Journal of Environmental Sciences Vol. 12, No. 1, pp. 81—85, 2000 ISSN 1001—0742 CN11—2725/X

Article ID: 1001-0742(2000)01-0081-05

Purification of AS-CMP effluent by combined photosynthetic bacteria and coagulation treatment

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Abstract: The effluent from the pulping of E. *urophylla* by alkali sodium sulfite chemi-mechanical process (AS – CMP) was characterized for its biodegradability by photosynthetic bacteria (PSB). Chemical coagulation post-treatment of biotreated wastewater was also studied. One-month continuous treatment in the laboratory indicated that the COD_{Cr}, BOD_5 and SS removals in biotreatment stages reached 56%, 83% and 89% respectively, and the CH_2Cl_2 extractives decreased from 10.7 mg/L to 7.7 mg/L. In chemical coagulation post-treatment stage, the effects of process conditions, such as coagulant dosage, pH value and the coordinated coagulation-flocculation treatment of three kinds of coagulants on coagulation effectiveness were discussed. The optimum operating conditions were given.

Key words: wastewater treatment; AS-CMP; E. *urophylla*; photosynthetic bacteria(PSB); flocculation; coagulation

CLC number: X703 **Document code**: A

Introduction

The pulp and paper industry is a major contributor to water pollution in China. In 1995, the wastewater discharged by pulp and paper industry accounted for 11% of the total industry wastewater. With the rapid development of China's pulp and paper industry, the environmental problems and wood resources shortage are becoming more and more serious. Fully utilizing the fast-growing wood, developing high yield pulping process and reducing the environment pollution are the main goals to developing China's paper industry. In the past decade, Eucalyptus has been cultivated widespreadly in South China(Wu, 1995). A research project of developing Eucalyptus chemi-mechanical pulping process is now being carried out in our college. The pollution loads of wastewater from chemi-mechanical pulping processes, such as CTMP, TMP, APMP and AS-CMP etc. are not so high as chemical pulping process, and the contents of organic compounds and chemicals of the effluent are too low to satisfy chemical recovery system, but the effluent must be treated to remove the pollutants before discharge.

The effluent from chemi-mechanical pulping processes can be treated by either aerobic or anaerobic method, or by a combination of the two. A number of studies(Wilson, 1988; Liu, 1993; Ruan, 1993) have been reported that both aerobic and anaerobic method have certain of disadvantages, for example, aerobic process requires more energy, nutrients and produces large of sludge, and as for anaerobic process, the high sulphocompounds contents of the effluent may have strong inhibition to anaerobic bacteria, the detoxification is not so sufficient as aerobic process and needs strict operation conditions.

Since 1967, many researches (Dutton, 1967; Taylor, 1983; Liu, 1991) revealed that photosynthetic bacteria (PSB) could obviously decrease the organic pollutants of industrial wastewater. The wastewater treatment process of PSB has many advantages over the traditional aerobic and anaerobic treatment.

In this study, PSB was used for E. *urophylla* AS-CMP effluent at a laboratory scale. The performance of this process was evaluated, and the chemical coagulation post-treatment of biotreated effluent was also studied.

1 Experimental

1.1 Pulping and AS-CMP effluent

The E. *urophylla* chips, which were from a seven-years-old tree, were pretreated in a 15L electrically heated digester with 15% sodium sulfite and 3% sodium hydroxide at 150—155℃ for 60 minutes. The spent liquor from the chemical pretreatment was reused and the chips were refined in a laboratory disc refiner at medium consistency. The all washed wastewater was collected for experiment. The effluent characteristics are listed in Table 1.

Table 1 The effluent characteristics

pH value	7.4—8.2
COD_{Cr}, mg/L	3300—3890
BOD_5, mg/L	1100—1300
$BOD_5:COD_{Cr}$	0.33—0.34
Colour, C.U.	2700—2850
SS, mg/L	346—673
Na_2SO_3, mg/L	372.7—485.0
Na_2SO_4, mg/L	0.72—1.07
VFA(based on acetic acid), mg/L	740—834

1.2 PSB treatment

The PSB treatment was conducted in two 17 liters up-flow reactors, which were filled with FH-4 type complex packing (diameter: 200 mm, bunch distance: 100 mm, porosity: 86%—95%). The entire system was operated at 30℃, the air flow supply was in a ratio of 1:8—1:10 for PSB treatment. Nitrations were added to meet a ratio of $BOD_5:N:P = 100:5:1$. Before pumping to PSB reactors, the wastewater was passed through an acidogenic pretreatment stage (Fig.1). The seeding sludge for acidogenic pretreatment was from Guangzhou Sewage Treatment Plant. Strains for PSB treatment were the mixed culture solution consisting of Rhodopseudomonas Palustris RH-01, RY-02, Rhodosporillum rubrum RS-01, and strain RW-01, RW-02 and RW-03 isolated by our laboratory.

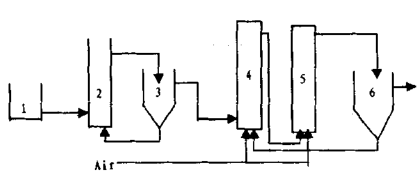

Fig.1 The flow sheet of biotreatment process
1. wastewater storage tank; 2. acidogenic pretreatment reactor; 3, 6. precipitating tanks; 4, 5. PSB treatment reactors

1.3 Analytic methods

The analytic methods for COD, BOD_5, SS and VFA were according to USA standard method(APHA, 1985). Colour was measured according to CPPA standard methods. The samples used for GC-MS were untreated effluent and PSB treated effluent. The samples were adjusted to pH=2 by 5% HCl and then extracted 3 times (1×300 ml + 2×150 ml) with CH_2Cl_2. The extractives were concentrated to approximately 1 ml, and were derived with diazomethane before GC-MS analysis.

1.4 Coagulation-flocculation treatment

Samples from biotreated effluent were taken for coagulation-flocculation studies. Experiments were conducted in 1 L beaker. The inorganic polymer flocculant, polyaluminum chloride(PAC), was provided by Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The cationic organic coagulant polyacrylamide (PAM) was supplied by SNF-Flocerger Company.

2 Results and discussion

2.1 PSB treatment

The characteristics of AS-CMP effluent are shown in Table 1. The pH value of the effluent ranged within 7.4—8.2. In previous study, we found that the pH value of the wastewater increased during the PSB treatment process, the suitable initial pH value for PSB treatment should be kept between 6.0—7.0. We adopted an aeidogenic pretreatment before PSB treatment, the acidogenic stage has three major purposes: reduce the inhibition of inorganic sulphocompounds to PSB, conversion of biodegradable organic compounds to volatile fatty aids, which are very easy to be degraded by PSB, and another purpose is to low the pH value. The acidogenic pretreatment reactor is a 9.5 L stirred tank with a retention time of 8 hours.

Fig.2 presented the variations of COD_{Cr}, BOD_5 and SS consistency of in-flow during the entire operating period. The removals of COD_{Cr}, BOD_5 and SS were demonstrated in Fig.3. From Fig.2 we can see that during the entire operating process, when COD_{Cr} concentration of fed effluent increased from 2500 to 4300 mg/L, the removals of COD_{Cr}, BOD_5 and SS changed in a narrow range, no upset operation was ever encountered, so this system had a good stability. During the third operation week, the COD_{Cr} concentration of in-flow was between 3600—3660 mg/L, the removals of COD_{Cr}, BOD_5 and SS reached 53.2%—56.1%, 78.0%—83.1% and 84.7%—89.6% respectively. We found that PSB concentration was a very important factor for keeping the stability of treatment process, the suitable living PSB concentrations were between 5.0×10^{9}—5.0×10^{10} in PSB treatment reactor.

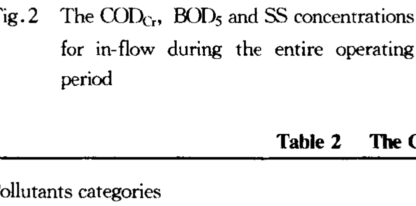

Fig.2 The COD_{Cr}, BOD_5 and SS concentrations for in-flow during the entire operating period

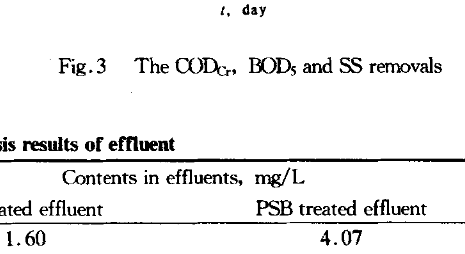

Fig.3 The COD_{Cr}, BOD_5 and SS removals

Table 2 The GC-MS analysis results of effluent

Pollutants categories	Contents in effluents, mg/L	
	Untreated effluent	PSB treated effluent
Alkanes	1.60	4.07
Saturated fat aids	0.084	n.d.
Unsaturated fat acids	0.097	n.d.
Phenols	1.83	0.14
4-OH-3-OCH_3-benzoic acids and 4-OH-3-OCH_3-benzaidelhydes	1.12	n.d.
4-OH-3-OCH_3-benzeneacetic acid	0.29	0.13
1,2-benzennedicarboxylic acid alkyl esters	3.02	1.02
Alkyl aromatics	0.48	0.18

It was found that the extractives of biotreated effluent decreased from 10.7 mg/L to 7.7 mg/L. In order to reveal the biodegradation of pollutants in the effluent, GC-MS has been used to analyze the extractives of untreated and PSB treated effluent. The detected organic pollutants are listed in Table 2.

From the results listed in Table 2, we can see that all the unsaturated fat acids, saturated fat acids, 4-OH-3-OCH_3-benzoic acid and 4-OH-3-OCH_3-benzaldehydes can be removed by PSB treatment. The content of phenols decreased from 1.83 mg/L to 0.14 mg/L. The results from GC-MS analysis indicated that PSB could degrade aromatic hydrocarbons under the experimental conditions. Except alkanes, other organic pollutants in the effluent detected by GC-MS reduced to a great extent after treated by PSB. Why did the alkane contents increase to a great extent? This may be the result of the cleavage of side chains and the break of benzenoid structure compounds during the biotreatment process.

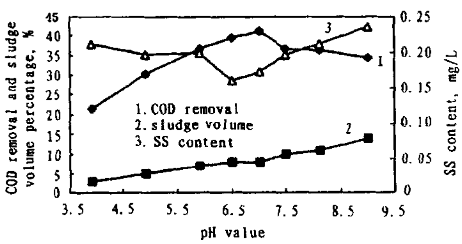

Fig.4 The relationship between pH value and the effectiveness of PAC coagulation

2.2 Coagulation-flocculation post-treatment

Fig.4 shows the effects of pH on the COD removal, sludge volume percentage and SS. From Fig.4 we can conclude that the suitable pH value of PSB treated wastewater was between 6.0—7.5. Sludge volume percentage increased with the increasing of pH value.

The relationship between PAC dosage and coagulation effectiveness is shown in Fig.5. From Fig.5 we can see that the COD removal, colour removal and sludge volume percentage increased with the PAC dosage. The high sludge volume percentage may lead to the operation difficulty of sludge disposal. On the other hand, the higher the PAC dosage, the higher cost for coagulant, so the dosage of PAC should be less than 120 mg/L, and at this dosage, the removal for COD_{Cr} is 35.8%, for colour is 33%. The results from above have shown that the coagulation results were not satisfied if only PAC was used.

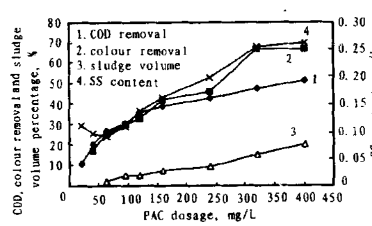

Fig.5 The relationship between PAC dosage and coagulation results

From above results, we know that PSB treatment can reduce BOD_5 and COD_{Cr} to a great extent, but had nothing to do with the colour and some organic compounds that were difficult for biodegradation. Table 3 indicates that the combined chemical coagulation-flocculation post-treatment of three kinds of coagulants had an excellent effect for further removal of the colour and

Table 3 The effects for a combined post-treatment of three kinds of coagulants

Dosage, mg/L			Removals, %			Sludge volume percentage, %
PAC	$AlCl_3$	PAM	COD	BOD_5	Colour	
80	80	3	49.3	44.3	50	10
80	120	3	54.8	51.0	58	14
80	180	3	63.4	58.9	75	17
60	120	3	51.3	50.7	65	13
100	120	3	57.5	51.8	70	16
120	120	3	64.6	59.1	73	17

Notes: the concentration of COD_{Cr}, BOD_5 and SS of PSB treated wastewater used for coagulation test were 1200 mg/L, 250 mg/L and 190 mg/L respectively, and the colour and BOD_5/COD_{Cr} of which were about 2900 C.U. and 0.28 respectively.

residual COD and BOD_5 in PSB treated effluent. When the dosages of coagulants were 80 mg/L for PAC, 180 mg/L for $AlCl_3$, and 3 mg/L for PAM, the COD_{Cr}, BOD_5 and colour removals reached 63.4%, 58.9% and 75%, respectively.

3 Conclusion

Results of this study showed that the effluent from E. *urophylla* AS-CMP process was susceptible to PSB treatment. The treatment process had good stability, needed less energy and performed well under high or shock hydraulic loads. When the COD_{Cr}, BOD_5 and SS concentrations of effluent were between 3300—3890 mg/L, 1100—1300 mg/L and 346—673 mg/L, the total COD_{Cr}, BOD_5 and SS removals for biotreatment reached 50%—56%, 77%—83% and 85%—89% respectively. The pollutants of the unsaturated fat acids, saturated fat acids, 4-hydroxyl-3-methoxyl-benzoic acid and 4-hydroxyl-3-methoxyl-benzaldehydes can be degraded completely. The content of phenols decreased from 1.83 mg/L to 0.14 mg/L.

PSB treatment process could not remove the colour, and the COD_{Cr} removal was less than 56%, the coagulation post-treatment was needed for abating colour and further reduction of COD_{Cr}. Results showed that the suitable pH value for PAC coagulation treatment was between 6.0—7.5. The combined chemical coagulation-flocculation post-treatment of three kinds of coagulants had excellent effects for further remove the colour and residual COD and BOD_5 in PSB treated effluent. At dosages of 80 mg/L for PAC, 180 mg/L for $AlCl_3$, and 3 mg/L for PAM, the COD_{Cr}, BOD_5 and colour removals reached 63.4%, 58.9% and 75% respectively.

Acknowledgements: This research program was supported by the Science Fund Committee of Guangdong Province, China. The authors wish to thank the Laboratory of Cellulose and Lignocellulosics Chemistry (LCLC), Guangzhou Institute of Chemistry for partly financial support for this research project.

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(Received for review August 17, 1998. Accepted November 23, 1998)