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The Efficiency of Amberjet 4200 Resin in Removing Nitrate in the Presence of Competitive Anions from Shiraz Drinking Water

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Abstract: The aim of this research is to study the feasibility of removing nitrates from water by means of anion exchange. In the purposed work an attempt was made to utilize strong basic anion resin to remove nitrate in the presence of competitive anion. Amberjet Cl⁻ 4200 ion exchange resin was used in a batch scale. The fixation rate of nitrate without the presences of any competitive anion was almost constant (94.60-96.43) when the nitrate concentrations are in the range of 100-150 mg L⁻¹. The fixation rate of nitrate in the presences of two competitive anions (sulphate and chloride) was reduced to 82% when the concentration of nitrate was 100 mg L⁻¹.

Key words: Nitrate, competitive anions, ion exchange, resin, drinking water

INTRODUCTION

Nitrate contamination in drinking water resources is an increasingly important problem in Iran. Elevated levels of nitrate in groundwater sources result from excessive use of chemical fertilizer, uncontrolled on land discharges of municipal and industrial wastewater, human and animal waste, run off septic tank and processed food (Samatya *et al.*, 2006; De Heredia *et al.*, 2006). Based on Assubaie study, nitrate and nitrite were the main sources of groundwater and soil pollution in Al-Hassa Oasis. Nitrate content of groundwater decreased with increasing depth. His study revealed that groundwater was more polluted due to application of organic manure and urea fertilizer than that of soil fertilized with organic manure alone (Assubaie, 2004). The high nitrate concentration in Saudi Arabia ground water may be due to the excessive use of nitrogen fertilizers and deep leaching properties of the nitrogen fertilizers (Al-Harbi *et al.*, 2006).

According to WHO (World Health Organization), drinking water must contain no more than 50 mg L⁻¹ of nitrate (Lohumi *et al.*, 2004) and EPA (Environmental Protection Agency) established a maximum contaminant level of 45 mg L⁻¹. European community recommends NO₃⁻ levels of 25 mg L⁻¹ (De Heredia *et al.*, 2006).

Excess of nitrate concentration cause several hygienic and environmental impacts (Lohumi *et al.*, 2004). This ion is stable and extremely soluble in water and can move easily through soil into water aquifer (Pintar *et al.*, 2001). These properties make it difficult to remove it using conventional water treatment technology. The ion exchange process seems to be suitable for small water suppliers contaminated by nitrate, because of its simplicity, effectiveness, selectivity, recovery and relatively low cost (Bae *et al.*, 2002). Typically, the increasing order of ion selectivity for an ion exchange resin is hydroxide <bicarbonate <chloride<nitrate< sulphate (Guter, 1997).

The removal of nitrate from a Netherlands ground water containing a relatively low amount of sulphate with two different resins, the sulfate selective resin Duolite A 165 and the nitrate selective resin Amberlite IRA 996, showed that the use of nitrate selective resins had not any advantages over the use of sulfate selective resins with respect to effluent nitrate concentrations. Though chloride concentrations in the treated water are lower in nitrate selective resin as compared with sulfate selective resin, sulfate concentrations were higher in the nitrate selective resin as compared with the sulfate selective resin. The nitrate selective resin can also be used for water with extremely high sulfate concentrations (Van der

Hoek *et al.*, 1988). Kim and Benjamin in their work on removing arsenate and nitrate from drinking water by strong base anion exchange resin (ASB-1, Anion exchange) found that, if the raw water contains substantial concentrations of sulfate or nitrate, the resin becomes exhausted quickly. The selectivity coefficient for sulfate over nitrate of a strong base anion exchange resin increased dramatically with increasing ionic strength, partially counteracting the decrease in SO_4/NO_3 separation factor predicted from mass action considerations (Kim and Benjamin, 2004). Boumediene and Achour studied the Purolite A 520 E ionic exchange resin for the denitrification of underground water which has a high concentration of nitrates and sulphates. Their study showed that the presence of high contents of sulphate and/or nitrate reduced the time of production of resin and resulted high contents of nitrate in the treated water (Boumediene and Achour, 2004). Treatment of high sulphate water with typical resins is difficult because the nitrate removal capacity of the resins is reduced by the sulphate ions. The use of selective resin, Amberlite IRN-78, for nitrate ion would be beneficial, using this resin also reduced nitrate peaking which occurred with conventional resin due to sulphate displacement of nitrate (De Heredia *et al.*, 2006). The nitrate removal efficiencies from aqueous solution by Purolite A 520E for NO_3^- , $NO_3^-:10SO_4^-$, $NO_3^-:10Cl^-$ and $NO_3^-:10Cl^-:10SO_4^-$ are 100, 96.6, 96.6 and 96.7, respectively (Samatya *et al.*, 2006). Terry used hydrotalcite, a clay mineral ion exchange media to remove nitrates and phosphates from aqueous solution. Removal was over 90% for 25 mg L⁻¹ nitrate, but decreased significantly at higher concentrations. Nitrate removals were significantly decreased by the presence of phosphates. However, second batch contact of the residual solution with fresh hydrotalcite was sufficient to reduce both phosphates and nitrates to below EPA standards (Terry, 2009). Another study used the Ion Exchange Membrane Bioreactor (IEMB) for removing nitrate from marine systems. The results demonstrated that the IEMB was able to remove naturally accumulated nitrate from water taken from a public marine aquarium to molecular nitrogen. This system reduced nitrate concentrations from 251 and 380 mg L⁻¹ to below 27 mg L⁻¹ exchanging it for chloride. They concluded that the IEMB proves to be a selective nitrate removing technology and minimizing the counter diffusion of anions other than nitrate and chloride (Matos *et al.*, 2009). This study aims at removing nitrate ion from Shiraz drinking water using a strong anionic exchange resin, Amberjet Cl⁻ 4200. For this purpose, a simple batch technique is used to find the optimum contact time, amount of resin, pH and temperature. The main objective

of this project is to examine Amberjet Cl⁻ 4200 to remove nitrate anion from water in the presence of competitive anions such as sulphate and chloride.

MATERIALS AND METHODS

Reagents: The research has been conducted in the environmental chemistry laboratory of School of Health and Nutrition of Shiraz University of Medical Sciences in May 2009. All chemical reagents were of analytical grade and were supplied by Merck. Macroporous strong base nitrate selective anion exchange resin Amberjet Cl⁻ 4200 used in this study was a commercial product furnished by Rohm and Hoss Inc. The resin is the anion type of macroporous structure with the matrix of styrene divinylbenzene copolymer and N⁺ (CH₃)₃ type which is specially designed for the removal of nitrates from water with more affinity for the nitrate ions than for the other anions. Physico-chemical properties of the resin are summarized in Table 1.

Analytical methods: Nitrate ions were determined by an Ultraviolet Spectrophotometric Screening method (Shimadzu model UV-Visible 120-02) at 220 nm (Eaton *et al.*, 2005). Sulphate ions were determined by a Turbidimetric method at 420 nm (Eaton *et al.*, 2005). Chloride ions were determined by the Argentometric method (Eaton *et al.*, 2005).

In order to determine the practicality of the resin to remove nitrate in the presence of sulphate and chloride from Shiraz water, the working nitrate, sulphate and chloride concentration were determined according to Shiraz water characteristics during years of 2004 to 2008. Selected concentration of nitrate sulphate and chloride are shown in Table 2.

Experiments: The suitable resin type was also chosen according to Shiraz water characteristics. Resin Amberjet Cl⁻ 4200 was selected for this study. The experiments were done on a batch scale. The pilot was a plexyglass container (75×30 cm) which was equipped with arrival valve, ion exchange container, resin bed, sieve (mesh 40), sand bed layer and outlet valve. The resin bed was on the top of antracit sand bed. The experiments were performed by passage of nitrate, sulphate and chloride loaded solutions through a resin bed on which nitrate ions are exchanged by chloride. Nitrate, sulphate and chloride concentration at the input and output samples were measured.

After determining the optimum detention time, resin amount, pH and temperature, the effect of competitive ions on the efficiency of nitrate removal by the resin was

Table 1: Physico-chemical properties of Amberjet Cl⁻ 4200 resin

| Type | Matrix | Physical form | Exchange capacity | Swelling | Moisture | Flow rate |
|------------------------------------|----------------------------------|-------------------|-----------------------------------|--|----------------------------------|--------------|
| N+ (CH ₃) ₂ | Styrene divinylbenzene copolymer | Insoluble, yellow | ≥1.30 eq/L (Cl ⁻ form) | Cl ⁻ -OH ⁻ about 30% | 49 to 55% (Cl ⁻ form) | 2 to 8 BV*/h |

Table 2: Selected concentration of nitrate, sulphate and chloride in water samples

| Cl ⁻ (mg L ⁻¹) | SO ₄ ²⁻ (mg L ⁻¹) | NO ₃ ⁻ (mg L ⁻¹) |
|---------------------------------------|---|--|
| 100 | 100 | 50 |
| 100 | 150 | 50 |
| 100 | 200 | 50 |
| 75 | 200 | 100 |
| 100 | 200 | 100 |
| 150 | 200 | 100 |

studied. The two anions of sulphate and chloride were chosen as competitive anions. The resin performance was determined for nitrate removal rate from aqueous solutions containing 50 and 100 mg L⁻¹ nitrate concentrations. To determine the effect of sulphate ions on the nitrate fixation rate, the sulphate concentrations were increased gradually, while the chloride concentration was constant. The effect of chloride ions on the nitrate removal rate was studied by increasing chloride concentration and maintaining the sulphate concentration constant.

RESULTS AND DISCUSSION

Table 3 shows the effect of influent nitrate concentration without the presence of competitive anions on nitrate fixation rate. Although the nitrate fixation rate was almost constant (94.60-96.43) when the nitrate concentrations are in the range of 100-150 mg L⁻¹, an increase in nitrogen fixation rate (5.73%) is observed.

Our preliminary study showed that a simple batch system, using a strong anionic ion-exchange resin, Amberjet Cl⁻ 4200 is able to remove nitrate concentrations in a wide range of pH and temperature with efficiencies of more than 90%. Variations in pH and temperature do not have a considerable effect on nitrate removal. In general, an increase in contact time increased the percentage of nitrate removal. In order to remove large amount of nitrate from aqueous solutions, the optimum contact time was 15 min with the nitrate fixation rate of 96.65%. Optimum resin weight was 7.5 g L⁻¹ with the nitrate fixation rate of 95.25%. In addition, the resin has the capability to remove high concentration of nitrate from water.

Table 4 showed the effects of the competitive ions sulphate and chloride on the fixation rate of nitrate. When nitrate and sulphate ions are both present in solution, the fixation rate of nitrate was decreased. The same trend of nitrate reduction was seen in the presence of chloride ion. Although the fixation rate of nitrate was reduced due to the presence of sulphate, the concentration of nitrate after passage through the ion exchange resin was always lower

Table 3: The effect of influent nitrate concentration without the presence of competitive anions on nitrate fixation rate

| Influent NO ₃ ⁻ concentration (mg L ⁻¹) | Nitrate fixation rate (%) |
|---|---------------------------|
| 50 | 90.70 |
| 75 | 94.60 |
| 100 | 95.25 |
| 125 | 95.76 |
| 150 | 96.43 |

Table 4: Nitrate fixation rate in the presence of chloride and sulphate ions

| Before Ion exchange | | | After ion exchange | | |
|---------------------|-------------------------------|------------------------------|--------------------|-------------------------------|------------------------------|
| Cl ⁻ | SO ₄ ²⁻ | NO ₃ ⁻ | Cl ⁻ | SO ₄ ²⁻ | NO ₃ ⁻ |
| 100 | 100 | 50 | 218 | 9 | 14 |
| 100 | 150 | 50 | 257 | 35 | 14 |
| 100 | 200 | 50 | 290 | 8 | 16 |
| 75 | 200 | 100 | 190 | 9 | 12 |
| 100 | 200 | 100 | 251 | 33 | 16 |
| 150 | 200 | 100 | 306 | 26 | 18 |

than standard permissible limit. In addition, the sulphate concentration in output samples was also decreased significantly. However the remarkable increase in output chloride concentration up to three times the initial concentration was seen. The reason for this increase was due to chloride base of resin. The contact of resin with solution containing nitrate, sulphate and chloride ions give a rise to the amount of chloride concentration due to the exchange between NO₃⁻ or SO₄²⁻ and Cl⁻. It can be concluded that as the chloride ion was increased, the nitrate fixation rate was reduced. Although the nitrate fixation rate was higher in the presence of chloride than sulphate ions, the problem of increasing chloride concentration in output samples was not resolved. Therefore, there is a limitation for using the resin. The chloride ion as the competitive ion had a remarkable effect on resin properties than sulphate. The more concentration of nitrate ions, less concentration of sulphate ions fixed.

When the ions, sulphate and chloride are both present in solution, the ratio of their concentration relative to the nitrate had a direct effect on the nitrate fixation amount. The more concentration of chloride and sulphate ions, the less concentration of nitrate ions fixed. The fixation rate of nitrate in the presences of two competitive anions (sulphate and chloride) was reduced up to 82% when the concentration of nitrate was 100 mg L⁻¹. The amount of nitrate ions fixed on the resin was decreased by 6% when SO₄²⁻ concentration was increased up to 2 times (200 mg L⁻¹) and the ration of chloride/nitrate concentration was equal to 2. When the sulphate concentration was constant (200 mg L⁻¹) and the ration chloride/nitrate concentration was 0.75, the nitrate fixation rate was increased up to 88%. The same trend is seen in

the presence of chloride and a reduction in the efficiency is seen. Though the efficiency of the nitrate removal is reduced, but this reduction does not mean lack of efficiency of the resin in the presence of sulphate and chloride. In all input nitrate concentrations, the nitrate level after the ion exchange is much less and acceptable according to standard limit, therefore, one can infer that though the resin does not act selectively, but the nitrate after removal is lower than the standard permissible level. Moreover, using this resin, the sulphate concentration in the output samples significantly decreases to 96% when the sulphate concentration was 200 mg L⁻¹ and the ration of chloride/nitrate concentration was equal to 2. But the remarkable point is increase in the chloride concentration in output samples to 2.9 times the original concentration due to presence of chloride base in the resin was observed. Therefore, one must seek a solution for the problem of increase in chloride concentration, since it leads into a limitation in the resin consumption. In the study of the effect of the competitive chloride ion on the fixation rate of nitrate, we see an efficiency reduction of nitrate. Therefore, one can conclude that by an increase in the chloride ion, the removal efficiency is reduced.

Van Der Hoek and his coworkers found that by using nitrate selective resin Amberlite IRA 996, lower chloride concentrations and higher sulfate concentrations in the treated water in nitrate selective resin as compared with sulfate selective resin (Van der Hoek *et al.*, 1988). Their results are in contradiction of our finding that high chloride concentration and low sulphate concentration in the treated water are observed by using anion exchange resin Amberjet Cl⁻ 4200. Boumediene and Achour found that the Purolite A 520 E ionic exchange resin that the presence of high contents of sulphate and/or nitrate reduced the time of production of resin and resulted high contents of nitrate in the treated water (Boumediene and Achour, 2004). Using ASB-1, anion exchange for removing arsenate and nitrate from drinking water is exhausted quickly by the presence of sulphate ion (Kim and Benjamin, 2004). Beltran de Heredia and his coworkers also found that the nitrate removal capacity of Amberlite IRN-78 resin was significantly reduced by the present of sulphate ion in water (De Heredia *et al.*, 2006). Their results are in support of our finding that nitrate fixation rate is reduced by the presence of high sulphate concentration. However, the nitrate removal efficiency from aqueous solution by using Purolite A 520E was 100% and in the presence of interfering ions such as chloride and sulphate was only reduced by 0.4% (Samatya *et al.*, 2006). Ion exchange resin Purolite A 520E has better performance in the presence of interfering ions than our anion exchange resin Amberjet Cl⁻ 4200.

Another researcher found that the hydrotalcite ion exchange resin has a capability of nitrate removing of over 90% for 25 mg L⁻¹ nitrate, but the nitrate removal capacity decreased significantly at higher nitrate concentrations and also by the presence of phosphates (Terry, 2009). However, our results showed that anion exchange resin Amberjet Cl⁻ 4200 has a better performance at high nitrate concentration than the hydrotalcite ion exchange resin. The ion exchange membrane bioreactor (IEMB) reduced nitrate concentrations from 251 and 380 mg L⁻¹ to below 27 mg L⁻¹ exchanging it for chloride. Although using IEMB has a good performance for removing nitrate, an increase in chloride concentration is observed (Matos *et al.*, 2009). Their results are in support of our finding that high nitrate fixation rate is achieved but the problem of high chloride concentration in the treated water is not resolved.

It is noteworthy that the Amberjet Cl⁻ 4200 resin used in our study has a better nitrate fixation rate, comparing with other resins used in other studies such as Amberlite IRN-78 resin, hydrotalcite ion exchange resin, the ion exchange membrane bioreactor (IEMB) and ASB-1 anion exchange, even in the presence of interfering ions such as sulphate and chloride ions. But its performance was lower, comparing to Purolite A 520E. Though the present study showed that the concentration of nitrate has decreased, the concentration of chloride ions has increased. Further research is needed to develop a method for reducing the chloride ion concentration in finished water.

CONCLUSION

The study presented in this study showed that the use of Amberjet Cl⁻ 4200 as anionic exchange resin permitted the removal of nitrate ions. The resin is more selective toward nitrate ions when this ion is present alone in solution. In the case of competitive ions (sulphate and chloride), it has been observed that the more concentration of these ions, the less amount of nitrate fixed. However, nitrate and sulphate concentration in all the output samples are less than standard limit. But the application of this resin in water containing high amount of chloride concentration was restricted due to the presence of chloride concentration more than standard limit.

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