Synthesis of modified melamine-formaldehyde resin

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Abstract:

In this paper, the conditions of modified melamine-formaldehyde resin (MF) used for a flocculent such as the ratio of reactant, reaction time, reaction temperature and the value of pi I, were studied. The preferable synthetic conditions were melamine : formaldehyde : acrylamide (mole) = 1:5:(2~3), reaction temperature 70°C, reaction time 4 h, pH 9.0.

Keywords: melamine-formaldehyde resin | flocculent | acrylamide (AM)

Article:

1 Introduction

Flocculent precipitation is an economical and convenient method widely adopted by a number of countries as an aid to improve the water quality. The polymer flocculent makes a very important action in water treatment because of good flocculent performance, decolorant potency and simple operation [l]. Cationic polymer flocculent, whose molecular chains comprise more active adsorption sites, has a more excellent behavior as a water-treatment chemical [2]. Because of all kinds of condition restricts, we require massive tasks in order to research the preparation of cationic polymer flocculent structure, mechanism and application. Melamine-formaldehyde resin is one of earlier industrialized products and the patent was got in 1935. It has affluent material resource and mature synthesis techniques to prepare MF. Due to good water-solubility and other characters, modified melamine-formaldehyde resin is widely used, for example, sulfonated melamine-formaldehyde resin is prepared for construction industry and papermaking industry to improve the fluidity of concrete and provide with a low moisture adsorption and a high tensile strength [3]; Zhu Lizhong probed into modified melamine-formaldehyde resin acting as flocculent in wastewater treatment [4]. In this paper, conditions of preparation such as the reactant ratio, reaction temperature, reaction time and the value of pH were studied. The results

prove that the modified resin exhibits positive and good water-solubility and is a novel flocculent to ensure the improvement of treatment processes.

2 Experiments

2.1 Materials

Melamine, formaldehyde (36%), acrylamide, hydrochloric acid (36%), sodium hydroxide (4 mol/L), distilled water and White Bole are all chemical pure.

2.2 Preparation of melamine-formaldehyde resin [5, 6]

Before add melamine and formaldehyde (36%) at a mole ratio of about 1.0 to 5.0 into a three-mouth flask, adjust the pH of formaldehyde solution using sodium hydroxide (4 mol/L). Then open the condensed water and control fixed temperature. After a period of time, an initial melamine-formaldehyde resin was formed. Adjust the pH of the system and add acrylamide solution (including some distilled water). After two hours, modified melamine-formaldehyde resin was prepared. The flocculating efficacy for modified MF resin is appraised by the Jar Test[7]. Use nephelometer to measure the turbidity of suspended wastewater and use spectrophotometer (λ = 400 nm) to test the absorbency. These data are main basis of the flocculating efficacy for modified MF resin.

3 Results and Discussions

3.1 Effect of reactant ratio on preparation

Acrylamide endows melamine-formaldehyde resin with water-solubility. Its quantity has an obvious effect on the water-solubility of resin. Table 1 shows the effect of reactant ratio on the flocculation behaviour. The turbidity removed rate is $T\% = (T_0 - T_1) / T_0 \times 100\%$ and the absorbency rate is $A\% = (A_0 - A_1) / A_0 \times 100\%$, in which T_0 is the initial turbidity, T_1 is the remnant turbidity, A_0 is the initial absorbency and A_1 is the remnant absorbency.

Table 1. Effect of reactant ratio on the flocculation behaviour

M:F:AM	State	T_0	T_1	$T\%$	A_0	A_1	$A\%$
1:6:8	Clear liquid	345	40.5	88.3	0.550	0.059	89.3
1:5:6	Clear liquid	262	27.5	89.5	0.450	0.074	83.6
1:5:5	Clear liquid	280	21.0	92.5	0.457	0.054	88.2
1:5:3.5	Clear liquid	350	35.0	90.0	0.603	0.080	86.7
1:5:3	Clear liquid	250	8.0	96.8	0.397	0.016	96.0
1:5:2	Clear liquid	250	8.0	96.8	0.346	0.014	96.0
1:5:1.5	Clear liquid	275	24.0	91.3	0.455	0.068	87.3
1:4.5:3							
1:4:3							

Note: M:F:AM is the ratio of melamine/formaldehyde/acrylamide, reaction time is 4 h, reaction temperature is 70°C.

Acrylamide is specifically mentioned, in the practice of this work, and is preferably used. Acrylamide is not added to the initial resin until an acrylamide/melamine mole ratio of about 2.0

to 3.0, based on the total amount of melamine, is reached. When the amount of AM is insufficient for the initial resin, surplus hydroxymethyl maybe makes the resin cross-linking and coacervation after graft modification. When the ratio is greater than 3. 0, after the reaction of graft the resin solution will include acrylmide monomer, which is toxin and probably makes environment contaminating during the wastewater treatment. With the proper amount, modified resin has a low viscosity and excellent water-solubility characteristics, making it preferable as a flocculent with low remnant turbidity. Furthermore the amount of formaldehyde has an important effect on the structure of resin and its solubility. Formaldehyde can be supplied in any one of its commonly available forms, and in this experiment it is generally used as a solution with a concentration of about 36 % formaldehyde in combination with a minor amount of alkali. The mole ratio of F/M is preferably 4.0 to 5 0. The low ratio will make the final resin a low molecular weight and the results of flocculation are unqualified. When the ratio is greater than 5.0, the solution has surplus free formaldehyde, which makes the resin unstable for storage and use. Moreover, free formaldehyde easily reacts with acrylamide, thus the rate of graft may be low, which increases the resin's solubility. Sum up, the more preferable ratio of melamine : formaldehyde : acrylamide 1:5:(2~3).

3. 2 Effects of reaction temperature and reaction time on Preparation

The main reaction includes two steps, polycondensation and graft. Fig. 1 shows the effect of reaction temperature on the flocculation behaviour of modified MF when the mole ratio is 1:5:3 and total reaction time is 4 h. Fig. 2 shows the effect of reaction time for the first step on the flocculi1tion behaviour of modified MF when the mole ratio is 1:5:3, reaction temperature is 70°C and reaction time for the second step is 2 h. Due to the low solubility of melamine in the first step, the mixture needs to be heated to about 60 °C to 70°C, preferably about 70 °C, and held for a time sufficient for formaldehyde to methylolate the melamine. Typically, the reaction time is among 1 h to 2 h and usually about 2 h in order to form a high polymer. In the second step add acrylamide solution to the remnant of the first stage. The temperature of the mixture is maintained about 70°C. The initial resin is grafted for a sufficient time to avoid instability. A suitable time for the graft step can be determined by experiments (in this paper select 2 h). See Fig. l and Fig. 2, the more preferable temperature is about 70°C and the total reaction time usually takes about 4 h.

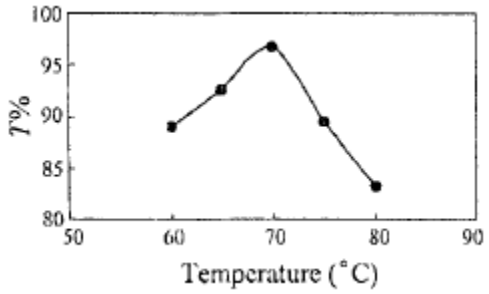

Figure 1. Effect of reaction temperature on the flocculation behaviour

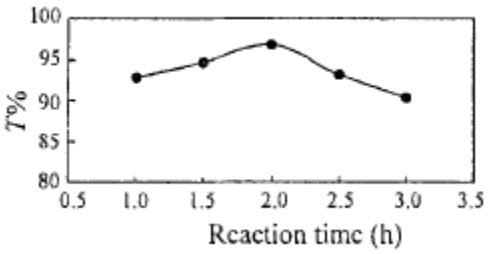

Figure 2. Effect of reaction time for the first step on the flocculation behaviour

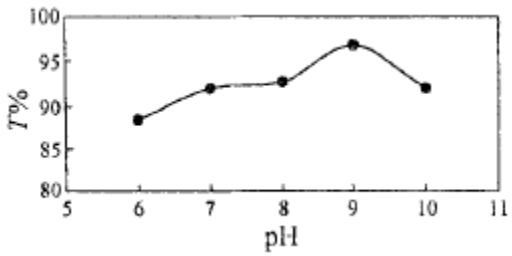

Figure 3. Effect of pH on the flocculation behaviour

3. 3 Effect of pH on preparation

Effect of pH on the flocculation behaviour is shown in Fig. 3, where the mole ratio is 1:5:3, reaction temperature is 70°C and the total reaction time is 4 h.

The value of pH has an important and complex effect on the reaction system of resin. Different pH can cause appearance of distinguished type reactions. During the first step when pH is greater than 10. 5, the reaction of Cannizzaro simultaneously will happen [8].

$2HCHO + H_2O \rightarrow HCOOH + HCH_2OH.$

The reaction of Cannizzaro decreases the amount of formaldehyde and then has an effect on the structure of modified resin. So it is necessary to select proper pH. Generally pH is about 8.0 to 10.0, preferably about 9.0. The alkaline condition of the reaction media is maintained or adjusted by Sodium Hydroxide. During the second step OH^- is initiator of graft reaction. In order to investigate the effect of pH on the water-solubility and stability of grafted polymer, we select several simple parallel-experiment shown in Table 2. The detail effect of pH on the graft step needs to be further studied.

Besides these factors, the adding speed of materials and the content of water probably affect the synthesis. Water can be added during the reaction or after the resin is prepared so that the final resin contains about 30 to 50%, preferably about 35 to 40%, resin solids.

Table 2. Parallel-experiment

Experiment	Procedure	Phenomenon	Remarks
1	After 2 h of polycondensation, adjust pH of about 9.7, add the solution of acrylamide.	The resin will dissolve and form clear and stable liquid.	OH^- is the initiator of graft reaction.
2	After 2 h of polycondensation, add the solution of acrylamide, without adjusting pH.	The resin concervation	Without the initiator the graft reaction doesn't happen.
3	After 2 h of polycondensation, adjust pH of about 9.7 without adding the acrylamide solution.	The resin concervation	The increase of resin's solubility is caused by acrylamide, not other factors.

4 Conclusions

(1) The modified melamine-formaldehyde resin is a novel flocculent. When treating the inorganic solids suspended wastewater, the turbidity removal rate may be reached 96%.

(2) The preferable condition of reaction is the mole ratio of melamine/formaldehyde/acrylamide of 1:5:(2~3), reaction temperature 70°C, total reaction time 4 h and pH of about 9.0.

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