Adsorption kinetics of nitrate ions on ion exchange resin

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HIGHLIGHTS

- Empirical and theoretical kinetic models described nitrate adsorption process well.
- The empirical model constants depended on the experimental conditions.
- Theoretical models described the experimental data with greater precision.
- Film diffusion model and particle diffusion model were the superior kinetic models.
- Column adsorption process was modeled satisfactorily by particle diffusion model.

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ABSTRACT

The aim of this study is to compare empirical (pseudo first-order, pseudo second-order, and Elovich models) and theoretical models (second order chemical reaction rate, film diffusion, and particle diffusion models) in the modeling of nitrate uptake by ion exchange resin. The modeling showed that the pseudo first and second order models describe the experimental kinetic data satisfactorily; however, the estimated rate constants varied significantly with the experimental conditions. In comparison with empirical models, theoretical models describe the experimental data with higher precision. In addition, the relative differences between the computed constants of each theoretical model are much less than the estimations of empirical models. The estimated constants of film diffusion model and particle diffusion model for different sets of experimental data were close to the average values, confirming that these models are indeed superior when it comes to the description of the kinetics of nitrate removal. Finally, the performance of ion-exchange column was evaluated using the particle diffusion model in conjunction with mass balance equation in column, with the results of the model predictions being compared to the experimental breakthrough curves. The selected mathematical equations reproduced the experimental breakthrough data very well.

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1. Introduction

Nitrate is one of the most common pollutants of water resources in many parts of the world. The elevated nitrate concentration in drinking water is a serious hazard to human health, causing abnormalities such as cancerous growths in the human digestion system and blue baby syndrome (also called methemoglobinemia) in infants less than six months old. Furthermore, the presence of nitrate and phosphate in waterways can stimulate eutrophication, which compromise the growth of algae and depletion of dissolved oxygen [1–6]. Natural and chemical fertilizers used in crop production, detergent manufacturing, uncontrolled land discharge of municipal wastewater, and industrial wastes have been identified as the main sources of nitrate in water sources [3,7–9].

Nitrate is a stable, highly soluble ion that is difficult to remove by conventional water treatment methods such as coagulation, flocculation, lime softening or surface adsorption processes [4,7,10–12]. Ion exchange is one of the most widely employed procedures used for removing nitrate, especially at points of entry into water distribution systems such as well sites. This process is simple to operate, design and monitor, while also being a cost-effective method for the direct treatment of groundwater at well sites [4,5,9,10,12–14]. Both conventional anion exchange resins and nitrate-to-sulfate selective ion exchange resins have been used in studies on nitrate removal. Several of these ion exchange resins have been reported in our previous work [15]. In almost all of these studies, the rate of nitrate removal has been

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described by empirical kinetic models such as pseudo first and second order models. These models have been originally derived for adsorption processes. However, these models do not provide any information regarding the real kinetics of ion exchange mechanisms, which are based on mass transfer resistances [5,13,16–23]. A suitable kinetic model can be used for design purposes to predict column behavior in water treatment plants [24–26].

In a recent study by Hekmatzadeh et al. [15], the equilibrium data obtained in different experimental conditions were modeled and compared using the Langmuir adsorption isotherm and the mass action law. Afterward, the breakthrough curves from column experiments were predicted based on the batch equilibrium data by using the mass action isotherm [15]. To the best of our knowledge, few efforts can be found in the literature to describe the ion exchange kinetic experimental data with both empirical and theoretical models and compare these models to each other. No comparison was found regarding nitrate ion removal using ion exchange resins. Additionally, relatively little research has been carried out to predict the nitrate breakthrough curve of a column experiment packed with ion exchange resin using a suitable kinetic model [3–5,9,13,14,20,27].

The main objective of this study is to investigate the rate of nitrate uptake by a selective resin using both empirical and theoretical kinetic models and compare the results to find the best kinetic models. The pseudo first-order, pseudo second-order, and the Elovich equations were the three empirical models considered for this study, while the second order chemical reaction rate, film diffusion, and particle diffusion models represent the theoretical models used to describe the kinetic data. Additionally, column performance was evaluated using a suitable kinetic model in conjunction with the mass balance equation in columns and the results of the model predictions were compared to the experimental breakthrough curves. In order to solve the model equations, a set of differential equations was solved numerically using the Crank–Nicholson scheme in MATLAB software and an optimization technique was employed to optimize the model parameter.

2. Experimental

2.1. Materials

IND NSSR resin, obtained from Ion Exchange India LTD, was used throughout the experiments. This product is a macroporous, strongly basic anion exchange resin with effective particle sizes of between 0.4 and 0.5 mm, suitable for the removal of nitrate from water. The resin has a styrene divinyl benzene copolymer matrix with the quaternary ammonium functional group and chloride as exchangeable anions. This resin has more affinity for nitrate ions in comparison with sulfate ions. Before use, the resin particles were washed with distilled water in order to remove any adhering dirt. Afterward, the resin particles were dried at an oven temperature of 60 °C for 24 h. The nitrate solutions used in the experiments were prepared synthetically by dissolving $NaNO_3$ powder in distilled water using Merck products. The concentration of the nitrate ions was analyzed via a HACH DR/5000 UV spectrophotometer instrument at a wavelength of 220 nm. The spectrophotometer was calibrated with reference solutions at specified nitrate concentrations. The accuracy of calibration was also confirmed using an ion chromatography instrument (Metrohm 761). For each experiment three samples were analyzed by UV spectrophotometer and the averages are reported in the manuscript. Before measurement, 50 ml of the samples was acidified with 1 ml of 1.0 N HCl in order to eliminate the effect of interfering ions.

2.2. Batch experiments

In order to investigate the adsorption performance of nitrate on resin particles, several batch kinetic experiments were carried out in duplicate using a temperature-controlled rotating shaker under different operating conditions. Specified amounts of dry resins, ranging from 0.05 to 0.5 g, were added to several glass bottles containing 200 ml of nitrate solution with initial nitrate concentrations of 58.9, 87.25, 119.4, and 153.2 mg/l. The sealed bottles were placed on the rotating shaker spinning at a speed sufficient to keep the bottle contents well-mixed. The samples were then withdrawn from the shaker at predetermined time intervals to measure the nitrate concentration. Moreover, three samples were analyzed for each experiment by means of a UV spectrophotometer and the averages were used for modeling purposes. After shaking, the resulting mixture of particles and solution was separated using a Whatman filter paper. In order to determine the sufficient rotating speed of the shaker, three sets of batch kinetic experiments were conducted at rotating speeds of 50, 80, and 120 rpm, respectively. In these experiments, the resin mass and the initial nitrate concentration were 0.15 g and 120.2 mg/l, respectively. The experimental kinetic data of these experiments were nearly overlapping and consequently the overall rate of adsorption was not influenced by the speed of the shaker in the range of 50 to 120 rpm. Therefore, the rest of the experiments were carried out at a fixed rotating speed of 50 rpm. In addition, batch equilibrium experiments were performed to determine the optimum resin dosage. Different precise amounts of resin (0.025 to 0.7 g) were added to 200 ml of nitrate solution and kept in shaker for 24 h to reach equilibrium. The experiments were carried with initial nitrate concentrations of 56, 87, and 118 mg/l. In all experiments, the temperature was kept at a constant 20 °C with a maximum tolerance of 0.1 °C. The solid phase concentration of nitrate on resin particles at any time, q_t (meq/g), was computed using the following mass balance equation:

$$q_t = \frac{(C_0 - C_t)V}{M} \tag{1}$$

where C_0 (meq/l) is the initial nitrate concentration in the solution, C_t (meq/l) is the concentration at any time, and V (l) and M (g) are the volume and the resin mass, respectively.

2.3. Column experiments

A schematic of the column setup used for the fixed bed experiments is shown in Fig. 1. Column tests at flow rates of 2.11, 1.40, and 0.69 l/h were performed using a glass column with an internal diameter of 3.6 cm. At both ends of the resin bed, a glass-ball layer was applied to avoid the loss of resin. The synthetic nitrate solution was introduced upwardly through the column at a specific flow rate to ensure the complete saturation of the resin bed. In addition, a peristaltic pump was used to preserve a constant flow rate during the experiments. The
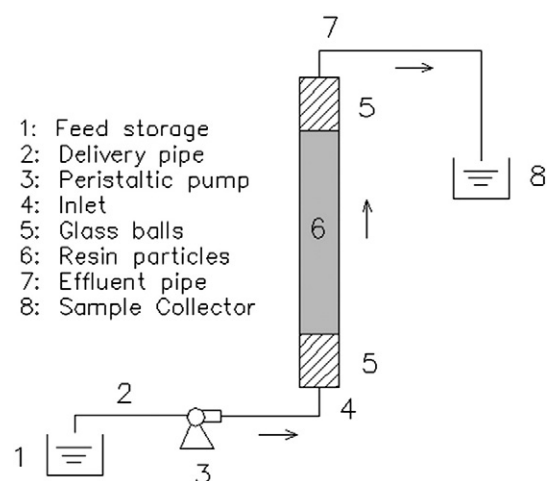

1: Feed storage
2: Delivery pipe
3: Peristaltic pump
4: Inlet
5: Glass balls
6: Resin particles
7: Effluent pipe
8: Sample Collector

Fig. 1. Experimental setup for column tests.