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Preparation and characteristics of quaternary amino anion exchanger from wheat residue

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ABSTRACT

Quaternary amino anion exchanger (QE) was prepared from wheat residue (WR) after reaction with epichlorohydrin and triethylamine in the presence of *N*,*N*-dimethylformamide and catalyst. The single influential factor experiments and orthogonal tests were carried out in order to obtain the optimal conditions for the preparation of wheat residue quaternary amino anion exchanger (WR-QE). The parameters of the influential factors, which included the types of catalysts, the amounts of WR and triethylamine, and experimental temperatures (activating temperature, catalytic temperature and reacting temperature) were also defined. The results indicated that pyridine was a suitable catalyst, and the catalytic temperature was a key factor of experimental temperatures. The optimal synthesis reaction parameters of dosages were WR:epichlorohydrin:pyridine:triethylamine = 2 g:20 ml:15 ml:30 ml. Optimal experimental temperature was 100 °C. Under these conditions, the nitrogen content of WR-QE was 6.0%, compared with WR of 0.4%. The yield was 556.3%. Nitrate removal was 89.1%; this was higher than the nitrate removal of wheat residue tertiary amino anion exchangers (WR-TE) of 6% –10%.

1. Introduction

Agricultural residues (AR) are regarded as abundant and available biological resources. While only 2–5% of AR in China is utilized in the industry, the remaining is burned without proper utilization, causing significant waste and pollution. Today, there is an increasing interest in AR for their low-cost and availability. AR have been utilized in the production of a diversity of chemicals, including activated carbon [1], ethanol [2] and ion exchangers [3].

Generally, ion exchangers are produced by polycondensation or polymerization [4] reactions which have several disadvantages such as long synthesis cycles, high costs, and reaction byproducts poisonous to the environment and humans. Further development of ion exchangers has been investigated, and some studies have exhibited the preparation of ion exchangers from AR, including sugarcane bagasse [5], peanut hull [6], apple pomace [7], sawdust [8], coconut husk [9], orange peel [10], banana pith [11] and pine bark [5].

Wheat residue (WR) is one of the major AR in China, which accounts for 15.2% of the AR. Therefore, large-scale use of WR for ion exchangers may reduce AR waste. The predominant constitutes of WR are cellulose (32.1%), hemi-cellulose (29.2%), lignin (16.4%), and other components (22.3%), making it a suitable chemical composition in comparison with other AR [12]. Cellulose, hemicelluloses and lignin structures have a large amount of easily available hydroxyl groups; these hydroxyl groups can be used for the preparation of various functional polymers [13].

Research about tertiary amino anion exchanger prepared from AR (AR-TE) has been reported in previous work [5,12,14], but there is no information concerning quaternary amino anion exchanger (QE) prepared from WR used for nitrate removal in the present literature. The main objective of this paper is to discuss the preparation of wheat residue quaternary amino anion exchanger (WR-QE) from WR after reaction with epichlorohydrin and triethylamine in the presence of *N*,*N*-dimethylformamide and catalyst. The optimal synthesis conditions were determined by batch experiments of single influential factor and orthogonal tests. The characteristics of WR-QE and its property for nitrate removal were studied, compared with those of the AR tertiary amino anion exchangers (AR-TE) studied by Orlando [12,14].

2. Materials and methods

2.1. Materials

WR was obtained from Liao Cheng, Shandong, China. The raw WR was washed with distilled water, dried at 60 °C for 6 h and sieved into particles ranging from 100 to 250 μm with bulk density of 250 kg m^{-3}.

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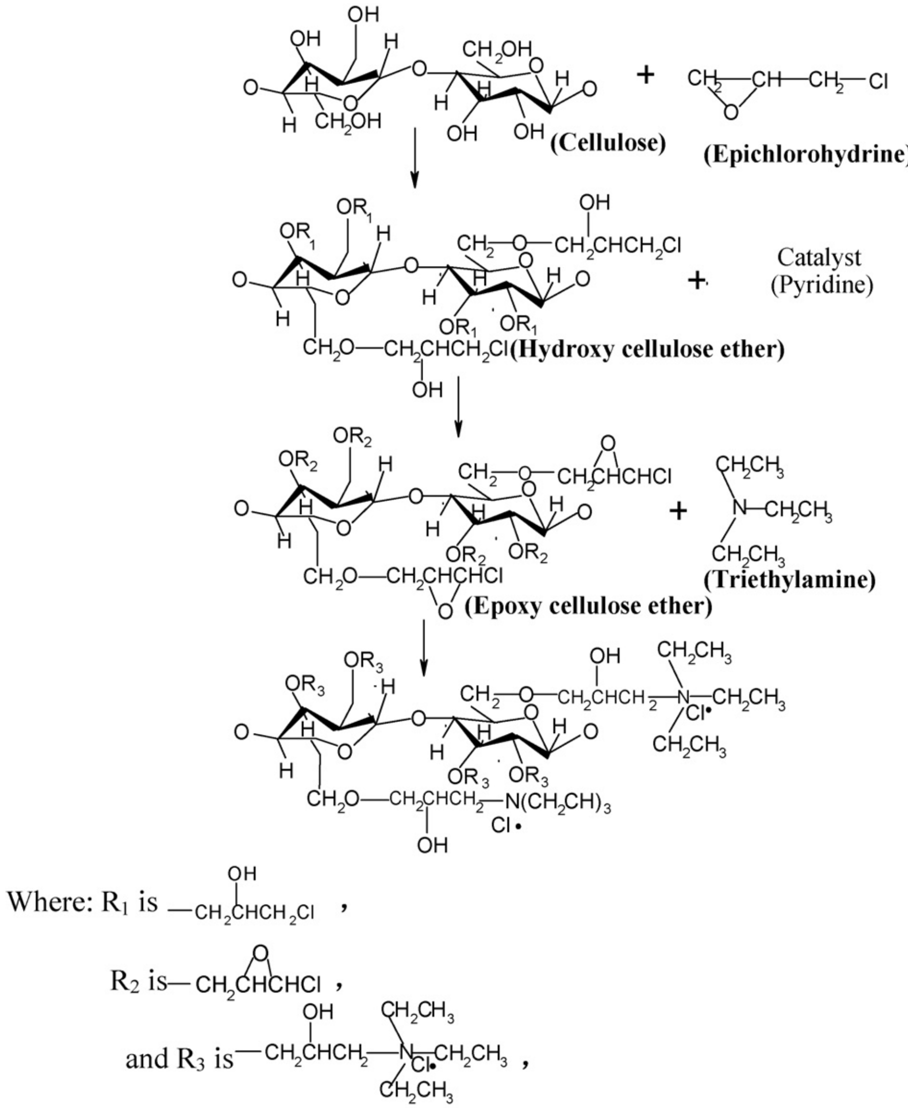

Fig. 1. Synthetic reactions of WR-QE.

2.2. Preparation of WR-QE

Batch experiments were conducted using WR with 20 ml of epichlorohydrin and 25 ml of *N*,*N*-dimethylformamide in a 250 ml three-neck round bottom flask at 50–100 °C for 1 h. Batch volumes (5–25 ml) of catalyst were added and the solutions were stirred for 1 h at 50–100 °C, followed by adding 15–40 ml of 99% triethylamine (w/w) for graft reaction, stirring the mixtures for 3 h at 50–100 °C.

The primary product was washed with 500 ml of distilled water to remove the residual chemicals, then dried at 60 °C for 12 h and sieved to obtain particles of less than 250 μm. The final product was obtained after a second cycle of washing, drying and sieving. It was used in all adsorption experiments [12,15].

The synthetic reactions of WR-QE using WR as a starting material are shown in Fig. 1 (cellulose as example). The reaction between epichlorohydrin and cellulose was induced after the hydroxyl groups in the cellulose molecule activated, producing hydroxy cellulose ether [16]. The hydroxy cellulose ether was then cyclized by the catalyst existing in the alkaline condition to produce the epoxy cellulose ether that was used as the intermediate in the reaction; the WR-QE was obtained after the graft reaction between epoxy cellulose ether and triethylamine [5,12].

2.3. Characteristics of WR-QE

2.3.1. The yield (%) and zeta potential (mV)

The yield of WR-QE can intuitively reflect the reaction efficiency of the preparation of WR-QE by comparing the dry weight of WR-QE and WR. The yield was determined gravimetrically using the following equation:

$$\text{Yield}\,(\%) = \frac{m_1}{m_0} \tag{1}$$

where m_1 and m_0 are the dry weight of WR-QE and WR, respectively. The lower bound of the yield is about 80% with the impurity in WR extracted after an unsuccessful synthesis, and the theoretic upper bound of the yield is evaluated at about 600–700% after the sufficient reaction of organic chemicals with WR.

The new anion exchanger prepared from WR is used for the removal of anionic pollutant. As a result, it is significant to determine the change of surface charge of WR-QE in comparison with WR. Zeta potential of WR-QE and WR were determined by electrokinetic analyzer (JS94H, Shanghai Zhongchen Digital Technical Apparatus Co., Ltd., China).