

Nitrate removal from water by new polymeric adsorbent modified with amino and quaternary ammonium groups: Batch and column adsorption study



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ABSTRACT

A new polymeric adsorbent (NDQ) modified with amino and quaternary ammonium groups was synthesized for the purpose of nitrate removal from water. Sorption kinetic and isotherm experiments were carried out in a series of batch experiments. Batch adsorption isotherms indicated that the maximum monolayer adsorption capacity of NDQ for nitrate was 221.8 mg/g which was higher than that of many other adsorbents reported in literature. Both ion-exchange and hydrogen bond played important roles in nitrate removal. The enthalpy change (-12.32 to -9.65 kJ/mol) and free energy change (-2.7 to -0.76 kJ/mol) indicated an exothermic and spontaneous adsorption process. Moreover batch adsorption kinetic curves indicated that both film and intra-particle diffusion processes were rate-limiting in the nitrate adsorption. It was observed that the adverse effect of co-existing anions on nitrate removal followed the order of $\text{SO}_4^{2-} > \text{HCO}_3^- > \text{Cl}^-$. In order to quantify the influence of operational conditions on the treatment efficiency, a series of fixed bed column experiments were conducted at different bed heights, flow rates and influent concentrations, and the breakthrough curves at various operational conditions were simulated and analyzed using different mathematical models. Finally, the adsorption-desorption assay showed a promising reusability of the NDQ.

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1. Introduction

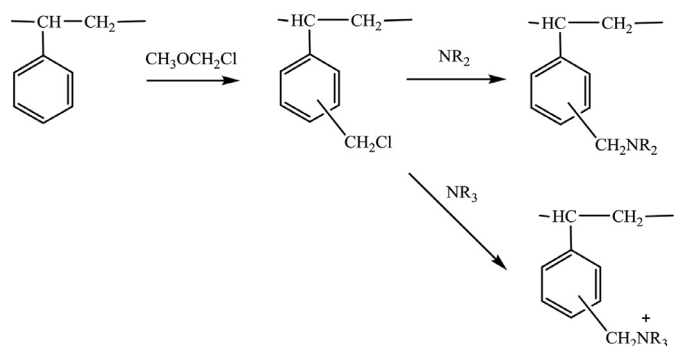
Water pollution due to the high concentrations of nitrogen species is a severe problem in recent years worldwide. Agricultural, industrial and household waste water are the major sources of nitrates in the surface and ground water. Many investigations indicate that high nitrate concentration in water is related to eutrophication in the aquatic environment [1–3]. Excessive level of nitrate in drinking water could potentially cause human health problems such as blue-baby syndrome in infants and stomach cancer in adults [2]. The recommended nitrate concentration limit in the drinking water by WHO and the Chinese Ministry of Health was 10 mg/l ($\text{NO}_3^- - \text{N}$) [4].

Many different techniques are used to remove nitrate from water including adsorption/ion exchange, biological de-nitrification, chemical denitrification, electrodialysis and reverse osmosis *etc.* [5–10]. Among these technologies, adsorption/ion exchange was

generally considered as one of the most simple and efficient method [11,12]. A number of natural and synthetic materials including carbon-based adsorbents [13,14], agriculture wastes [15,16] and synthetic resins [17,18] were used as adsorbents for the nitrate removal from various wastewater and surface water. However, most of these adsorbents exhibited relatively low removal efficiency due to the high solubility of nitrate. During the last decade, polystyrene anion exchange resins have become more popular due to the high adsorption capacity and simple operation. The synthetic process of polystyrene anion exchange resin is presented in the Scheme 1. Usually the chloromethyl content of the chloromethylated cross-linked polystyrene (P-Cl) ranges from 10% to 20% [19], which limits the modification of excessive amine groups on the P-Cl. Therefore, the total ion-exchange capacity (TEC) of major anion exchange resins reported in literatures ranges from 2.0 to 4.0 meq/g [19–23]. It is known that the adsorption capacity of anion exchange resin for nitrate is dependent on its TEC. Thus, new method to prepare anion exchange resin with high anion exchange capacity still remains to be developed.

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Scheme 1. Synthetic method of traditional polystyrene anion exchange resin ('R' represent of alkyl).

In the present work, a new type of polystyrene resin NDQ modified with both amino and quaternary ammonium groups was synthesized by a special method in this work. Compared with traditional anion exchange resin, NDQ has higher TEC and adsorption capacity for nitrate. The present study is focused on the following aspects: (1) adsorption behavior of nitrate using NDQ, including the thermodynamic and kinetics, in batch experiments; (2) the influence of pH and coexisting anions on nitrate adsorption by NDQ; (3) modeling of fix-bed column adsorption experiments with different bed heights, inlet concentrations and flow rate; (4) evaluation of reusability of NDQ for five adsorption–desorption cycles.

2. Material and methods

2.1. Materials

Chloromethylated cross-linked polystyrene (P-Cl) was purchased from Aladdin Reagent Company Limited in Shanghai. 3-chloro-2-hydroxypropyltrimethylammonium chloride (analytical-grade) and hexamethylenetetramine were purchased from J&K Scientific Ltd. All other organic chemicals were analytical-grade. Stock

solution of nitrate was prepared by dissolving 1.000 g of sodium nitrate in 1 l of deionized water.

2.2. Preparation and characterization of NDQ

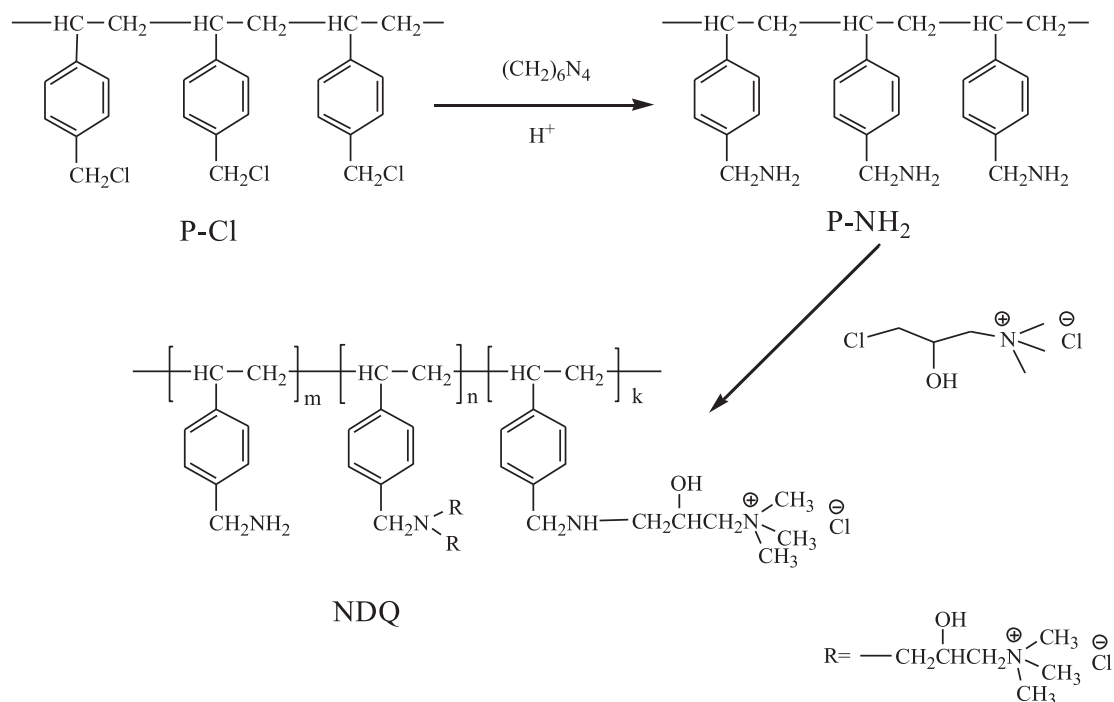
The preparation of NDQ was described as follows and shown in Scheme 2:

- (1) Amination: 5.0 g P-Cl was immersed into the mixture solution of ethanol and chloroform for 5 h. Then 5.0 g of hexamethylenetetramine was added into the flask. The reaction mixture was mixed at 318 K for 7 h continuously. Afterwards, the copolymers was first washed with ethanol and then with 100 ml HCl solution (37.5%) with agitated stirring for 2 h. Then NaOH was added in order to maintain the pH > 14 in the reaction solution for 3 h. At the end, the mixture was filtered and washed with deionized water to harvest the Rs-Ph-CH₂-NH₂ (P-NH₂).
- (2) Quarternization: 2.0 g P-NH₂ was added into the mixture of 3-chloro-2-hydroxypropyltrimethylammonium chloride and 2 M NaOH. The mixture was then stirred at 343 K for 2 h. The product (NDQ) was filtered and washed with 1 M NaCl solution.
- (3) Nitrate concentration was determined using the Dionex ICS-1000 ion chromatography (United States). FT-IR spectra of P-Cl, P-NH₂ and NDQ were analyzed by a spectrophotometer (NICOLET 6700 FT-IR), and the spectra were recorded in the wave number ranging from 400 to 4000/cm. BET tests were carried out at 77 K to determine the surface area and the pore size based on BJH model using Micromeritics ASAP 2020 (U.S.). The TEC of NDQ was determined following the method described by Zhou et al. [22].

2.3. Batch experiments

2.3.1. Adsorption isotherms

Nitrate solutions of various concentrations were prepared by successive dilution of the stock solution in deionized water. Equilibrium adsorption of nitrate using NDQ were conducted in 150 ml



Scheme 2. Preparation process of NDQ (*m*, *n* and *k* represent of the numbers of each unit).

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