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STUDY ON TREATMENT OF ALKALINE BLACK LIQUOR USING SULPHATE REDUCING BACTERIA

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Abstract. Alkaline pulping liquors are the problematic for environment due to their toxicity and poor biodegradability. During last decade, anaerobic treatment technology has been successfully applied to various types of pulp and paper industry effluents. In the present study, the treatment of highly toxic pulping liquors in lab-scale has been done using sulfate reducing bacteria (SRB) isolated from sediment samples of pulp and paper mills in Vietnam. This treatment could reduce 70 - 75% of COD after three weeks. The COD removal could achieve 82 - 88% by subsequent aerobic treatment in 48 hours. COD of treated water was 80 - 90 mg/l.

1. INTRODUCTION

Black liquors in modern intergrated pulp and paper mills are burnt for chemical recovery and steam generation. In Vietnam, small-scale pulp and paper mills producing more than two third of total pulp capacity (more than one hundred thousand tons per year) have no recovery line and treatment of pulping liquor before discharging to the receiving water.

Alkaline pulping liquors are the problematic for environment due to their toxicity and poor degradability. The research has led to the proposal of a detoxification stragegy denominated upfront dilution, based on the sequenced anaerobic-aerobic treatment of the pulping liquors [1,2,3,4,5]. In this study, the treatment of highly toxic pulping liquors in lab-scale has been done using sulphate reducing bacteria (SRB) isolated from sediments of pulp and paper mills in Vietnam.

2. MATERIALS AND METHODS

2.1. Bacteria

Sulphate reducing bacteria were isolated from sediments of pulp and paper mills on the Posgate B medium in anaerobic tubes. This medium contained (in grams per liter): KH_2PO_4, 0.5; $CaSO_4$, 1.0; $MgSO_4.7H_2O$, 2.0; $FeSO_4.7H_2O$, 0.5; NH_4Cl, 1.0; Sodium lactate 3.5; ascobic acid 0.1; yeast extract 1.0; agar 15. After sterilization at 121 $^\circ$ C in 30 minutes, the medium was supplemented with 1 mL of trace element solution and 1 mL of vitamins solution per liter. PH was adjusted to 7.2 by using 5% solution of $NaHCO_3$ and Na_2S (5% solution) was added for oxygen removal.

Aerobic bacteria were isolated from sediments of pulp and paper mills on the Meat - Pepton - Agar (MPA) medium. This medium contained (in grams per liter): meat extract 3.0; pepton 10; NaCl, 5.0; agar 15 - 20. The medium was sterilized at 121 $^\circ$C in 30 minutes.

2.2. Preparation of effluents

Pulping black liquors from three pulp and paper companies (Viet Tri, Hoang Van Thu and Van Diem) were diluted with tap water. Nutrients ware added in the ratio BOD_5 : N : P = 100 : 2 : 0.1

2.3. Analytical methods

Waste sample were analyzed for COD, SS and pH according to American Public Health Association standard methods.

3. RESULTS

Alkaline pulping liquors were shown to be highly eliminated during aerobic waste water treatment and were problematic for anaerobic treatment due to their toxicity to methanogens and their relatively large fraction of inert lignin.

The research on biodegradation of the lignocellulosic solid waste was investigated under both methane producing and sulphate reducing conditions. It was shown that the total carbon mineralization under sulphate reducing condition was 2 - 4 times higher than in methane producing condition. The degradation of lignin, which is generally considered recalcitrant under anaerobic condition, was also detected under sulphate reducing condition [6].

a. Study on distribution of microorganisms in sediments from pulp and paper mills

For total bacterial counts, 10 g of each sediment was mixed in 90 mL of sterilized water contained 0.9% NaCl. The solution was shaked for 1 hours and then was diluted to the folder of 1...10.

Added 1 mL of each diluted solutions to anaerobic tubes. Filled the tubes with the prepared Posgate B medium and sealed with a rubber septum. After incubation at 37 $^\circ$C in the period of 4 - 7 days the formed colonies of SRB were counted. These isolated colonies were removed using Pasteur pipet and transformed to new tube contained Posgate B medium.

Transfered 1 mL of each above diluted solutions onto petri dishes contained MPA medium. These dishes were incubated at 37 $^\circ$C in 48 hours. The formed colonies were counted. The number of counted SRB and aerobic bacteria was given in Table 1.

CFU = Colony Forming Unit

Numbers of SRB in sludges polluted black liquors were higher than of sample in nature and aerobic bacteria were especially high. The chosen bacteria (VT, HVT_2 and VD_2) were natively tested and mixed for the growth on the Posgate B medium contained

Table 1. *Total bacterial counts in sludge polluted black liquors*

Pulp and paper mill	SRB strain	Total counts (CFU/g)	
		SRB	aerobic bacteria
Viet Tri	**VT**	1.5 x 10^4	2.6 x 10^{10}
Hoang Van Thu	HVT_1	3 x 10^5	1.8 x 10^9
	HVT_2	2.5 × 10^6	
Van Diem	VD_1	2.3× 10^6	1.4 × 10^{10}
	VD_2	1.5 × 10^7	

black liquors insteed of sodium lactate and with deducted $FeSO_4$. The growth of these bacteria was examined on the optical density at the wave length of 600 nm (OD_{600nm}).

Table 2. *The growth of isolated SRB in Posgate B medium containing black liquors*

Sample	SRB	The growth of SRB (OD_{600nm})		
		1 week	2 weeks	3 weeks
Viet Tri	VT	0.159	0.204	0.132
	VT+HVT_2+VD_2	0.122	0.162	0.138
Hoang Van Thu	HVT_2	0.168	0.212	0.162
	VT+HVT_2+VD_2	0.145	0.217	0.147
Van Diem	VD_2	0.167	0.228	0.167
	VT+HVT_2+VD_2	0.122	0.162	0.111

It was shown that the SRB were able to develope on the medium contained black liquor as carbon sourse by the following reaction:

Organic matter + $SO_4^{2-} \xrightarrow{SRB}$ CO_2 + Sulphide

The produced sulphide by the oxidation of the lignin will be distributed in the aqueous phase in three species, i.e. H_2S, HS^- and S^{2-}. The hydrogen sulphide species can be controlled by an increased pH. At higher pH nearly all the sulphide will be as HS- in the aqueous phase [6]. During treatment pH of media was increased from 7.2 to 8.8 - 9 after three weeks (Table 3).

Table 3. *The change of pH during alkaline black liquor treatment*

Sample	SRB strain	pH		
		1 week	2 weeks	3 weeks
Viet Tri	VT	7.59	8.30	8.42
	VT+HVT_2+VD_2	8.74	8.84	8.93
Hoang Van Thu	HVT_2	7.42	8.82	8.78
	VT+HVT_2+VD_2	8.59	8.82	8.90
Van Diem	VD_2	7.42	8.86	8.86
	VT+HVT_2+VD_2	7.58	8.83	8.70

b. Study on biodrgadability of alkaline black liquors

Pulping black liquors from three pulp and paper mills were analyzed for COD, BOD_5, SS and pH. The results were shown in Tab.4

Table 4. *Wastewater characteristics of some pulp and paper mills in Vietnam*

Paper mill	***COD, mg O_2/L***	***BOD_5, mg O_2/L***	***SS, mg/L***	***pH***
Viet Tri	113800	59900	42000	12.6
Hoang Van Thu	152600	72600	36000	10.6
Van Diem	109200	52900	40000	11.6

These paper mills used alkaline pulping method have neither recovery line nor wastewater treatment due to very small capacity and economic problem. Their black liquor effluents directly discharge to the rivers and cause heavy pollution to the aquatic lives and people living at the delta of the rivers.

The chosen strains were used for treatment of pulping black liquor from the native paper mills in the anaerobic - aerobic sequence. The black liquors were diluted to the initial COD of about 600 mg O_2/L and added with 1% (v/v) of culture medium. Anaerobic treatment is performed in plastic bottles at room temperature (about 30 ° C) by the native strains. The samples were analyzed for COD and the result is given in Fig. 1.

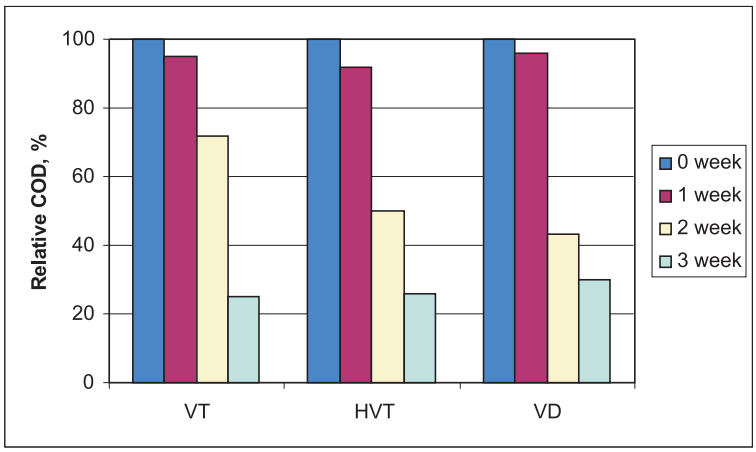

Fig. 1. Removal CODs of pulping black liquors during treatment by SRB

An attempt was made using mixed three strains for the treatment of the pulping black liquor. The COD was analyzed.

Using mixed sulphate reducing trains did not show better efficiencies compared to using separate strains. The estimated removal of COD is 70 - 75%. After detoxification by anaerobic treatment, the wastewater samples were added with aerobic bacterial culture (1% v/v) and shaken for two days. The treatment efficiencies during anaerobic – aerobic treatment are shown in Fig. 2.

Table 5. *Removal of CODs of pulping black liquors by native and mixed strains*

Sample	SRB strain	Removal of COD (%)		
		1 week	2 weeks	3 weeks
Viet Tri	VT	4.8	27.7	75.6
	VT+HVT_2+VD_2	5.7	36.8	56.0
Hoang Van Thu	HVT_2	8.3	45.9	74.4
	VT+HVT_2+VD_2	5.6	47.6	71.8
Van Diem	VD_2	4.1	57.5	70.1
	VT+HVT_2+VD_2	4.0	42.0	70.3

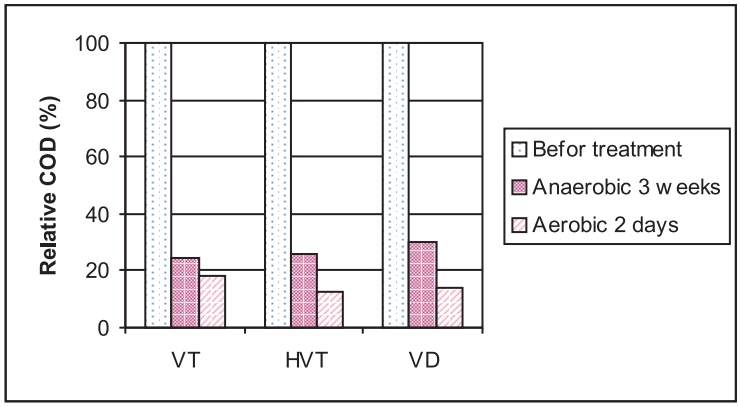

Fig. 2. The anaerobic (SRB) – aerobic treatment efficiencies of pulping effluents

Anaerobic – aerobic treatment of pulping effluents by strains isolated from the sludge of pulp and paper mills improved COD removal to 82 - 88%. The discharged effluents have COD in the range of 80 - 90 mg/L, which is accepted by the column B of TCVN 5945 -1995.

An attempt was made in treating more toxic black liquor. The black liquor was diluted to COD of about 1000 mg O_2/L. The result of anaerobic - aerobic treatment was given in the table 6.

Table 6. *Removal of CODs of pulping black liquors by VT and mixed strains, %*

Strain	***Anaerobic 3 weeks***	***Aerobic 2 days***
VT	81.9	90.5
VT+HVT_2+VD_2	63.8	87.8
Blank	1.0	1.5

The treatment efficiency was higher in case of more concentrated black liquor. The adequate pulping black liquor concentration should be found under specific conditions.

4. CONCLUSION

Pulping black liquors are toxic and poor biodegradable. These effluents can be treated in anaerobic (SRB) – aerobic sequence. The discharged water is acceptable. Using SRB can decrease the "green house effect" by reducing formation of methane and carbon dioxide. Besides, SRB can precipitate the heavy metals in the form of sulfide salts. This study should be enlarging to pilot scale before it can feasible for both technique and economy.

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