

Nitrate removal from water by ion exchange

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Summary

High concentrations of nitrate in water, both in surface and in groundwater, is a consequence of geological composition of soil or human activity. Increased concentrations of nitrate in drinking water is a serious hazard to human health, causing abnormalities such as cancerous growth in human digestion system, while excessive nitrate intake via drinking water can cause methemoglobinemia in infants. Furthermore, the presence of nitrate in aquifers can stimulate eutrophication, which compromise the growth of algae and depletion of dissolved oxygen. Natural and chemical fertilizers 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. Nitrate is a stable, highly soluble ion that is difficult to remove by conventional water treatment methods such as coagulation and flocculation. The ion exchange is the most widely used procedure for removing nitrate from water. In this research the possibility of removing nitrate from water was examined by using commercial ion exchangers: Duolite A7 and Relite A490, respectively. The influence of the initial concentration of nitrate (10, 50 and 100 mg/l), the contact time (15 - 1440 min) and the mass of the ion exchanger (0.1 to 0.6 g) was also examined.

Keywords: nitrate, water, nitrate removal, ion exchange

Introduction

Groundwater is the most common source of drinking water in many parts of the world. However, in the last few decades, there is an increasing concern about the quality of groundwaters due to the presence of toxic pollutants such as inorganic anions, metal ions, synthetic organic chemicals and others (Velizarov et al., 2004). Elevated nitrate concentrations in the environment can cause various damages to humans and aquatic life (Sowmya and Meenakshi, 2014). The most common sources of nitrate in surface and groundwater are mainly from human and animal wastes and the use of fertilizers. In addition, municipal and industrial wastewater discharged on land are potential cause of high nitrate concentrations. High nitrate concentrations can stimulate heavy algal growth using eutrophication in water bodies. After ingestion of water or plants with high nitrate concentrations, acute poisoning in cattle can occur within few hours (Bhatnagar and Sillanpää, 2011). In humans, elevated nitrate concentrations can cause methemoglobinemia in infants and the formation of carcinogenic nitrosoamines (Lundberg et al., 2006). Having in mind that serious consequences are linked to high nitrate concentrations in water for human consumption, various environmental regulatory agencies have set a maximum contaminant level of 50 mg/L of NO_3^- in water for human consumption (Council Directive 98/83/EC, 1998).

Nitrate is a highly soluble and stable ion in water. Therefore, some techniques have been employed for efficient removal from water, such as adsorption, ion exchange, reverse osmosis and biological treatments. Some of these methods have high operational costs (Kalaruban et al., 2016). The ion exchange process seems to be the most suitable for small water suppliers because of its simplicity, effectiveness and relatively low cost. There are several nitrate selective resins which have proven to have affinity for the following ions $\text{NO}_3^- > \text{SO}_4^- > \text{Cl}^- > \text{HCO}_3^-$. The ion exchange process involves passage of nitrate loaded water through a resin bed containing strong base anion exchange resins on which nitrate ions are exchanged for chloride until the resin is exhausted (Samatya et al., 2006).

In this paper, adsorption properties of Duolite A7 and Relite A490 for nitrate removal were investigated.

Materials and methods

Materials

Strong base nitrate selective ion exchange resin Relite A490 was kindly provided by Resindion S.r.l., and A490 weak base anion exchanger Duolite A7 by Dow Chemical Company. Relite A490 is a porous strongly basic anion exchange resin having an outstanding selectivity for nitrate. This resin allows good kinetics exchange and resistance to physical, thermal and osmotic shocks as well as organic fouling.

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Its composition complies with the existing food processing rules and regulations. Its physical properties and specifications are reported by the suppliers given in Table 1.

Duolite A7 is a phenolic weak base anion resin that is highly resistant to physical attrition. The highly porous structure of this hydrophilic resin makes it useful both for reversible adsorption of large organic molecules and for acidity removal. The properties of Duolite A7 are given in Table 1.

In the designed experiments, all the reagents were of analytical grade. Model nitrate solutions were prepared by dissolving KNO₃ in deionized water.

Batch-mode sorption studies

The batch sorption experiments were conducted by shaking various amounts of resin (0.1 – 0.6 g) with 100 mL of KNO₃ solution (10, 50 and 100 mg/L) in a shaker for 24 h at 25 °C, after which the resin was separated from the sample by vacuum-filtration. The residual nitrate concentration was analyzed using a spectrophotometer (Analytik Jena Specord 200, Germany). The nitrate reduction *R* as a percentage was calculated as

$$R = \frac{c_0 - c_r}{c_0} \cdot 100 \quad (1)$$

where *c*₀ is the initial nitrate concentration (mg/L) and *c*_r is the residual nitrate concentration (mg/L).

The effect of the resin dose

Varying amounts (0.1 – 0.6 g) of Relite A490 and Duolite A7 were mixed with 100 mL of nitrate solution (50 mg/L, pH 5.4). The samples were shaken for 24 h and the residual nitrate concentrations were measured.

The effect of contact time

The effect of contact time was examined by shaking 100 mL of nitrate solution (50 mg/L, pH 5.4) and 0.6 g of resins for various times (15, 30, 60, 120, 240 and

360 minutes). The samples were filtered and the residual nitrate concentrations in the filtrate were analyzed by the spectrophotometric method.

The effect of the initial nitrate concentration

Model nitrate solutions with 10, 50 and 100 mg/L NO₃⁻ were prepared by diluting stock KNO₃ solution.

100 mL of each solution was mixed with 0.6 g of resin for 24 h. The maximum sorption capacity *q* (mg/g) was calculated as

$$q = \frac{c_0 - c_r}{m} \cdot V \quad (2)$$

where *c*₀ and *c*_r are the initial and residual nitrate concentration (mg/L), *V* is the volume of sample (0.1 L) and *m* is the mass of resins (0.6 g).

Sorption kinetics

The sorption kinetics of the ion exchange resins was described by the pseudo-second order kinetic as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

where *k*₂ is the pseudo-second order rate constant (g/mg min), *q*_e is the equilibrium adsorption capacity (mg/g) and *q*_t is the adsorption capacity (mg/g) at any time (min). Integrating Eq. (3) for boundary conditions *q* = 0 at *t* = 0 and *q* = *q*_t at *t* = *t* gives

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

By plotting *t/q*_t vs. *t* a linear plot with a slope 1/*q*_e and an intercept 1/*k*₂*q*_e² is obtained, which can be used in determining parameters *k*₂ and *q*_e (Keränen et al., 2013).

Table 1. Physico-chemical properties of resins Relite A490 and Duolite A7

Resin	Relite A490	Duolite A7
Matrix	porous copolymer styrene-DVB	phenol-formaldehyde polycondensate
Functional group	quaternary ammonium group	secondary amine
Physical form	light yellowish, opaque beads	tan, opaque granules
Particle size	0.3 – 1.18 mm	≤ 2
Uniformity coefficient	1.7	< 2
Ionic form	Cl ⁻	free base
Total exchange capacity	0.9 eq/L	> 2.1
Operating pH range	0 - 12	0 - 8
Operating temperature range	5 – 100 °C	max 40 °C

Results and discussion

The effect of the resin dose

The resin dosage is important parameter because it determines the capacity of an ion exchanger for a given initial concentration of the adsorbate under operating conditions (Xu et al., 2010). To find the optimum amount of resin concentration, which can completely remove nitrate from aqueous solution, a batch-mode adsorption study was performed. The results of the experiments with varying amounts of resins are presented in Fig. 1. In general, an increase in resin dosage increased the percentage of nitrate removal. A slight optimum in the resin dose for Relite A490 was found to be 6 g resin/L, although over 80% reductions were achieved with as little as 4 g/L, while the optimum resin dose for Duolite A7 was 6 g resin/L with 60% removal efficiency. Samatya et al. (2006) achieved similar results. They observed increased percentage of nitrate removal with the increment of resin dose. Xu et al. (2010) investigated the adsorption of phosphate ions on prepared ion exchangers from wheat residue, and reported that with increasing the resin dosage, more sorption sites are available for sorption, thus resulting in higher removal efficiencies. Nevertheless, the adsorbate removal will not increase much if the dosage of resin is higher of that resin dosages when constant sorption is achieved. On Fig. 1 it can be clearly seen that in the case of Relite A490, a constant sorption at 4 g/L was achieved, and every further increment of resin dose does not have significant impact on higher nitrate uptake.

The effect of contact time

As expected, during various contact times (15, 30, 60, 120, 240 and 360 minutes) the highest nitrate removal efficiency was achieved after 360 minutes (70% with Relite A490 and 40% with Duolite A7) (Fig. 2.). No difference between Relite A490 and Duolite A7 after 15, 30 and 60 minutes can be observed. In both cases, a slight drop in removal efficiency can be seen after 240 minutes of sorption. A contact time of 120 – 360 min was sufficient to achieve equilibrium. Therefore, a 24 h contact time was used in all the experiments to ensure equilibrium.

The effect of initial nitrate concentration

Adsorption of nitrate ions on Relite A490 and Duolite A7 was investigated at various initial concentrations of 10, 50 and 100 mg/L at resin dose of 6 g/L, reaction temperature of 25 °C and contact time of 24 h (Fig. 3).

With increasing the initial nitrate concentration, the efficiency of nitrate removal decreases in both tested resins from 92.23 to 80.78% for Relite A490 and from 81.26 to 40.39% for Duolite A7. The decrease in process efficiency may be attributed to the insufficient sorption sites on the surface area.

The maximum sorption capacities varied from 6.51 mg/g for Duolite A7 to 13.02 mg/g for Relite A490. Orlando et al. (2002) obtained capacity of 16.8 mg/g (as NO_3^- -N) for Amberlite IRA-900, while Chabani et al. (2006) obtained 14.8 mg/g (as NO_3^- -N) for Amberlite IRA-400.

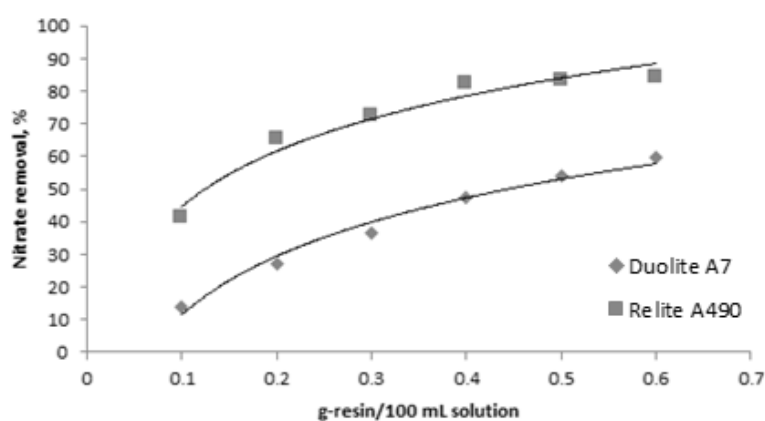


Fig. 1. The effect of resin amount on removal of nitrate from aqueous solution

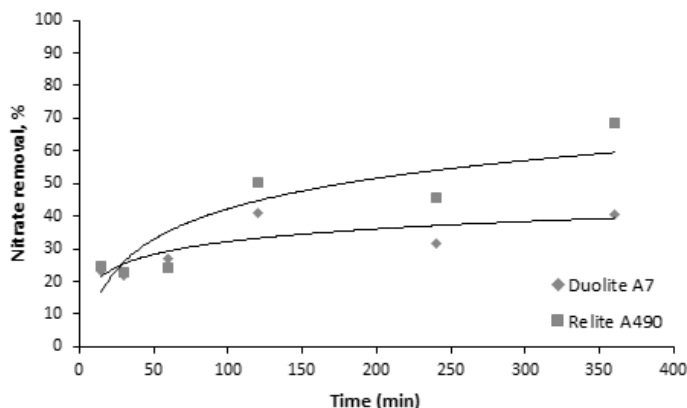


Fig. 2. The effect of contact time on nitrate removal efficiency

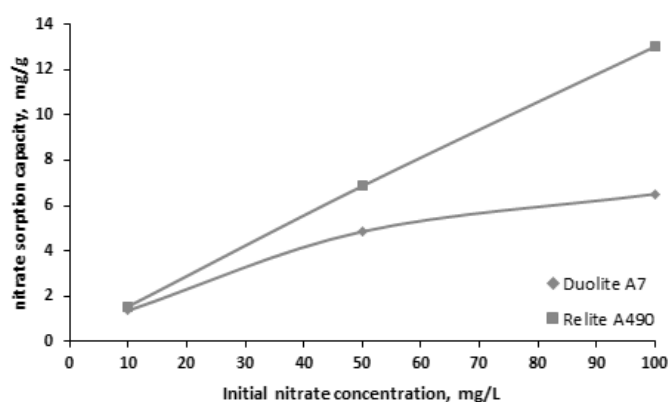


Fig. 3. Maximum nitrate sorption capacities of Duolite A7 and Relite A490

Table 2. Parameters and coefficients of determination of the linearized pseudo-second order kinetic model

Resin	q_e (mg/g)	k_2 (g/mg min)	R^2
Duolite A7	5.068	0.0018	0.9692
Relite A490	7.391	0.0010	0.9781

Sorption kinetics

The experimental data were fitted in the linear pseudo-second order model. The values of constants, q_{m2} and k_2 , were calculated from the slope of the plot t/q_t versus t (Table 2). The model fitted the data well with coefficients of 0.9692 and 0.9781, respectively. Relite A490 achieved the highest equilibrium sorption capacity ($q_e=7.391$).

Conclusions

In this study, nitrate removal from aqueous solutions was investigated by two ion exchange resins, Duolite A7 and Relite A490. From the results obtained it can be concluded that with increasing the resin dose, the removal efficiency also increases. By increasing the initial nitrate concentration, the

sorption capacity increased, while the nitrate removal efficiency decreased for both, Relite A490 and Duolite A7. The data fitted well in the pseudo-second order kinetic model with $R^2 > 0.97$. The future aim is to study removal of nitrate and other ions from real wastewater samples.

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