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Nitrate adsorption by stratified wheat straw resin in lab-scale columns

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HIGHLIGHTS

- A resin prepared from wheat stalk was pilot-scale produced and applied in a column.
- The column was stratification-packed with different lengths of resins.
- Adams–Bohart and Thomas models were applied for analyzing all these parameters.

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ABSTRACT

A continuous adsorption study for nitrate removal was carried out by using pilot-scale produced wheat straw anion resin in batch lab-scale columns. Effect of resin widths on column adsorption was first evaluated and then a stratification-packed column with different widths of resins was applied. The nitrate uptakes by different bed depth (3.6, 5.6 and 9.8 cm) of stratified columns were 35.3, 28.1 and 23.2 mg/g, respectively. The better performance for this stratified column was observed at neutral condition, and marginally decreased with pH variation on both acidic and basic sides. The nitrate adsorption capacity was optimum at lower flow rates. In addition, Adams–Bohart and Thomas models were applied for analyzing all these parameters. The results showed that the Thomas model was suitable for the description of breakthrough curve at all experimental conditions, while Adams–Bohart model was only for an initial part of dynamic behavior of the column.

1. Introduction

Water pollution due to the excessive discharge of nitrate from agricultural application and mineral industries has become a serious environmental problem worldwide [1,2]. Excess nitrate in ground water may cause the eutrophication of aquatic environment [3]. Eutrophication comprises the growth of algae and depletion of dissolved oxygen, which in turn affects the aquatic life [1]. In addition, drinking water containing excess nitrate may cause various health problems such as infant methemoglobinemia and cyanosis syndrome [1,4]. Considering the health effects, a guideline value of 45 mg/L of nitrate (equivalent to nitrate-nitrogen of 10 mg/L) was suggested by WHO as maximum permissible level of nitrate in drinking water [4].

Several physicochemical (chemical reduction, coagulation, adsorption, electrodialysis, filtration, reverse osmosis) and biological processes (bacterial assimilation, harvesting of algae, oxidation ponds) have been developed for the removal of nitrate from drinking water and wastewaters [5–12]. Among them, adsorption techniques are promising since they allow economical and simple operation. In addition, most adsorptive materials are regenerable so adsorption techniques cause less sludge production and fewer disposal problems. Recently, some adsorbents that prepared from natural waste materials (especially from biomass waste materials) have been used for the removal of nitrate. Various biomass waste materials, such as rice bran, wheat bran, sawdust of various plants, groundnut shells, coconut shells, walnut shells, cotton seed hulls, waste tea leaves, sugarcane bagasse, chinese reed, giant reed, banana, orange peels, soybean hulls, sugar beet pulp, and cotton stalks have been tried [13–19]. These biomaterials can be easily activated into some porous-structure adsorbents (activated carbons) or modified into anion exchange resins by cross-linking with some functional groups so as the adsorption capacity for nitrate as well as rate adsorption is enhanced.

Some biomaterials based activated carbons have been commercially used for anions removal. However, rare literatures were reported regarding to pilot-scale or commercial products of biomaterials based anion exchange resins. In our previous work, coir stalk, cotton stalk, giant reed and wheat stalk have been lab-scale produced and these biosorbents have shown excellent adsorption capacities for various anions [9,20–22]. As a continuation of our previous work, an anion resin originated from wheat stalk was pilot-scale produced in this research and its adsorption capacity for nitrate in fixed-bed column was intensively

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investigated. The stratification-packed column with different widths of resins was particularly designed. Nitrate adsorption characteristics in the fixed-bed column were studied by varying the influent parameters, such as bed depth, influent concentrations, flow rates and pH. These parameters were then analyzed using Adams–Bohart and Thomas models.

2. Methods and materials

2.1. Preparation of WS-AR in pilot-scale reactor

The pilot-scale production of wheat stalk anion resins was conducted in a jacketed enamel reactor (1 m^3). All chemicals used in pilot-scale test were industrial grade. Wheat straw was purchased from Zhouping, Shandong province, China. The virgin wheat straw was smashed to pieces with 0.02–0.5 cm by the vertical type mill. These smashed wheat straw (100 kg) was then transferred into the reactor and preheated at 85–90 °C by the water bath heating.

Epichlorohydrin (32 kg) and N,N-dimethylformamide (20 kg) were first fed into the reactor by the dosing system (Fig. 1) and all mixtures were stirred for 2 h at 90 °C. Ethylenediamine (5 kg) and dimethylamine (25 kg) were then added in sequence and the whole system was further operated for 3 h. Thereafter, the products were dried by the pneumatic dryer and then were sieved to three different widths of resins (0.02–0.05 cm, 0.05–0.2 cm and 0.2–0.5 cm).

2.2. Fixed-bed column studies

An organic-glass column with length of 20 cm and internal diameter of 1.2 cm was employed for the fixed-bed column adsorption studies. Effect of resin widths on column adsorption was first investigated. As shown in Fig. 2, three different resins with widths of 0.02–0.05 cm, 0.05–0.2 cm and 0.2–0.5 cm were filled into their respective columns. The filled resins in all three columns were 1.0 g. In particular, a stratified column packed with different widths of resins (0.3 g, 0.4 g and 0.3 g of resins with width of 0.02–0.05 cm, 0.05–0.2 cm and 0.2–0.5 cm, respectively) was also used in this test (Fig. 2). The flow rate, influent nitrate concentration and pH were constant at 10 mL/min, 100 mg/L and 6.0, respectively. Samples were collected at regular intervals. The nitrate concentration was determined spectrophotometrically according to the Brucine-sulfanil colorimetric method [9], using a UV–visible spectrophotometer (model UV754GD, Shanghai).

In addition, effects of the following column parameters on nitrate adsorption were also investigated. (i) Effect of bed depth: bed depth (stratified column) was varied between 3.6 cm (1.0 g), 5.6 cm (1.6 g) and 9.8 cm (2.8 g), keeping flow rate, influent nitrate concentration and pH constant at 10 mL/min, 100 mg/L and 6.0, respectively. (ii) Effect of pH: the influent pH was monitored at 3.0, 6.0, 8.0 and 11.0, while flow rate (10 mL/min), influent nitrate concentration (100 mg/L), and bed depth (3.6 cm) were held constant. (iii) Effect of flow rate: flow rate was controlled within 5–25 mL/min with influent nitrate concentration, pH and bed depth constant at 100 mg/L, 6.0 and 3.6 cm, respectively.

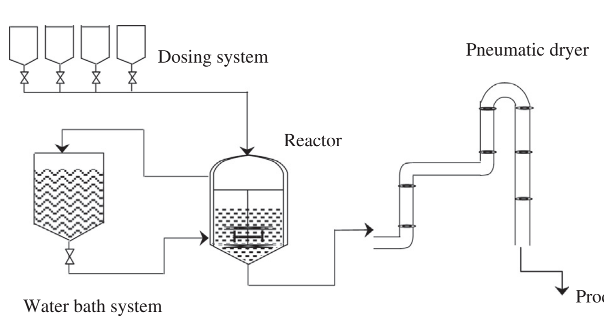

Fig. 1. Preparation of wheat stalk anion resins in pilot-scale test.

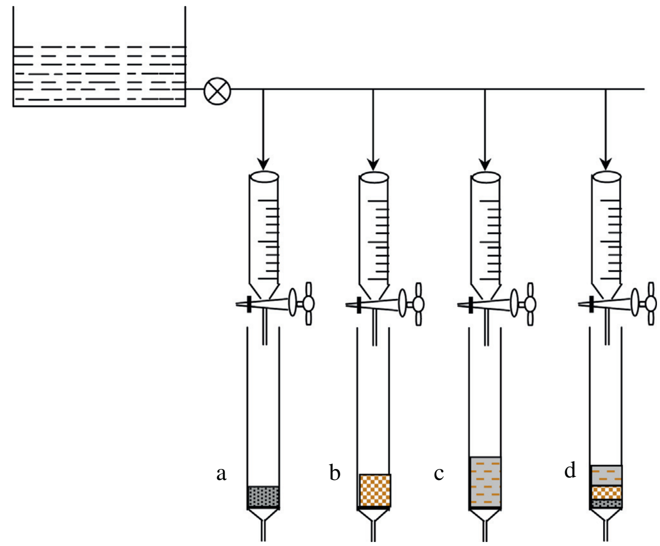

Fig. 2. Experimental set up for fixed-bed column study (resin widths and stratified column tests) (a) column with resin width of 0.02–0.05; (b) column with resin width of 0.05–0.2; (c) column with resin width of 0.2–0.5; and (d) stratified column.

2.3. Column data analysis

The performance of column is usually evaluated with the concept of breakthrough curve. The effluent adsorbate concentration (C_t) from the column that reaches about 5% of the influent adsorbate concentration (C_0) is the breakthrough point. The point where the effluent concentration reaches 95% is usually called the "point of column exhaustion". The breakthrough curve can be obtained by plotting the dimensionless concentration C_t/C_0 versus time or volume of the effluent. The effluent volume, V_{eff} (mL), is calculated from the following equation:

$$V_{\text{eff}} = Qt_{\text{total}} \tag{1}$$

Total mass of nitrate, q_{total} (mg), adsorbed at specific column parameters can be calculated from following equation:

$$q_{\text{total}} = \frac{Q}{1000}\int_0^{t_{\text{total}}} C_{\text{ad}}dt = \frac{Q}{1000}\int_0^{t_{\text{total}}} (C_0 - C_t)dt \tag{2}$$

where Q is the volumetric flow rate (mL/min), t_{total} is the total flow time (min), C_{ad} is adsorbed nitrate concentration (mg/L). The integral in Eq. (2) is equal to the area in the breakthrough curve.

Maximum capacity of the column or equilibrium nitrate uptake per unit mass of resin, $q_{eq(exp)}$ (mg/g), is calculated as following:

$$q_{\text{eq(exp)}} = \frac{q_{\text{total}}}{M} \tag{3}$$

where M is the dry weight of resin packed in the column (g).

Total amount of nitrate passing from the column (m_{total}) and total removal percentage of nitrate (Y%) are calculated from the following equation:

$$m_{\text{total}} = \frac{C_0 Q t_{\text{total}}}{1000} \tag{4}$$

$$Y(\%) = \frac{q_{\text{total}}}{m_{\text{total}}} \times 100 \tag{5}$$