Enhanced removal of suspended colloidal particles from turbid water using a modified microbial flocculant

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Abstract. Microbial flocculant (MBF), as an efficient, environmental friendly and biodegradable flocculant, has been widely studied in water treatment. The cationic modification of MBF would improve its charge neutralization and extend its application. In this study, the effect of mAM:mDMDAAC, mMBF:m(AM+DMDAAC), reaction temperature and initiator dosage on the molecular weight of modified MBF were investigated. The optimal synthesis condition was obtained. Modified MBF performed well in the removal of suspended colloidal particles from water. It possessed the potential application in the surface water treatment.

1. Introduction
Coagulation-flocculation as an important technology has been widely applied in water treatment [1]. A great deal of flocculant/coagulant has been studied to improve their performance. Microbial flocculant (MBF) is one of flocculant with the advantages of high treatment efficiency, environmental friendliness and biodegradation. MBF is extracted from extracellular organic matter of bacteria [2]. It containing numbers of anion functional group has been used in the removal of heavy metals from water [3]. It is potentially applied in the surface water treatment as well. But before that, the modification of MBF should be carried out to graft some cationic group into its molecular chain. It is able to neutralize negative charge in the water and improve flocculation efficiency, which is rarely investigated.

In this study, a modified MBF was synthesized by grafting acryl amide (AM) and diallyl dimethyl ammonium chloride (DMDAAC) with MBF via redox initiation system. In the synthesis, mAM:mDMDAAC, mMBF:m(AM+DMDAAC), reaction temperature and initiator dosage playing essential roles for the molecular weight of modified MBF were studied. Flocculation performance of modified MBF was investigated in the turbid water treatment.

2. Materials and Methods

2.1. Synthesis of modified MBF
A modified MBF was synthesized via redox initiation system in aqueous solution. Predetermined amounts of MBF, AM and DMDAAC were sequentially completely dissolved and thoroughly mixed in deionized water. The pH of miscible liquids was adjusted to 3.0 by sodium hydroxide (0.1 mol•L⁻¹) or hydrochloric acid (0.1 mol•L⁻¹). And then, potassium persulfate (0.1 mol•L⁻¹) and sodium hydrogen sulfite (0.1 mol•L⁻¹) were added into the reaction system with vigorous stirring. After deoxygenating by pure nitrogen (N₂) for 20 min, the sealed reaction vessel was placed in water bath with constant reaction temperature for 6 h. Modified MBF was obtained by purifying in ethyl alcohol and drying in vacuum oven at 50°C until constant weight.

2.2. Measurement of intrinsic viscosity and calculation of molecular weight
Intrinsic viscosity of modified MBF was measured by Ubbelohde viscometer with capillary diameter of 0.5-0.6 mm. The measurement process and calculation of molecular weight had been described in previous research [4].

2.3. Flocculation experiments
Kaolin was used to prepare the turbid water. Kaolin powder was firstly sieved through a 200-mesh sifter, and then it was added into deionized water with vigorous stirring for overnight. The turbidity of water was 51.1±0.4 NTU after settling for 30 min. Flocculation experiments were carried out using a six-paddle gang stirrer (Wuhan Meiyu Instrument Co., Ltd, China). The 0.1 mL commercial polyaluminium chloride (PAC, Fidelity Water Purification Material Co., Ltd, China) with the concentration of 2g•L⁻¹ and a certain amount modified MBF of 1g•L⁻¹ were added into turbid water. The mixed solution was stirred at a high speed of 300 rpm for 1 min and then at a low speed of 40 rpm for 10 min. After settling for 30 min, the turbidity of supernatant water was measured using a 2100P turbidity meter (HACH, USA). The removal rate was calculated using Eq. (1):

\[
\text{Removal rate} \ (% ) = \left( 1 - \frac{T_2}{T_1} \right) \times 100\% \tag{1}
\]

where, T₁ and T₂ are the initial and the final turbidity in the water respectively.

3. Results and Discussion

3.1. Effect of mAM:mDMDAAC on modified MBF
AM played an important role in the graft copolymerization of MBF and DMDAAC. The reactivity of AM was often higher than cationic monomer. It acting as a chain enhanced DMDAAC grafting on the MBF. Thus, increasing the amount of AM would improve intrinsic viscosity and molecular weight of modified MBF, which had been represented in Figure 1. When the mass ratio of AM and DMDAAC decrease, electrostatic repulsion caused by cationic monomer obviously increase, and reaction was impeded. In most cases, there was a positive correlation between intrinsic viscosity and molecular weight in polymers. The positive correlation had also been found in this study.
3.2. Effect of reaction temperature on modified MBF

Temperature influenced reaction activity and reaction rate in the copolymerization. Free radicals generated in the redox initiation system were few and molecular diffusion was slow at low temperature (Figure 2). In this condition, the reaction time was increased, and the molecular weight of copolymer was undesirable. The molecular weight would increase with the increase of temperature. However, the high temperature markedly improved the amount of free radical, which caused cross-linking reaction and implosion [4]. The synthetic modified MBF possessed bad solubleness and low molecular weight. Furthermore, high temperature enhanced the collision of free radical and made the chain reaction end.

Figure 2. Effect of reaction temperature on intrinsic viscosity and molecular weight of modified MBF

3.3. Effect of initiator dosage on modified MBF

The initiator dosage was another factor to affect the amount of free radical. At the low initiator dosage, the insufficient primary free radicals were hard to react with the surrounding MBF and monomer and yielded MBF free radicals and monomeric free radicals. Chain initiation was slowed down. The reaction efficiency and molecular weight were low (Figure 3). Increasing initiator dosage was contributed to form the long copolymer chain and obtain outstanding modified MBF. But supernumerary initiator greatly increased the number of free radical and caused cross-linking,
implosion and chain termination like high temperature [5]. The low molecular weight was also found in this case.

Figure 3. Effect of initiator dosage on intrinsic viscosity and molecular weight of modified MBF

3.4. Effect of mMBF:m(AM+DMDAAC) on modified MBF

The molecular weight of MBF was larger than that of monomer. Increasing mass ratio of MBF and AM+DMDAAC was able to enhance the molecular weight of modified MBF (Figure 4). However, the reaction activity of MBF was low, and the formation of MBF free radical was harder compared with the formation of monomer free radical. Therefore, the high ratio of MBF and AM+DMDAAC conversely impeded the copolymerization.

Figure 4. Effect of mMBF:m(AM+DMDAAC) on intrinsic viscosity and molecular weight of modified MBF

3.5. Flocculation performance of modified MBF in turbid water treatment

There were lots of suspended colloidal particles in the simulative turbid water. These colloidal particles mostly carried negative charge in their surface. Cationic inorganic coagulant and organic coagulant would neutralize the surface charge of colloidal particles and accelerate them crashing, aggregating and settling. The modified MBF possessing cationic group and anion group was also able to conduce to charge neutralization. Furthermore, the modified MBF had the strong adsorption and bridging in the removal of colloidal particles. The low dosage of modified MBF with few inorganic coagulants and the acceptable flocculation performance was discovered in Figure 5.
4. Conclusions
A cationic modified MBF was prepared via grafting AM and DMDAAC onto molecular chain of MBF. The optimum preparation condition, mAM:mDMDAAC of 5:1, reaction temperature of 60°C, initiator dosage of 3 mL and mMBF:m(AM+DMDAAC) of 0.8:4.2, was investigated. In this condition, modified MBF possessed the highest molecular weight. The high molecular weight and cationic functional groups both contributed to the outstanding flocculation performance in the turbid water treatment. The removal rate of turbidity was able to reach 95.6% with low dosage of MBF and PAC.

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