Separation and Purification Technology 158 (2016) 62–70

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Removing nitrate from water using iron-modified Dowex 21K XLT ion exchange resin: Batch and fluidised-bed adsorption studies

Mahatheva Kalaruban, Paripurnanda Loganathan, W.G. Shim, Jaya Kandasamy, Gayathri Naidu, Tien Vinh Nguyen, Saravanamuthu Vigneswaran *

Faculty of Engineering, University of Technology Sydney (UTS), P.O. Box 123, Broadway, NSW 2007, Australia

ARTICLE INFO

Article history:
Received 8 September 2015
Received in revised form 11 November 2015
Accepted 11 December 2015
Available online 11 December 2015

Keywords:
Nitrate
Adsorption
Dowex
Ion exchange resin
Adsorption models
Fluidised-bed adsorption

ABSTRACT

Elevated concentrations of nitrate in surface waters can cause eutrophication, while in drinking water they pose a threat to human health, especially causing blue baby syndrome in infants. An anion exchange resin – Dowex 21K XLT – was surface modified by incorporating Fe (Dowex-Fe) and tested to remove nitrate from aqueous solutions in batch and fluidised-bed adsorption experiments. Solution pH in the 4.0–7.5 range had no effect on nitrate adsorption. The adsorption data at pH 6.5 fitted well to the Langmuir model with maximum adsorption capacities of 27.6 mg N/g, and 75.3 mg N/g for Dowex and Dowex-Fe resins, respectively. Energy dispersion spectrometry and zeta potential measurements indicated that the increase in adsorption due to Fe impregnation was caused by additional surface positive charges induced on the resin by Fe. In both batch and fluidised-bed experiments, nitrate adsorption capacity declined markedly when sulphate was added, but phosphate and chloride additions had little effect. Batch kinetic data fitted well to the pseudo-first, pseudo-second and homogeneous surface diffusion models. Data from the fluidised-bed experiments satisfactorily fitted to the Thomas and plug-flow models. More than 95% of adsorbed nitrate was desorbed by 1 M KCl in all three adsorption/desorption cycles and the resins were successfully regenerated in each cycle with little reduction in adsorption capacity. No significant reduction in the Fe content of Dowex-Fe occurred during the regeneration.

1. Introduction

Nitrate is a contaminant that greatly affects the quality of water. Nitrate concentration in surface water and groundwater increases because of excessive use of inorganic and organic fertilisers in agriculture, and input from animal wastes and leakages from sewerage systems. One of the most serious environmental problems concerning nitrate pollution is eutrophication of natural water bodies such as rivers and lakes; it affects fish and other aquatic life and recreational use of water [1]. High nitrate levels in drinking water can also cause 'blue baby syndrome' or methemoglobinemia especially in infants. Severe methemoglobinemia can result in brain damage and death [2,3]. The nitrate concentration limit recommended for drinking water by WHO and the European Union is 50 mg/L (11.3 mg N/L) [4]. In Australia, the recommended nitrate limit is 50 mg/L for infants up to 3 months old and 100 mg/L for adults and children over the age of 3 months [5].

Several nitrate removal technologies have been used in water treatment, for example ion exchange, reverse osmosis, adsorption and chemical and biological methods [6,7]. Of these methods, adsorption is the best choice because of its relatively low operational costs, simplicity, and minimal production of waste [8]. However, this method's efficiency depends highly on the type of adsorbent. Nitrate removal studies have been conducted in the past with several adsorbents such as ion exchange resins, zeolite, fly ash, red mud and agricultural wastes [6]. Of these materials, strong base anion exchange resins generally have high nitrate adsorption capacity [9]. Indion NSSR [10], Amberlite IRN-78 [11], Amberlite IRA 400 [12], Imac HP555 [13], and Purolite A100 [14] are some ion exchange resins that have been used to remove nitrate. However, most studies on ion exchange resins for removing nitrate have been conducted in static batch experiments, while only a few were done in dynamic column experiments. These latter ones are more relevant to water treatment conditions in the field.

Recently, Nur et al. [15] compared the nitrate adsorption capacities of the anion exchange resins, Dowex 21K XLT, Purolite A520E, Purolite A500P and Purolite FerrIX A33E in batch experiments. They found that Purolite A520E and Dowex 21K XLT had the

---

* Corresponding author.
E-mail address: s.vigneswaran@uts.edu.au (S. Vigneswaran).

http://dx.doi.org/10.1016/j.seppur.2015.12.022

highest nitrate removal efficiencies of 75% and 70%, respectively, from a solution containing 20 mg N/L for an adsorbent dose of 1.5 g/L. However, they conducted a detailed nitrate adsorption study using column mode experiments only on Purolite A520E. For this reason a similar study is needed on Dowex 21K XLT.

The adsorption capacity of anion exchange resins can be increased by impregnation of metals which increases the surface positive charges [7]. Increment of positive charges on the surface would increase the adsorption of negatively charged ions such as nitrate by electrostatic attraction. For example, Namasivayam and Sangeetha [16] impregnated Zn on coconut coir pith and found that the adsorption capacity for nitrate increased from a negligible amount to 10.3 mg NO_3^-/g. They reported that the improved adsorption capacity was due to increased positive charges, surface area and pore volume of the adsorbent by adding metal ions. In another study, granular activated carbon (GAC) produced from coconut shells was modified with $ZnCl_2$ and tested for nitrate removal [17]. The adsorption capacity significantly increased via this metal impregnation method. No studies, however, have been conducted on metal impregnation on anion exchange resin for removing nitrate, although a few such studies have been reported for phosphate removal [18,19]. For the adsorption process to be cost-effective the adsorbent needs to be satisfactorily regenerated for repeated use. Such studies on modified ion exchange resins are also rare.

The objectives of the research were to: (i) study the efficiency of nitrate removal from synthetic water using iron-modified and unmodified Dowex 21K XLT ion exchange resin in batch and fluidised-bed adsorption experiments; (ii) model the equilibrium, kinetics and column data on nitrate removal; (iii) determine the effect of pH and co-existing anions on the adsorption of nitrate; and (iv) investigate desorption of nitrate from the resin and the regeneration of adsorbent for multiple reuse.

2. Materials and methods

2.1. Ion exchange resin

Dowex 21K XLT, a strong base anion exchange resin was obtained from Dow Chemical Pte Ltd., USA [20]. It consists of a quaternary methylamine functional group with chloride as the counter ion, which gives it the ability to exchange with other anions. The physical state of the Dowex anion exchange resin was yellow spherical beads with particles 0.3–1.2 mm in diameter and a density of approximately 1.08 g/mL.

Dowex resin was modified by impregnation of iron (Dowex-Fe). In the impregnation method, 10 g Dowex resin was mixed with 1 L of $FeCl_3{\cdot}6H_2O$ (2.0 g Fe^{3+}/L) for 1 h in a shaker at a speed of 120 rpm [19]. Then pH was increased to 8.0 by slowly adding 1 M NaOH solution for 3 h. The mixing speed was reduced to 30 rpm and the suspension was continuously mixed for 24 h. The resin was then filtered and rinsed with deionised water to remove unreacted Fe and dried in an oven set at 45 °C for 24 h.

2.2. Feed solutions

Synthetic water was prepared using Milli-Q water and ANALAR grade KNO_3 to obtain a concentration of 20 mg N/L for use in the batch experiments. The ionic strength was maintained at 1×10^{-3} M NaCl and the pH adjusted to 6.5 using a HQ40d portable pH metre by adding dilute HCl and NaOH. These ionic strength and pH were chosen because local storm waters were reported to have this ionic strength (electrical conductivity 0.74 dS/m) and average pH of 7.0 which is close to the pH selected [21]. For the ion competition studies the synthetic water was prepared with ANALAR grade KH_2PO_4 and Na_2SO_4. For the fluidised-bed adsorption studies an aqueous solution containing 20 mg N/L was prepared using tap water instead of Milli-Q water. This is because large volumes of Milli-Q water required for the long-term column study were not available. The pH of this solution was 6.5–7.5.

2.3. Nitrate analysis

Nitrate concentration was analysed by an ion chromatograph (Model 790 Personal IC) equipped with an auto sampler and conductivity cell detector. The ion chromatograph was cleaned before the analysis using a mobile phase solution (Na_2CO_3, $NaHCO_3$), diluted sulphuric acid and Milli-Q water.

2.4. Characteristics of materials

Scanning electron microscope (SEM) images and energy dispersion spectrometry (EDS) results were obtained using the scanning electron microscope (Zeiss Supra 55VP Field Emission) in conjunction with energy dispersion spectrometry operated at 15 kV. This instrument was employed to examine the dried Dowex, Dowex-Fe and nitrate adsorbed materials. The BET surface area and porosity were measured by Micrometrics 3 Flex surface characterisation analyser at 77 K.

Zeta potential measurement was conducted to determine the electrical potential at the boundary of the hydrodynamic shear plane of the charged adsorbents. The zeta potential is related to the surface charge on the adsorbents. The Dowex and Dowex-Fe were ground to a smaller size so they could be suspended, and 0.1 mg of these materials were added to 100 ml Milli-Q water and pH adjusted to 4–8 using dilute HCl and NaOH solutions. The flasks were agitated at a speed of 120 rpm and then zeta potential was measured using a Zetasizer nano instrument (Nano ZS Zen 3600, Malvern, UK). A chemical analysis was conducted to determine the Fe content in Dowex-Fe. 0.1 g of Dowex-Fe was ground and then heated with 5 ml HNO_3 and 5 ml HCl at 100 °C for 5 h. The samples were then diluted to 40 ml with 30 ml Milli-Q water and Fe concentration was determined by microwave plasma-atomic emission spectrometer (Agilent 4100 MP-AES).

2.5. Batch studies

Equilibrium adsorption and kinetic adsorption experiments were conducted using the modified and unmodified anion exchange resin Dowex 21K XLT. All adsorption experiments were conducted at 24 ± 1 °C.

2.5.1. Equilibrium adsorption

To 100 ml synthetic water containing 20 mg N/L and ionic strength of 1×10^{-3} M NaCl at pH 6.5 in a set of glass flasks, different amounts of adsorbents were added to provide adsorbent dosages of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 g/L. The flasks were agitated in a shaker at 120 rpm for 24 h. The supernatant solution was then filtered using filters with 1.2 μm openings and analysed for nitrate using an ion chromatograph analyser (Model 790 Personal IC). The amount of nitrate adsorption at equilibrium, q_e (mg/g), was calculated using the equation given below [22]:

$$q_e = \frac{(C_0 - C_e) \cdot V}{M} \tag{1}$$

where C_0 is initial concentration of nitrate (mg N/L), C_e is equilibrium concentration of nitrate (mg N/L), V is volume of solution (L) and M is mass of adsorbent (g).

Percentage adsorption was calculated using Eq. (2) as follows: