



Research Journal of
**Environmental
Sciences**

ISSN 1819-3412



Academic
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Counterion Effects on Nitrate Adsorption from Aqueous Solution onto Functionalized Polyacrylonitrile Coated with Iron Oxide Nanoparticles

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ABSTRACT

Batch adsorption experiments were conducted to evaluate the effects of the initial nitrate concentration, ionic strength and contact time on the nitrate removal efficiency by functionalized polyacrylonitrile coated with iron oxide nanoparticles (PAN-Oxime-Fe₂O₃). All tests were performed in 100 mL solution at constant temperature of 25°C and mixing rate of 150 rpm. The residual nitrate concentration in the solution was determined spectrophotometrically. Statistical analyses were performed on data using SPSS16 software by applying Kruskal-Wallis tests using Excel software. The results showed that the adsorption of nitrate was influenced by counterions. Finally, experimental data were analyzed using adsorption isotherm. The results show that nitrate removal efficiency increases with an increase in the initial nitrate concentration and contact time and decreases in the presence of other ions.

Key words: Counterion, nitrate, adsorption, polyacrylonitrile, nano-Fe₂O₃

INTRODUCTION

Nitrate, a high water soluble ion, which is known as the most widespread groundwater contaminant in the world, imposing a serious threat to drinking water supplies and promoting eutrophication (Majumdar and Gupta, 2000; Tate and Arnold, 1990). High NO₃ concentrations in drinking water sources can lead to a potential risk to environment and public health (Romano and Zeng, 2009). Studies have shown that excess NO₃ in drinking water may also be responsible for causing diverse kinds of cancers in humans. In humans, increasing NO₃ concentrations in drinking water causes two adverse health effects like induction of "blue-baby syndrome" (methemoglobinemia), especially in infants and the potential formation of carcinogenic nitrosamines (Majumdar and Gupta, 2000). Due to the adverse effects and serious health problems are imposed with excess NO₃ concentrations in drinking water, various environmental regulatory agencies including the U.S. Environmental Protection Agency (U.S. EPA) have regulated a Maximum Contaminant Level (MCL) of 10 mg L⁻¹ of NO₃ in drinking water (USEPA, 2000). Besides nitrate, a number of inorganic anions have been found in potentially harmful concentration in water bodies. These inorganic contaminants can be present at the same time in different levels. Fluoride, nitrate, sulphate, chloride and carbonate are major inorganic anions which co-exist with their

related cations like iron, calcium and magnesium in natural waters. The removal of these ions are often a challenging task due to their physio-chemical properties since their interfere with the removal of other ions from aqueous phase (Smith *et al.*, 2002). Therefore, the effect of other ions on nitrate removal by a novel adsorbent, which its great potential on nitrate removal was presented in our earlier study (Nabizadeh *et al.*, 2013) is investigated.

MATERIALS AND METHODS

Adsorbent preparation: Hydroxylamine hydrochloride (16 g), sodium carbonate (12 g) and 0.4 g of PAN powder were added to a 250 mL bottle to which 100 mL of deionized water was added and shaken. The reaction was carried out at 70°C for 120 min. After reaction, the resultant was filtered and let to dry. Fe₂O₃ was coated on PAN functionalized by adding 0.2 g of selected Fe₂O₃ and 100 mL deionized water in a sealed bottle. The solution was shaken at 70°C for 120 min. The resultant was filtered and dried in a vacuum oven at 60°C. PAN functionalized-Fe₂O₃ was used as an adsorbent. The characteristics of PAN-oxime-nano Fe₂O₃ was studied by XRD, FTIR and SEM in our earlier study (Nabizadeh *et al.*, 2013).

Batch adsorption experiments: Aliquots of nitrate with initial concentrations in the range from 20-200 mg L⁻¹ were placed in beakers with 0.03 g PAN-oxime-nano Fe₂O₃. The suspensions were shaken at 150 rpm for 24 h (25 ± 2°C). The supernatant was separated by centrifugation for 30 min at 2000 rpm. An aliquot of the supernatant was analyzed by UV-visible spectrophotometer Lambda 25 (PerkinElmer). Each experiment was conducted in triplicate under identical conditions to confirm the results and was found reproducible (experimental error within 5%). The amount of the dye uptake and percentage of dye removal by the adsorbent were calculated by applying Eq. 1 and 2, respectively:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$R = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where, C₀ and C_e are the initial and equilibrium concentrations of nitrate in solution (mg L⁻¹) respectively, V is the volume of the solution and m is the mass of the adsorbent (g).

Counter ion studies: In order to study the effects of different anions on nitrate removal, pure grade salts Na₂SO₄, NaCl, Na₂CO₃ and NaF and deionized water were used to prepare the anion concentration of 100 and 200 mg L⁻¹. Fe₃(PO₄)₂, Ca₃(PO₄)₂, Mg₃(PO₄)₂ were used to prepare the cation concentration of 20, 50 and 100 mg L⁻¹. The aliquots were stirred in the presence of nitrate with the same concentration for 24 h. Nitrate removal was measured spectrophotometrically and its removal percentage were compared with the situation of non co-existing ions.

RESULTS AND DISCUSSION

Effect of contact time and initial nitrate concentration: The adsorption equilibrium isotherm is important for describing how the adsorbate molecules distribute between the liquid and solid phases. The adsorption isotherm of nitrate on PAN-oxime-nano-Fe₂O₃ is shown in Fig. 1.

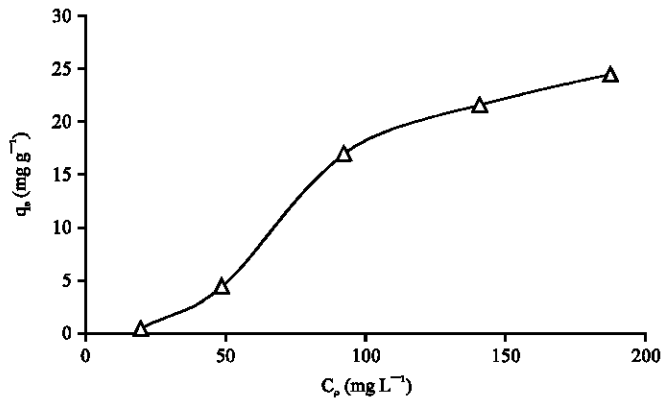


Fig. 1: Adsorption isotherm of nitrate onto PAN-oxime-nano-Fe₂O₃

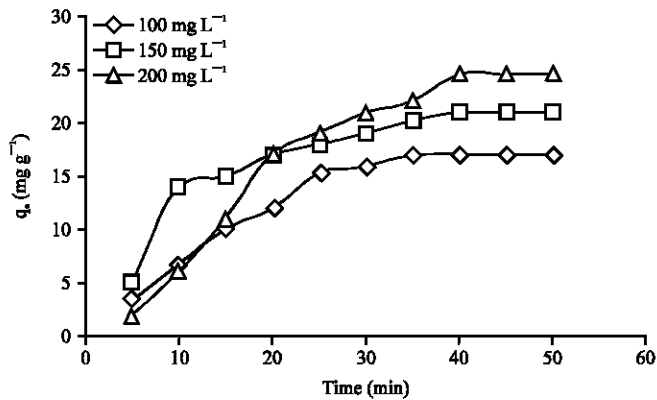


Fig. 2: Effect of contact time and initial nitrate concentration on sorption of nitrate

As shown in Fig. 1, the equilibrium uptake increased with increasing equilibrium nitrate concentration over the experimental concentration range. A maximum experimental adsorption capacity of 16.95 mg g⁻¹ was observed for nitrate (100 mg L⁻¹) on PAN-oxime-nano-Fe₂O₃ at 25±2°C. The initial sharp rise in the isotherm indicates the availability of readily accessible sites for adsorption. However, as the nitrate concentration increases a plateau is reached, indicating virtually no more sites remain available for further adsorption. The initial concentration provides an important driving to overcome all mass transfer resistances of the nitrate between the aqueous and solid phases. The effect of contact time on nitrate adsorption (100 mg L⁻¹) is shown in Fig. 2. The quantity of adsorbed solute (mg g⁻¹) increased with increasing time of contact and reached equilibrium after 40 min. It was noticed that nitrate removal increased with time and then gradually decreased with lapse of time until saturation. The nitrate adsorption was initially speeded up to 20 min and then it became slow. Therefore, the optimum contact time for adsorption of the fluoride was considered to be 20 min. Nitrate adsorption by the selected adsorbent increased when the initial nitrate concentration increased from 100-150 and 200 mg L⁻¹ (Fig. 2). This can be related to the increase in the driving force of the concentration gradient, as an increase in the initial fluoride concentration.

Adsorption isotherms: Adsorption isotherms are equations for description of equilibrium phase between sorbent and an aqueous solution. Freundlich models are empirical models for rough

sorbents which are applicable for systems with a single dissolved material. Langmuir isotherm can be used for physical sorption in a single layer. In the present study experimental data of adsorption equilibrium was described by use of Langmuir and Freundlich isotherms and could be shown as Eq. 3 (Hameed *et al.*, 2007):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \quad (3)$$

where, C_e (mg L^{-1}) is the equilibrium concentration, q_e (mg g^{-1}) is the amount of adsorbate adsorbed per unit mass of adsorbate and q_m and b are the Langmuir constants related to adsorption capacity and rate of adsorption, respectively.

Equation of Freundlich isotherm (Eq. 4) can be expressed as:

$$\text{Ln}q_e = \frac{\text{Ln}K_f + 1}{n \text{Ln}C_e} \quad (4)$$

where, q_e is the amount of nitrate adsorbed at equilibrium mg g^{-1} and C_e is the equilibrium concentration. K_f and n are Freundlich constants. The Langmuir and Freundlich constants were calculated and are listed in Table 1. According to the obtained results (Table 1), the experimental data fitted well to Langmuir isotherm. So this adsorption model was employed as the best for describing the characteristics of adsorbent in nitrate removal from the aqueous solutions. Another important parameter, R_L , the separation factor or equilibrium parameter, is determined from Eq. 5:

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

where, b is the Langmuir Constant and C_0 (mg L^{-1}) is the highest nitrate concentration. The value of R_L shows this type of isotherm to be either favourable ($0 < R_L < 1$) or unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$) (Zheng *et al.*, 2008). The R_L value in the present calculated as 0.367, which confirms that adsorption of nitrate by this material is favourable under the conditions of this research.

Table 1: Constant of Freundlich and Langmuir isotherms of nitrate

Parameters	Values
Langmuir model: $\frac{1}{q_e} = \frac{55.6}{C_e} - 0.478$	
q_m (mg g^{-1})	2.09
b (l mg^{-1})	0.0086
R^2	0.983
Freundlich model: $\text{Ln } q_e = 0.504 \text{ Ln}C_e + 3.337$	
K_f (mg g^{-1})	16.17
$(\text{L mg}^{-1})^{1/n}$	1.98
$n R^2$	0.936

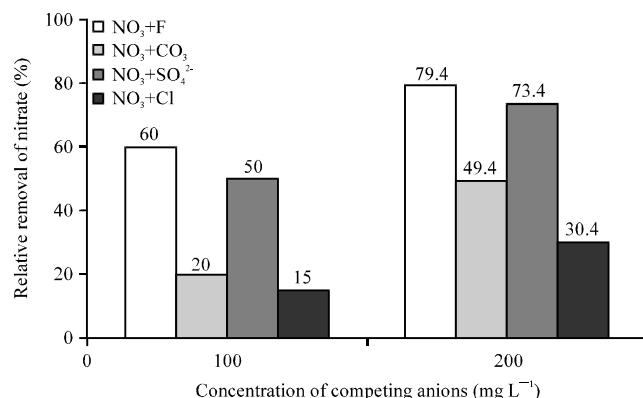


Fig. 3: Effect of different anions on nitrate removal

Table 2: Statistical results of the effect of various anions and cations on removal efficiency

	N	Minimum	Maximum	Mean	SD	p-value
Anions						
Fluoride	20	58	80	69.5	9.99	0.000
Carbonate	20	20	50	35.65	14.53	
Sulphate	20	48	75	61.1	12.29	
Chloride	20	15	32	23	8.25	
Cations						
Iron	30	72	90	80	4.64	0.000
Calcium	30	88	99	93	3.48	
Magnesium	30	90	95	92.66	2.089	

Counterion effects: Contaminated water usually contains several other co-existing ions along with nitrate, which may compete with nitrate for the active adsorption sites. Thus, it is weighty to investigate the possible interference of these ions (CO₃, Cl, F, SO₄, Ca, Mg and Fe) on nitrate removal by adsorbent. It would be important to assess the suitability of PAN-Oxime-nano Fe₂O₃ for field applications. The effects of various co-existing anions are represented in Fig. 3. The results indicated that the anions have substantial effect on nitrate removal. The presence of chloride affected the nitrate removal potential by adsorbent up to 85%. This indicated that chloride is the greatest competitor for nitrate followed by carbonate, sulphate and fluoride. This indicates that the outer spherically sorbing anions especially chloride, carbonate and sulphate can significantly interfere the sorption of nitrate at lower concentration where they compete for the limited amount of sorption sites on adsorbent. Moreover, fluoride which is an inner-spherically sorbing anion, showed little interference on nitrate sorption. The adsorption mechanism of the anions onto adsorbents is significantly dependent on the physico-chemical properties of anions and their interaction with the adsorbent surface (Marcus, 1997). Kraskal-Wallis test was used for analyzing and determining the effect of ionic strength as the variable on the removal efficiency. The result is in Table 2. As shown the mean removal efficiency for chloride and iron, two ions which showed predominant importance on nitrate removal, are 23 and 80%, respectively. Characteristic of anions such as the solubility, ionic radius, hydration energy and bulk diffusion coefficient are imperative for the selective adsorption of anions. The immobilization of anions onto the adsorbent also relies on the size of the adsorbent pores, which in some cases is similar or smaller than the ionic and/or hydrated dimensions of the anions which results in selective anionic adsorption and further results

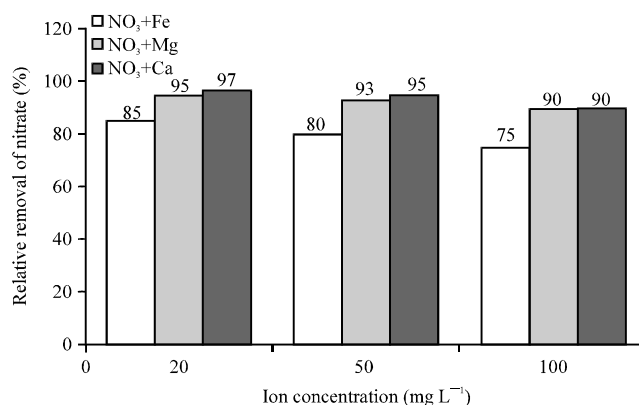


Fig. 4: Effect of different cations on nitrate removal

in the formation of inner-sphere, outersphere complexes and electrostatic or hydrogen bonding of the anion with the adsorbent surface. The hydrated radius of anions explains the adsorption behavior of anions to a small extent. The hydrated ion radius impede the ions to approach to close the interface, the 'depletion region' (Langmuir, 1997). For nitrate this hydrated radius is 5.1×10^{-10} m which is significantly much greater than hydrated radius of other anions leading to its less adsorption. Chloride has the highest diffusion coefficient, thus the formation of inner sphere complexation is expected. At higher values (200 mg L^{-1}) the effects of anions were less noticed. Figure 4 shows the effect of various commonly found cations on nitrate removal. As evident, magnesium and calcium did not greatly reduce the adsorption capacity. Unlike calcium and magnesium, nitrate removal substantially decreased in the presence of iron (Fe). Contrary to what observed in the cases of anions, nitrate removal capacity reduced as cation concentration increased and at 100 mg L^{-1} , around 5-10% reduction in nitrate removal efficiency was observed.

CONCLUSION

The adsorption process by PAN-Oxime-nano Fe_2O_3 can be a good alternative in treating solution containing nitrate. The nitrate removal efficiency is highly sensitive to the presence of other ions. The result shows that solution containing high co-ions showed lower removal efficiency than those having low ionic concentration. Nitrate removal decreased according to the affinity of anions on the adsorbent surface in the following order: $\text{Cl} > \text{CO}_3 > \text{SO}_4 > \text{F}$. The adsorption capacity is high in the initial times but it decreases with further increase in the adsorption time. The data of adsorption of nitrate ions follow Langmuir isotherm ($R^2 = 0.98$).

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