of 75-80% and 75% was observed by Bhatti working on methanolic wastes and dairy wastes (Bhatti, 1996). The rest of the gas content is mainly carbon dioxide, because these two gases, methane and carbon dioxide, are produced during anaerobic digestion. A portion of hydrogen gas is also produced if the system is not working properly due to the presence of hydrogen-producing acetogens, which will provide unfavorable conditions for the conversion of volatile fatty acids to acetate other than to methane. In this study the average percentage of methane was observed as about 62% of the biogas. The lowest gas composition of methane can be attributed to the recalcitrant properties of the substrate which is mainly composed of lignin. An average gas conversion rate calculated is was 0.88 L-CH_4/g-COD_{rem}-day.

Conclusions

For the optimum design of UASB reactor treating actual NSSC pulping effluent to obtained more than 30% COD removal, the required OLR and HRT is 4.5 kg-COD/m^3-day and 20 hours, respectively. To improve the treatability performance of UASB reactor further investigation are needed to know the exact behavior of lignin-COD during the course of degradation and is recalcitrant behavior. As the lignin-COD could not be degraded easily in a UASB reactor alone, therefore post-treatment is essential for the safe disposal of such wastes.

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