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Optimization of preparing a high yield and high cationic degree starch graft copolymer as environmentally friendly flocculant: Through response surface methodology

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ABSTRACT

To pursue effective and environmentally friendly flocculant, a bio-copolymer was prepared by starch grafting with acrylamide (AM) and dimethyl diallyl ammonium chloride (DMAAC) through an initiator system $\text{KMnO}_4/\text{HIO}_4$. The initiation and grafting reaction were optimized by the Response Surface Methodology. In the initiation reaction, the optimum condition was KMnO_4 at 0.28 mmol, HIO_4 at 0.25 mmol, and the temperature at 67.64 °C, when the highest copolymer yield of 13.43 g was obtained from 4 g raw starch. In the grafting reaction, the optimum condition was the temperature at 68.71 °C, (AM + DMAAC)/starch anhydroglucose units molar ratio at 2 and the AM / (AM + DMAAC) molar ratio at 0.34, when the copolymer had the maximum cationic degree of 1.54 meq/g. The optimized preparing method had a high grafting efficiency of $97.12 \pm 0.14\%$ and high raw material utilization. The flocculation ability of the optimized graft copolymer was also tested. The result showed the graft starch was effective to remove reactive dyes and disperse dyes from wastewater. The dye removal efficiency of the graft starch was nearly 10% higher than polyacrylamide. Therefore, through the optimization of initiation and grafting reaction, the graft starch was a promising environmentally friendly flocculant.

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1. Introduction

Flocculation is an important wastewater treatment technology [1]. With environmental protection requirements becoming stricter, inorganic and synthetic organic polymer flocculants have been criticized for their non-biodegradability and the possibility of pollution [2]. Therefore, the demands for more environmentally friendly flocculant have been increasing. New types of sustainable natural biopolymer flocculants have been continuously developed and reported [3, 4]. Natural macromolecular polysaccharides, such as starch [5], chitosan [6], cellulose [7] and lignin [8], are widely adopted as the backbones to prepare organic polymer flocculants because of their accessibility. To improve the flocculation properties, modifications of these natural polymers are frequently required [9, 10].

Starch, as one of the most abundant and accessible polysaccharide, is a promising candidate for sustainable materials. The modification of starch is convenient with the reactive groups on the starch backbone [11]. Many modification methods have been applied to starch, such as acylation [12], esterification [13], oxidization [14], cross-linking [15] and grafting [5]. Among them, starch grafting with other organic

monomers is a convenient and effective approach of modification [16]. To acquire important flocculation properties, for instance, to increase cationic charges, starch was grafted with cationic monomers DMAAC (dimethyl diallyl ammonium chloride) [17]. To increase molecule weight and degree of crosslinking, starch was grafted with AM (acrylamide) [18].

An initiator system is often required for starch graft copolymerization reaction. Common initiators include cerium ammonium nitrate [19], azobisisobutyronitrile [20], $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ [21], potassium persulfate [22] and so on. An improved $\text{KMnO}_4/\text{HIO}_4$ initiator system is reported to have the advantages of low cost and high grafting efficiency [5]. KMnO_4 can oxidize primary alcohol groups on the starch backbone to aldehyde groups. Aldehydes react easily with manganese ions to produce free radicals. HIO_4 as an oxidant can open the C_2-C_3 bond of the glucose unit and form two aldehyde groups simultaneously. Consequently, one glucose unit could provide three active sites for the starch grafting reaction through the initiator system. This is more efficient than other methods typically only forming two active sites. However, further optimization for this initiator system has not been considered. In particular, the amounts of the initiators and the temperature in the reaction are not optimized, which would significantly influence the generation of free radicals and the grafting efficiency [23]. Additionally, after initiation stage, the optimization for conditions of the grafting reaction stage

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has not been reported, the lack of which might lead to low effectiveness of the copolymerization reaction and the inferior flocculation properties of the copolymer flocculant.

Response surface methodology (RSM) is an optimization tool with statistical experimental designs. This method is used to establish a continuous variable surface model to evaluate the factors that affect specific processes and their interactions to determine the optimal level range [24]. RSM based on Box-Behnken Design (BBD) can carry on the experiment with the number of factors within 3–7 and the number of experiments within 15–62 times. When the number of factors is the same, the number of experiments required for BBD is less than that for the Central Composite Design [25]. Therefore, RSM-BBD has been successfully applied to various process optimizations in a convenient manner [26].

In this paper, a starch graft copolymer flocculant was successfully prepared through the initiator system $\text{KMnO}_4/\text{HIO}_4$. Starch was copolymerized with AM and DMDAAC in the grafting reaction to enhance the flocculation properties. The RSM-BBD was used to optimize and analyze the important parameters of the initiation reaction (KMnO_4 , HIO_4 and temperature) to improve the yield of graft products. Then the RSM-BBD were further used to optimize the important parameters of the grafting reaction (temperature, AM / (AM + DMDAAC) molar ratio, (AM + DMDAAC) / starch anhydroglucose units (AGU) molar ratio) to improve the cationic degree of the copolymer flocculant. To test the flocculation ability of the copolymer, the optimized graft starch was used to remove reactive dyes and disperse dyes from wastewater.

2. Materials and methods

2.1. Materials

All chemicals were obtained from National Pharmaceutical Group Corporation, Beijing, China, including potato starch, KMnO_4 , HIO_4 , AM, DMDAAC, PAM (polyacrylamide) (non-ionic), PDMDAAC (poly-dimethyl diallyl ammonium chloride), P(AM-DMDAAC) (poly(acrylamide- dimethyl diallyl ammonium chloride)), poly-aluminum ferric chloride (PAFC), reactive dyes and disperse dyes. All chemicals were A.R. and used without further purification. Ultrapure water was used throughout the overall study to prepare aqueous solutions.

2.2. Graft copolymerization reaction

The potato starch (4 g) was dried at 105 °C for 24 h, before it was stirred with pure water in a four-necked flask at 85 °C for 30 min to obtain a gelatin solution. After cooling to 65 °C, nitrogen gas was filled to remove oxygen in the reactor. At the same time initiators KMnO_4 and HIO_4 were added. After 15 min of initiation, certain amounts of DMDAAC monomers and AM monomers were added. In cases that AM needed large addition, a part of it was dissolved previously and added slowly at a velocity of 1.0 mL/min. After adjusting the pH to 1 with sulfuric acid, the reaction continued for 3 h. After the reaction, the mixture was neutralized with NaOH and cooled to ambient temperature. The grafted product was settled with anhydrous ethanol, filtered, dried at 50 °C under vacuum to a constant weight (denoted as m_1), and ground into powder. Free AM and DMDAAC and reaction by-products, i.e., PAM homopolymers, PDMDAAC homopolymers and AM-DMDAAC copolymers, were then removed by Soxhlet extraction with 50/50 (v/v) acetic acid and methanol for 18 h [27]. The purified product was further washed with ethanol for three times and dried at 50 °C to a constant weight (denoted as m_2).

2.3. Experimental design

2.3.1. Optimization of initiation conditions

Radicals generated by the initiators are essential for the grafting [28]. Therefore, the amounts of initiators and the reaction temperature are

Table 1
RSM design variables and levels for optimization of initiation conditions.

Variables	Levels		
	−1	0	1
X_1 : Quantity of KMnO_4 (mmol)	0.10	0.20	0.30
X_2 : Quantity of HIO_4 (mmol)	0.05	0.15	0.25
X_3 : Initiation reaction temperature (°C)	40	55	70

significant factors that influence the grafting efficiency. To optimize these reaction conditions comprehensively, a BBD (by Design Expert 8.0.6) with three variables and three levels for each variable was applied, as shown in Table 1. The response of the BBD was the yield of purified product (i.e., m_2 in Section 2.2).

2.3.2. Optimization of grafting conditions

As AM is non-ionic but DMDAAC is cationic, the relative amount of the monomers added to the grafting reaction will affect the cationic degree of the grafted copolymer, which is an important flocculation property. A BBD was applied, as shown in Table 2, with AM / (AM + DMDAAC) molar ratio, (AM + DMDAAC) / starch AGU molar ratio, graft reaction temperature as variables, and the cationic degree as the response.

2.4. Grafting efficiency and cationic degree determination

The quantity of monomers successfully grafted onto the starch backbone can be reflected by calculating the graft efficiency [5], as shown in Eq. (1):

$$GE = m_2/m_1 \times 100\% \quad (1)$$

where GE is the grafting efficiency, m_1 (g) is the weight of crude products, m_2 (g) is the weight of purified products (see Section 2.2).

The cationic degree is an indicator of the charge neutralization ability of cationic flocculant. It was determined by titration. 0.2 g starch graft product was dissolved in 100 mL deionized water. 1 mL of K_2CrO_4 solution were added as indicator. The solution was then titrated with 0.05 mol/L AgNO_3 solution after pH was adjusted to 6.5–7.2 by sulfuric acid. The cationic degree (CD) was calculated as Eq. (2) [17]:

$$CD = C \times (V_{\text{AgNO}_3} - V_0)/m_2 \quad (2)$$

where CD (meq/g) is the cationic degree, C (mol/L) is the concentration AgNO_3 solution, V_{AgNO_3} (mL) is the volume of consumed AgNO_3 , V_0 (mL) is the volume of consumed AgNO_3 in blank test, m_2 (g) is the weight of purified products (see Section 2.2).

2.5. Model fitting and statistical analysis

A multiple quadratic model was established for each BBD, indicating the effect of variables on the response, as illustrated by Eq. (3).

$$Y = A_0 + \sum_{i=1}^3 A_i X_i + \sum_{i=1}^3 A_{ii} X_i^2 + \sum_{i=1}^2 \sum_{j=i+1}^3 A_{ij} X_i X_j \quad (3)$$

Table 2
RSM design variables and levels for optimization of grafting conditions.

Variables	Levels		
	−1	0	1
X_1 : Grafting reaction temperature (°C)	65	70	75
X_2 : (AM + DMDAAC) / starch AGU molar ratio	2	4	6
X_3 : AM / (AM + DMDAAC) molar ratio	0.3	0.5	0.7

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