

Research on Preparation of flocculants for Sugar Factory Wastewater Treatment

Abstract Polyacrylamide, formaldehyde and carbamide or guanidine carbonate were used as raw materials, cationic polyacrylamide flocculants were synthesized with Mannich reaction, effects of technical conditions on rate of turbidity removal were investigated, and synthesis technics was optimized. Experimental results showed that the flocculation properties of the products prepared with Mannich were better than ones of blank experiments (polyacrylamide). In the same dosage of flocculants, consumption of polyacrylamide in the products was smaller than (or equal to) 1/10 of polyacrylamide (blank experiments), reducing flocculation cost greatly. In the real waster-water treatment of sugar factories with the prepared products under optimum conditions, the turbidity removal rates was approaching to 90% or greater than 90% showing flocculation effectiveness was better. In addition, the wasterwater of sugar factories was treated with prepared products and the removal of COD was 10~30%, which showed that using flocculating agents could reach the purposes of wasterwater pretreatment.

Key Words flocculant, polyacrylamide, carbamide, guanidine carbonate, wastewater

INTRODUCTION

Sugarcane grows mainly in south and southwest of China, specially in Guangxi, Yunnan, Fujian, and Guangdong, among which Guangxi province is the largest producer of cane sugar in China and there are 96 sugar factories in the province. Sugar industries play an important role in economic development of country, but effluents released produce a high degree of organic pollution in both aquatic and terrestrial ecosystems and cause health hazards. There are two major wastewater sources: one is from sugar mills, and the other is from the cane molasses distilleries. The sugar factories in Guangxi are the biggest water consumers and effluent generators. On averages, 20-30 tones of water are needed for one ton of sugar^[1]. With the growth in sugar production, the environmental problems associated with sugar factories are also increased.

The wastewater, from sugar mills and the cane molasses distilleries, contains high concentrations of organic materials, and is high acidity and deep color. Its solid content reaches 10%~12%. Therefore, it is necessary to carry out sugar wastewater flocculation treatment before aerobic treatment, in order to reduce the concentration of COD, the solid content, and the load of aerobic treatment.

In this work, polyacrylamide, formaldehyde and carbamide or guanidine carbonate were used as raw materials, cationic polyacrylamide flocculants were synthesized with Mannich reaction. This study had the advantages of simple preparation, high efficient wastewater treatment, low drug consumption and low cost of wastewater treatment.

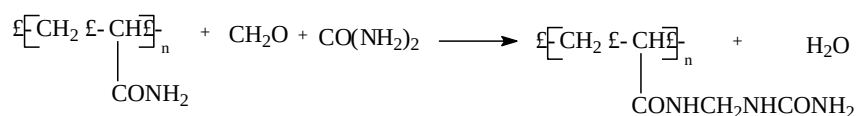
EXPERIMENTAL PROCEDURES

MATERIALS

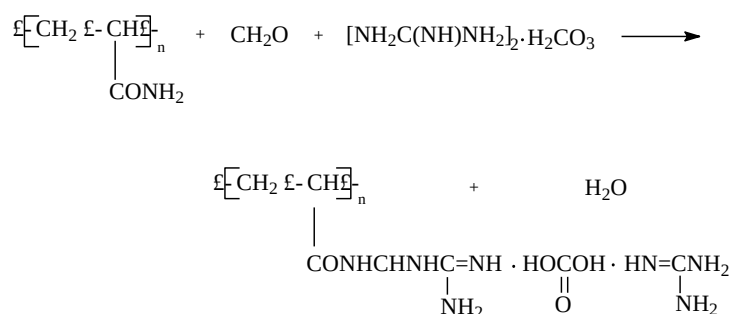
Polyacrylamide(300W molecular weight, reffered to as PAM(300W)), carbamide(AR), guanidine carbonate (AR) and formaldehyde(40% by weight)(AR) were obtained by a local market.

SYNTHESIS

Polyacrylamide, formaldehyde and carbamide or guanidine carbonate were used as raw materials, cationic polyacrylamide flocculants were synthesized with Mannich reaction. The over-all reaction is presumed to be



or



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44 PROCEDURE

45 To a stirred reactor which provided with a reflux condenser, 60ml H₂O, 2g PAM(300W), formaldehyde (40%
46 by weight) and urea or guanidine carbonate was proportionally added. The reaction temperature was kept at
47 20~60°C for 1h. Then pH value of the reaction mixture was adjusted to 5.5 with acetic acid, and the reaction
48 continued for 3~6h at this temperature. Finally, pH was adjusted to 7.5 with NaOH, the reaction continued for a
49 certain time and products were obtained. The reaction mixtures were used as flocculants for sugar wastewater
50 flocculation treatment.

51 ANALYTICAL METHODS

52 Turbidity was determined by spectrophotography according to GB 13200-91^[2]. The determination of
53 flocculation effectiveness was measured according to Y/T 5796-93^[3].

54 RESULTS AND DISCUSSION

55 Taking the turbidity removal as the object function, and the conditions such as reaction temperature, reaction
56 time, molar ratio of formaldehyde to amine, amine as variable factors, we evaluated the effects of these four factors
57 on the function. Experiments were carried out by using the orthogonal table of L₁₆(4⁴×2³)^[4] [i.e., an orthogonal table
58 of 16 rows (16 times of test), 7 columns (4 factors and 3 empty columns: A= reaction temperature, B= reaction time,
59 C= formaldehyde/ amine, D= amine), 4 levels: 20°C, 30°C, 40°C, 50°C; 2h, 3h, 4h, 5h; 2.0, 2.2, 2.4, 2.6; 2 levels: 9g
60 carbamide, 27g guanidine carbonate], whose levels and factors are shown in Table 1. The orthogonal test results
61 and range analysis are shown in Table 2.

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Table 1 Levels and factors in orthogonal test

	A	B	C	D
Levels	Reaction temperature	Reaction Time	formaldehyde/ amine	Amine (g)
	(°C)	(h)	(mol/mol)	
1	20	2	2.0	9 (carbamide)
2	30	3	2.2	27(guanidine carbonate)
3	40	4	2.4	
4	50	5	2.6	

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Table 2 Orthogonal test results and range analysis*

Test number	A	B	Empty column	C	D	Empty column	Empty column	turbidity removal %
1	1	1	1	1	1	1	1	83.18
2	1	2	2	2	1	2	2	77.09
3	1	3	3	3	2	1	2	68.80
4	1	4	4	4	2	2	1	78.00
5	2	1	2	3	2	2	1	76.17
6	2	2	1	4	2	1	2	72.48
7	2	3	4	1	1	2	2	55.18
8	2	4	3	2	1	1	1	69.57
9	3	1	3	4	1	2	2	72.81

10	3	2	4	3	1	1	1	82.48
11	3	3	1	2	2	2	1	72.10
12	3	4	2	1	2	1	2	73.80
13	4	1	4	2	2	1	2	74.97
14	4	2	3	1	2	2	1	54.50
15	4	3	2	4	1	1	1	52.40
16	4	4	1	3	1	2	2	68.67
K_1	307.0 8	307.1 4	306.92	266.6 7	561.3 9	575.90	587.05	
K_2	273.4	286.5 5	273.55	293.7 3	570.8 3	556.32	545.16	
K_3	301.1 9	248.4 8	261.48	296.1 2				
K_4	250.5 4	290.0 4	290.26	275.7 0				
k_1	76.77	76.79	76.73	66.67	70.17	71.99	73.38	
k_2	68.35	71.64	68.39	73.43	71.35	69.54	68.14	
k_3	75.3	62.12	65.37	74.03				
k_4	62.64	72.51	72.56	68.92				
R	56.54	58.66	45.44	29.45	9.44	19.58	41.90	
optimum	A ₁ B ₁ C ₃ D ₂ or A ₁ B ₁ C ₃ D ₁							

* Dosage of flocculants: 15mg/L

K_i : Sum of turbidity removal of the level i

k_i : Average of K_i

R (range): $R = k_{\max} - k_{\min}$

With range analysis of effects of each factor on the rate of turbidity removal, we found that, among these factors, the order of influence upon turbidity removal was as follows: reaction time > reaction temperature > molar ratio of formaldehyde to amine > carbamide or guanidine carbonate.

According to the conclusion of the orthogonal test, the optimum conditions were determined by this test. The optimum conditions as follows:

reaction temperature: 20°C;
 reaction time: 2h;
 molar ratio of formaldehyde to amine: 2.4:1;
 amine: 9g carbamide or 27g guanidine carbonate

Through repeated experiments under the optimum conditions, the rate of turbidity removal could reach 90% or greater than 90%, when the dosage of flocculants (solid content) was 10mg/L, which shows that the synthesized flocculants was high flocculation efficiency.

In the real waster-water treatment of sugar mills with the prepared products under optimum conditions, the experimental results are shown in Figure 1(the waster-water from Naning sugar mill: deep color; turbid; COD 562.85mg/L). It indicates that the turbidity removal rates of products are greater than ones of PAM(300W)(blank experiments). When the dosage is 15 mg/L, the turbidity removal rates of blank experiments, products from urea or guanidine carbonate are 77.14%, 94.95% or 92.93% respectively, which shows flocculation effectiveness better. In the same dosage of flocculants, consumption of polyacrylamide in the products was smaller than (or equal to) 1/10 of polyacrylamide (blank experiments), reducing flocculation cost greatly. When the dosage of PAM(300W)(blank experiments) is 10mg/L, the consumption of polyacrylamide(the product from urea) is 1mg(the reaction mixture(g): 2g polyacrylamide+60g H₂O +27g formaldehyde(solution)+9g urea =98g; the ratio of polyacrylamide: 2/98=0.02; solid content of the products: about 20%; the additive amount of the product for flocculation: 10/0.2=50mg; the consumption of polyacrylamide: 50*0.02=1mg). Through analysis, it is known that the synthetic products have high efficiency, less consumption of polyacrylamide and low cost of administration, which can save the cost of water treatment.

In addition, the wasterwater of sugar mills was treated with prepared products and the removal of COD was 10~30%, which showed that using flocculating agents could reach the purposes of wasterwater pretreatment.

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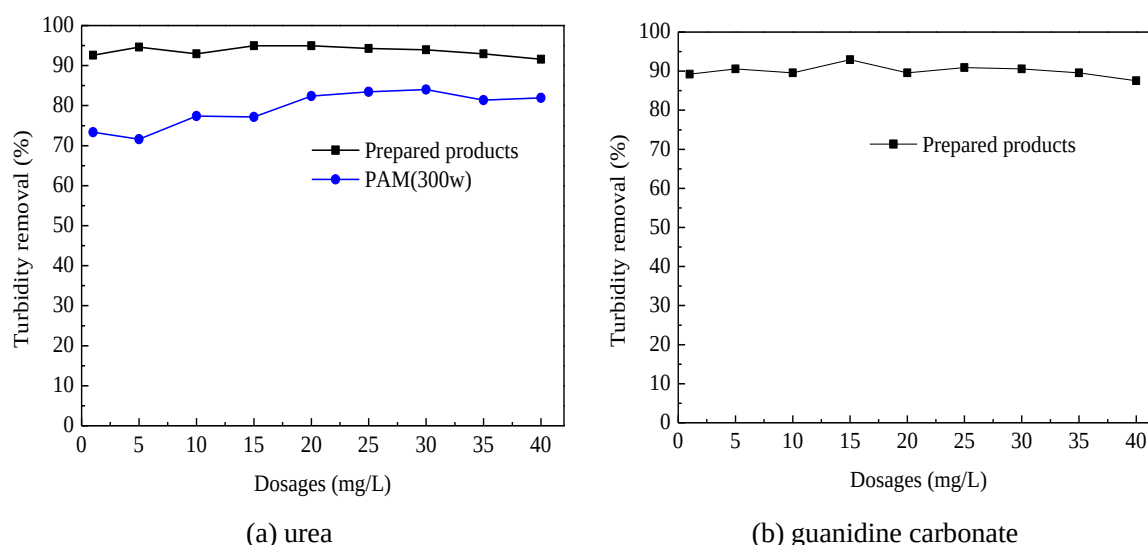


Fig1 Real wastewater treatment of sugar factories with prepared products under optimum conditions

96 CONCLUSIONS

97 1.By orthogonal test main technical parameters of preparing flocculants were optimized. The optimum
 98 conditions were as follows: reaction temperature: 20°C; reaction time: 2h; molar ratio of formaldehyde to amine:
 99 2.4:1; amine: 9g carbamide or 27g guanidine carbonate.

100 2. In the same dosage of flocculants, consumption of polyacrylamide in the products was smaller than (or equal
 101 to) 1/10 of polyacrylamide (blank experiments), reducing flocculation cost greatly. In the real waster-water
 102 treatment of sugar factories with the prepared products under optimum conditions, the turbidity removal rates were
 103 approaching to 90% or greater than 90%, showing flocculation effectiveness better. In addition, the wastewater of
 104 sugar factories was treated with prepared products and the removal of COD was 10~30%, which showed that using
 105 flocculating agents could reach the purposes of wastewater pretreatment.

106 3.This study had the advantages of simple preparation, high efficient wastewater treatment, low drug
 107 consumption and low cost of wastewater treatment.

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