# Effects of Methanol on the Treatability of Black Liquor using UASB Reactor

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**Abstract:** This study was conducted on a laboratory scale UASB (upflow anaerobic sludge blanket) reactor, treating an actual pulping effluent at an organic loading rate and hydraulic retention time of 2.1 kg-COD/m3d and 44 hours, respectively. To investigate the impacts of methanol, it was subjected to the reactor with the feeding solution (substrate) in concentration ranging from 100 mgTOC/l to 700mgTOC/l. It was observed that the overall TOC and COD removal efficiency of the reactor was improved gradually from 36% and 34% to 57% and 55%, respectively, by increasing the concentration of methanol up to 600 mgTOC/l, but very little effects of methanol on the removal efficiency of lignin were observed. The lignin removal efficiency of the reactor slightly changed from 25% to 31%. The gas conversion rate was found to be improved slightly from 0.31[L-CH4/g-CODrem.day] to 0.34 [L-CH4/g-CODrem.day], with an average methane composition of 61%. Hence, addition of methanol to the reactor can improve the black liquor degradation up to certain extent.

**Key words:** Black liquor, methanol, UASB, lignin, TOC

## Introduction

The pulping effluent, 'black-liquor', is a major source of environmental pollution. When combined with the chlorinated compounds black liquor 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 (APHA, AWWA and WEF 1998; Savant, Abdul-Rahman and Ranadi 2005). Therefore, the treatment of black liquor is essential, since it is a serious environmental problem, especially for Pakistan where a majority of the paper manufacturing industries discharges effluent without any treatment (Savant, Abdul-Rahman and Ranadi 2005; Rintala 1992; Xiao, Boltan and Pan 2007). Although the physio-chemical methods, like chemical recovery plants or the de-lignification process, give promising results in terms of the black liquor treatment, these processes are not viable for the developing countries in terms of their cost. In developing countries more emphasis should be paid to biological treatment processes (Bhatti 1995b).

The 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, Sproul and Atkins 1964), therefore, 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, after the knowledge gained during the operation of several anaerobic treatment units all over the world (Schellinkhout 1993; Fatima, Gohary and Fayza 1999).

**Nomenclature**

| | |
|---|---|
| AOX | Absorbable Organic Halides |
| COD | Chemical Oxygen Demand |
| $CH_4$ | Methane |
| HRT | Hydraulic Retention Time |
| NSSC | Neutral Sulfide Semi-Chemical |
| TOC | Total Organic Carbon |
| OLR | Organic Loading Rate |
| VSS | Volatile Suspended Solids |
| UASB | Upflow Anaerobic Sludge Blanket |

One of the most attractive anaerobic options available for high strength sewage is the upflow anaerobic sludge blanket (UASB) reactor, which acts as a compact system for removal and digestion of sewage organic components. Full scale UASB reactors are in operation now in India, Colombia and Brazil. They have been applied world wide for a variety of wastes, including pulp and paper mills effluent (Driessen, Tielbaard and Vereijken 1994; Vieira 1988; Chernicharo 2001; Wiegant 2001). The pulping effluent COD removal efficiency of single-stage UASB reactors and multi-stage anaerobic reactors is about 45-65% (Lettinga *et al* 1980; Rintala, Sanz Martin and Lettinga 1991; Dangcong and Qiting 1993) and 65-75%, respectively (Latola 1985). The multi-stage anaerobic processes are giving comparatively better results in terms of the COD removal efficiency, but they are not recommended for the developing countries because of their high capital and maintenance cost. They require a high level of skill operation; thus, the best option is to use a single stage anaerobic process (Bhatti 1995b).

Since black liquor alone cannot be easily degraded due to recalcitrant material present in it (Sharma 1992), this study was designed to observe treatability of black liquor, particularly lignin, under anaerobic conditions in the presence of an easily biodegradable substance like methanol (Bhatti 1995a). The main objective of the study was to investigate the removal efficiency of UASB reactor in terms of its COD and lignin removal by introducing methanol with the feeding solution (pulping effluent) to the reactor.

## Material and Methodology

*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°C. The reactor was also equipped with a gas solid separator (GSS) and a mixer.

*Substrate and Nutrients*

Actual pulping effluent and methanol was 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. 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 1995a).

| 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. Concentration of Various Nutrients Added to the Feed Solution.

## Operating Conditions of the Reactor

i. Temperature was controlled at about 32±2oC, similar to that of the actual effluent for the pulping section of the mills.
ii. pH of about 7.13±0.21 was maintained in the reactor, by adding NaHCO3 to the feed solution.
iii. Loading Rate; the reactor working under a constant loading rate of 2.1 kg-COD/m3day (1.33 kg-TOC/m3day) was subjected to methanol, ranging in concentration from 100 mg-TOC/l to 700 mg-TOC/l in step-wise loading rates, in order to avoid organic (methanolic) loading shocks to the system.
iv. Hydraulic Retention Time kept constant at 44±2.5 hours.
v. Ratio (v/v): M (Methanol): BL (Black Liquor) :: 1:4

*Monitoring and Analysis*

pH, temperature, influent and effluent COD and TOC, influent and effluent lignin concentration, gas production and methane composition were monitored regularly; 2-3 times weekly. Gas was collected over tap water saturated with NaCl. All analyses were carried out according to the Standard Methods (APHA, AWWA and WEF 1998)

## Results and Discussion

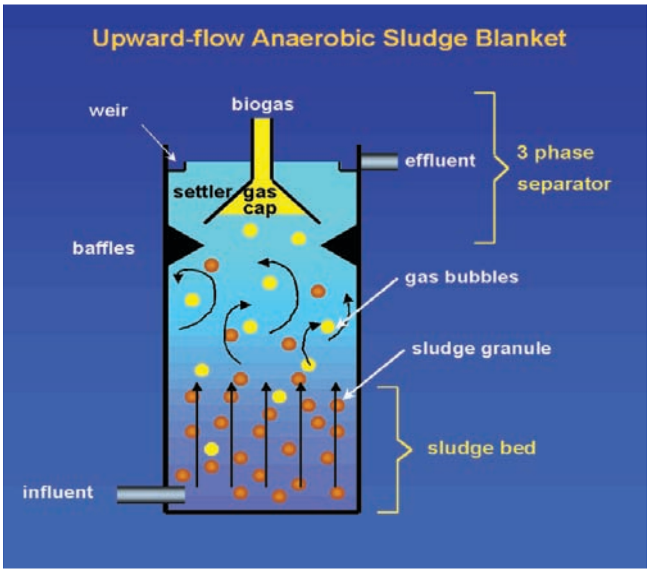
*Treatability study of the UASB system*

pH is the most important and principle operating parameter of anaerobic digestion. An optimum pH of "5.5 to 6.0" for the processes of anaerobic digestion in UASB reactor, working on methanol, was previously reported by Lettinga *et al* (1980), but since, the methanolic bacteria are highly restricted to the neutral pH for their optimum growth (Bhatti 1995a); therefore, in this study the pH of the reactor was kept around neutral by adding an external buffer in the form of NaHCO3 addition to the feed solution. Thus, the average pH of the reactor throughout the study observed was about 7.13±0.21.

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, but since, at lower levels of OLR, the impacts of HRT are not prominent (Bhatti 1995a), therefore, the OLR and HRT of the reactor were constant at 2.6±0.59 kg-COD/m3d and 44.48 hours, respectively, to clearly investigate the effects of methanol on the treatment efficiency of the reactor.

The methanol was added to the reactor, gradually, in step-wise, from 100 mgTOC/l to 700 mgTOC/l. It was observed during the study that the addition of methanol to the reactor increased its efficiency up to certain limits. As shown in the Figures 2 and 3, the removal efficiency of TOC and COD goes on increasing gradually from 36% and 34%, respectively during the first week when no methanol was added, to 57% and 55%, respectively, at 45th day of operation, when the concentration of methanol was increased up to 600 mgTOC/l. But, no visible change was observed on the

Figure 1. The upward-flow anaerobic sludge bed (UASB) reactor concept.



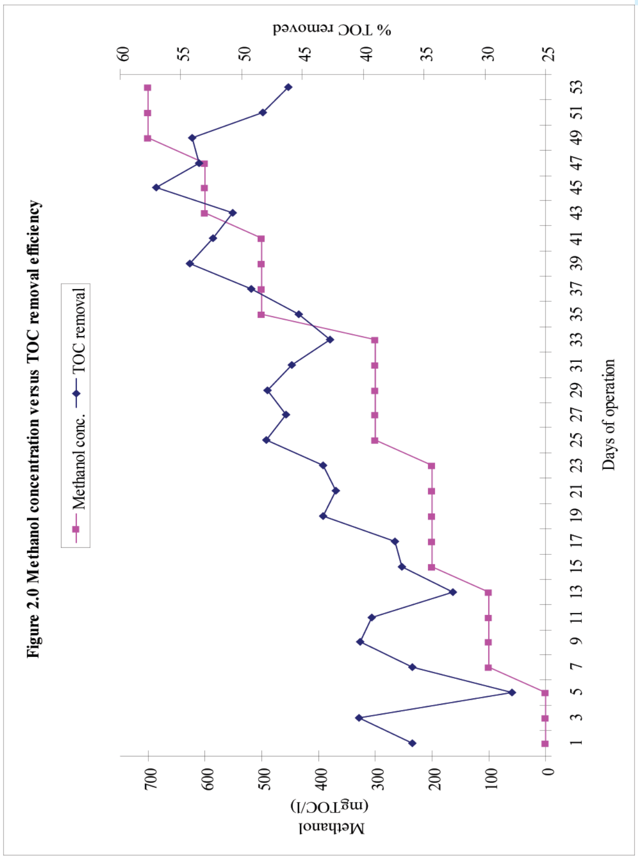



Figure 2.0 Methanol concentration versus TOC removal efficiency

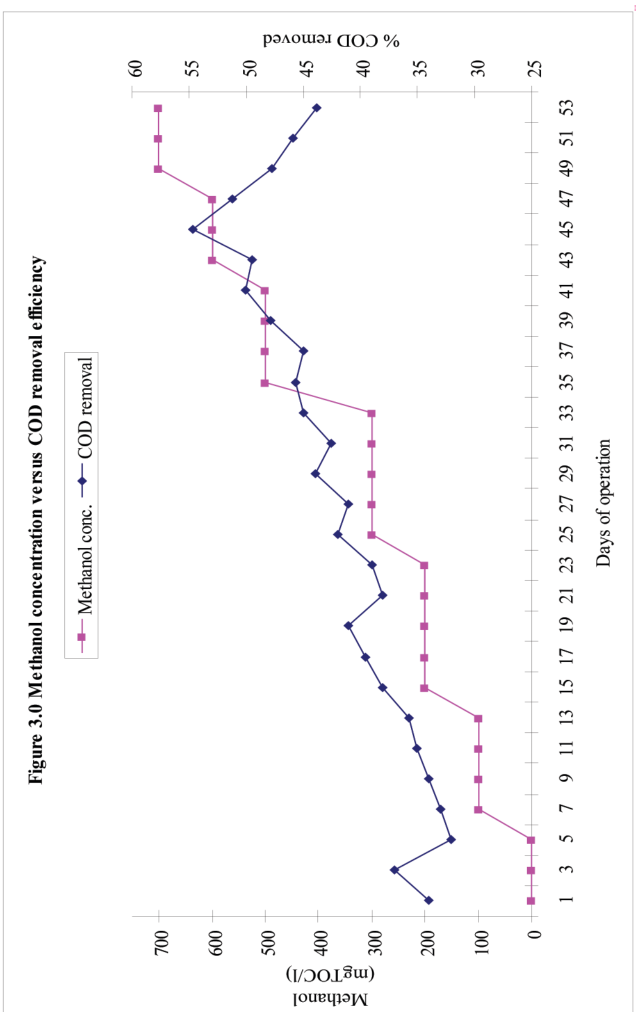



Figure 3.0 Methanol concentration versus COD removal efficiency

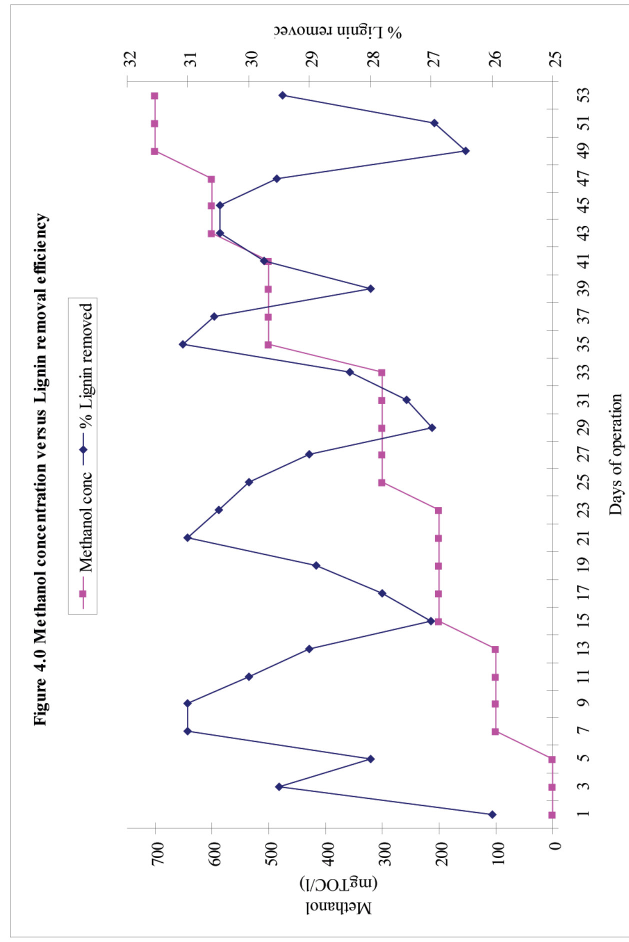



Figure 4.0 Methanol concentration versus Lignin removal efficiency

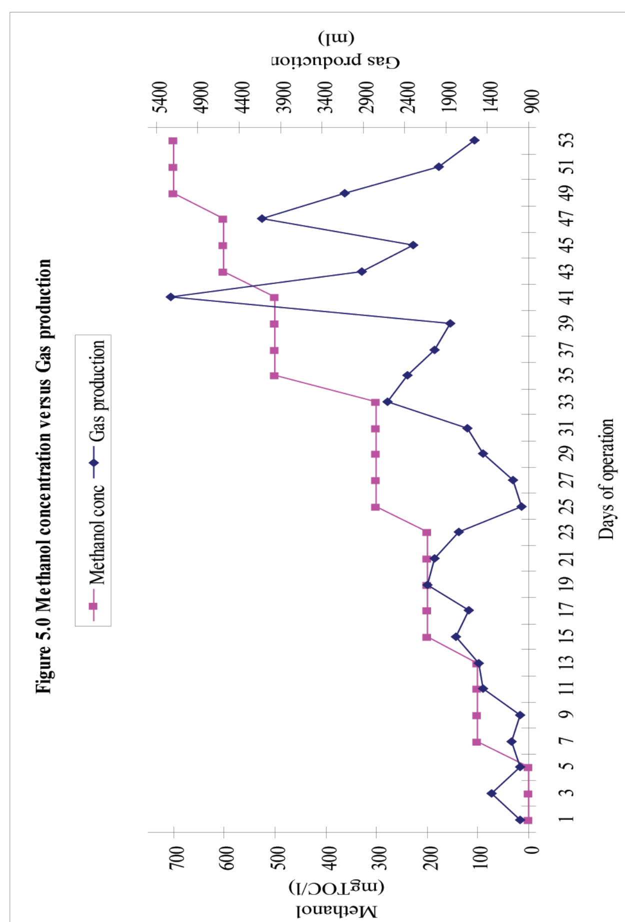
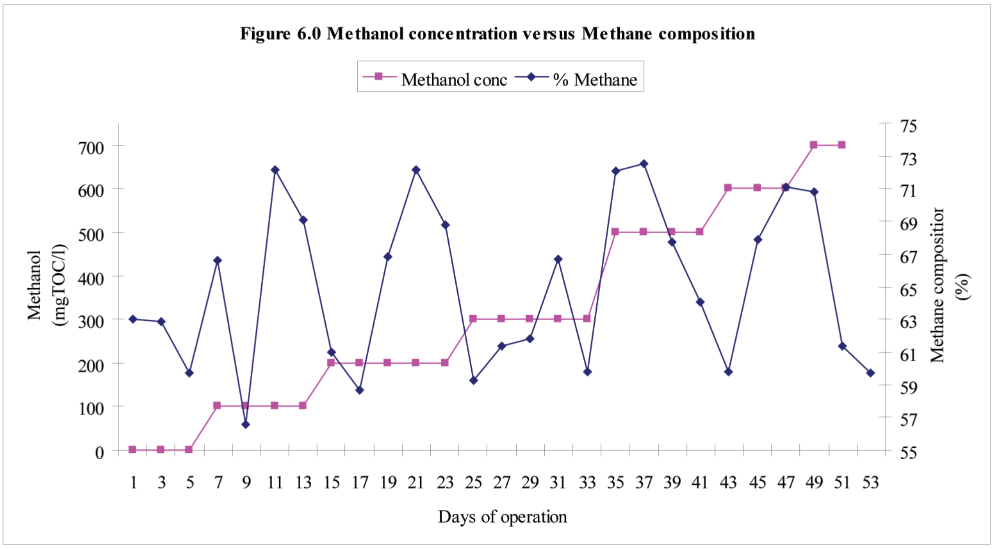



Figure 5.0 Methanol concentration versus Gas production




lignin removal efficiency of the reactor due to methanol, as shown in the Figure 4. The lignin removal efficiency slightly changes from 25% to 31% during the course of study.

In every step of increasing the concentration of methanol, there was initially a slight decrease noticed in the treatability that might be due to the accumulation of organic acid within the reactor. But later on, the system would set up and the treatability would increase under the particular methanolic concentration. And it was noticed that for every step there was an increase in the TOC and COD removal efficiency of the reactor after establishing steady state conditions under a given concentration of methanol.

The minimum TOC and COD removal efficiency of the reactor was observed on the 5th day of operation as 28% and 32%, respectively. It might be due to the upset of the degradation process during acclimatization stage. By introducing more methanol beyond 600 mgTOC/l, there was an abrupt decrease in the TOC and COD removal efficiency of the reactor observed, particularly on 53rd day of operation, as 46% and 44%, respectively, when methanol at a concentration of 700 mgTOC/l was introduced. Indicating that the system could not sustain further high shocks of methanol. This might be due to the fact that at the initial startup of the reactor, during acclimatization process, methanol was not used as source of carbon with the substrate (black liquor). Otherwise, a much higher concentration of methanol (up to 80% of TOC) removal has been reported by Bhatti (1995a,b), working on purely methanolic wastes using UASB reactor.

Results from the identical kind of studies, as shown in the Table 2, indicate that the relatively low removal efficiency of UASB reactor for the black liquor COD (or TOC) 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 (Sharma 1992).

### *Gas Production*

The gas was collected in a smaller system saturated with NaCl solution. The average gas collected was observed to be 3005 mL/day, [0.34 L-$CH_4$/g-$COD_{rem}$.day]. It was noticed that by introducing methanol to the system the total gas production and methane composition was slightly increased from 0.31[L-$CH_4$/g-$COD_{rem}$.day] to 0.34 [L-$CH_4$/g-$COD_{rem}$.day], with an average methane composition of 61%. The time course of gas production and methane composition is shown in the Fig. 5-6, respectively. The low gas production observed was 1593ml on the first day of operation with about 61% of methane composition. The lowest gas production and gas composition of methane can be attributed to the recalcitrant properties of the substrate which is mainly composed of lignin at the start of the experiment. By increasing methanol concentration to the feeding solution, the gas production and methane composition slightly increased. The maximum gas production was observed on the 41st day of operation, as 8149 ml corresponding to 500 mgTOC/l of methanol, at which the methane composition observed was 71.2%, indicating an improved acclimatization of the sludge within the reactor. But an abrupt decrease was noticed both in the gas production and methane composition during the last weeks, when the methanol

| Author [Ref] | Year | Wastewater Type | COD reduction (%) | Methane production ($m^3$/kgCOD removed) |
|---|---|---|---|---|
| Lettinga | 1984 | Soda pulping liquor | 45-50 | |
| Latola | 1985 | Pulp and Paper mill effluent | 60-75 | 0.25-0.38 |
| Rintala | 1991 | Sulfide rich pulp and paper mill effluent | 55 | |
| Bhatti | 1995 | Methanol | 80%* | 0.30 |
| Present Study | 2007 | 23% Methanol + 77% NSSC pulping effluent from paper mill | 55 | 0.34 |
| * TOC = Total Organic Carbon | | | | |

Table 2. Performance Evaluation of UASB for Same Type of Wastes.

concentration was increased to 600-700 mgTOC/l, which is mainly due to the accumulation of nonviable recalcitrant material of black liquor in the reactor and high organic shocks of methanol to the process that adversely effected the overall methanogenic activity of the sludge.

## Conclusion

The addition of an easily biodegradable substance, like methanol, can improve the overall COD and TOC removal of the system, but the lignin COD removal efficiency remains unchanged. The treatability of the black liquor, not only alone but even with the addition of an easily biodegradable substance like methanol, in an upflow sludge blanket reactor seems to be technically not feasible. A long-term comprehensive study is required to know about the exact behavior of lignin during the course of degradation, particularly under an anaerobic process.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