

Nitrate removal from water using complex of activated carbon with Fe³⁺

Aboalfazl Azhdarpoor, Leila Khosrozadeh and Mohammadreza Shirdarreh

ABSTRACT

Pollution of surface and ground waters with nitrate is a serious issue in many regions of the world. Therefore, this study attempts to investigate the extent of nitrate removal from aqueous solutions using a new complex of activated carbon. The effects of operating parameters such as pH of solution (3 to 9), adsorbent dosage (0.4 to 5 g in 50 mL), contact time (5 to 300 min) and initial concentration of nitrate (50 to 300 mg L⁻¹) were studied. The highest efficiency of nitrate removal (95.4%) was related to application of modified activated carbon to a solution with pH of 7 and 100 mg L⁻¹ nitrate concentration. Increasing the amount of modified activated carbon from 0.5 to 1 g in 50 mL promoted removal of nitrate from 82.6% to 94.1%. Furthermore, increasing contact time from 5 to 30 min improved removal efficiency from 76.6% to 92.3%. The obtained experimental data were compatible with the Langmuir isotherm model. In general, the results demonstrated that employing Fe³⁺-modified activated carbon can be considered as a new method of nitrate removal from aqueous solutions due its convenience, safety and high efficiency.

Key words | activated carbon, adsorbent, aqueous solutions, nitrate

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INTRODUCTION

In recent years, the presence of high quantities of nitrate (NO₃⁻) in surface and ground waters has become a serious global concern (Zhang & Angelidaki 2013). Nitrate pollutant can enter water resources as a result of the disposal of urban and industrial wastes and agricultural activities which excessively consume pesticides, chemical fertilizers and manure. High concentrations of nitrate in drinking water can cause health issues, such as methemoglobinemia in infants, bladder and gastric cancers and liver dysfunction (Loganathan *et al.* 2013). In this respect, the World Health Organization (WHO) have declared the permitted concentration of nitrate in drinking water to be 50 mg L⁻¹ (Islam & Patel 2010; Azhdarpoor *et al.* 2018). Due to the solubility and stability of nitrate in water, it has a very low tendency to get adsorbed and precipitate (Ensie & Samad 2014).

To date, several physical, chemical and biological methods have been applied to remove nitrate from water, e.g. ion exchange, reverse osmosis, electrodialysis, denitrification, nano-filtration, adsorption by residues of

agricultural products and a combination of ozone and activated carbon filters (Yang & Lee 2005). Current technologies like ion exchange and reverse osmosis are not selective for nitrate and generate secondary brine wastes. Biological processes are in need of the addition of a carbon source and disposal of biomass waste. Among these approaches, surface adsorption has been employed more due to operational convenience, simplicity of design and economic considerations.

Adsorption by activated carbon is efficient in eliminating a broad spectrum of pollutants (Nunell *et al.* 2015). To increase the adsorption surface of activated carbon for removal of ionic pollutants, such as nitrite and nitrate, there is still a great possibility for research. Some methods of activated carbon treatment involve application of acid, cationic surfactant, metals, metallic ions and heat. These methods change the physical and chemical properties of activated carbon and, therefore, enhance the adsorption of nitrate (Cho *et al.* 2011; Ota *et al.* 2013).

Despite the applicability of these approaches, few studies have focused on FeCl_3 complexes to modify activated carbon and remove nitrate. In the current study, FeCl_3 was used to modify granules of activated carbon and increase its adsorption surface. Then, to evaluate the extent of nitrate removal, the parameters that are effective on nitrate adsorption capacity including pH, adsorbent dosage, contact time and initial concentration of nitrate were investigated.

MATERIALS AND METHODS

Synthesis of modified activated carbon

In this study, we used granulated activated carbon with 10 to 20 mesh, effective size of 1 mm and uniformity coefficient of 1.18, produced by Kimia Carbon Co. of Arak (Iran). A modified procedure was developed to impregnate AC with iron. To prepare modified activated carbon, 48 g of unmodified activated carbon (AC) was added to a 400 mL solution of FeCl_3 (0.5 M) and stirred for 24 h at 150 rpm. Then, the solution was filtered and the resultant activated carbon was kept in an oven for 5 h, at 105 °C. Then, to treat the modified activated carbon (AC-Fe^{3+}), it was immersed in 400 mL NaOH solution (0.5 M) for 3 h and, subsequently, rinsed with 400 mL HCl solution (0.5 M) for 3 h. At the end, AC-Fe^{3+} was washed with deionized water several times and dried in the oven for 3 h, at 65 °C. All the experimental reagents used in the present study were of analytical grade (Merck Company).

Analysis

Concentration of nitrate ions was measured by a UV spectrophotometer (HACH DR/5000) at a wavelength of 220 nm, according to the standard method. X-ray diffraction (XRD) was performed to determine the crystalline and non-crystalline phase of the adsorbents and scanning electron microscopy (SEM) was conducted to analyze the morphology and size of the activated carbon particles (Noori Sepehr *et al.* 2013). For SEM, samples were first prepared using an ultrasonic dispersion of sorbent powder in ethanol and then dropped on a Cu grid. Then, a sputtering coating (Q150R-ES, Quorum Technologies) was added to the samples on the grid.

Nitrate removal experiment

All nitrate experiments were repeated twice under batch conditions. The stock solution of nitrate (2,000 mg L^{-1}) was prepared by dissolving NaNO_3 in deionized water. The pH of the nitrate solution (100 mg L^{-1}) was adjusted to a range of 3 to 9 with HCl or NaOH (both 0.1 M) and then 1.5 (or 3) g of AC-Fe^{3+} was added to 50 (100) mL of nitrate solutions and stirred for 45 min at 150 rpm. After that, the solution was filtered using 0.45 micron Whatman paper and concentration of the remained nitrate was measured using UV spectroscopy. The amount of adsorbed nitrate (mg.g^{-1}) can be calculated by the following Equation (1). In this equation, C_0 is the initial concentration of nitrate (mg L^{-1}), C_e refers to the concentration of the nitrate ions that have remained in the solution after adsorption (mg L^{-1}), m is the mass of the adsorbent (g) and V relates to the volume of the solution (L).

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

Effect of adsorbent dosage

In this stage, different amounts of the adsorbent (0.5 to 4.0 g) were added to 50 mL nitrate solutions with 100 mg L^{-1} concentration and pH of 7 and stirred for 45 min to equilibrate. Then, the samples were filtered and nitrate concentrations of the filtrate solutions were measured. Evaluations of the adsorption isotherms were conducted using different amounts of AC-Fe^{3+} (0.5 to 4.0 g) and 100 mL nitrate solutions (200 mg L^{-1}) at pH of 7.

RESULTS AND DISCUSSION

Adsorbent characteristics

SEM images of AC and AC-Fe^{3+} are shown in Figure 1(a) and 1(b). As can be observed, small pieces of carbon exist among the main pores of the activated carbon granules before modification. After modifying the granules with FeCl_3 , crystals of iron have grown around the small carbon pieces, which have caused an increase of particles inside the activated carbon granules. In other words, the small carbon pieces

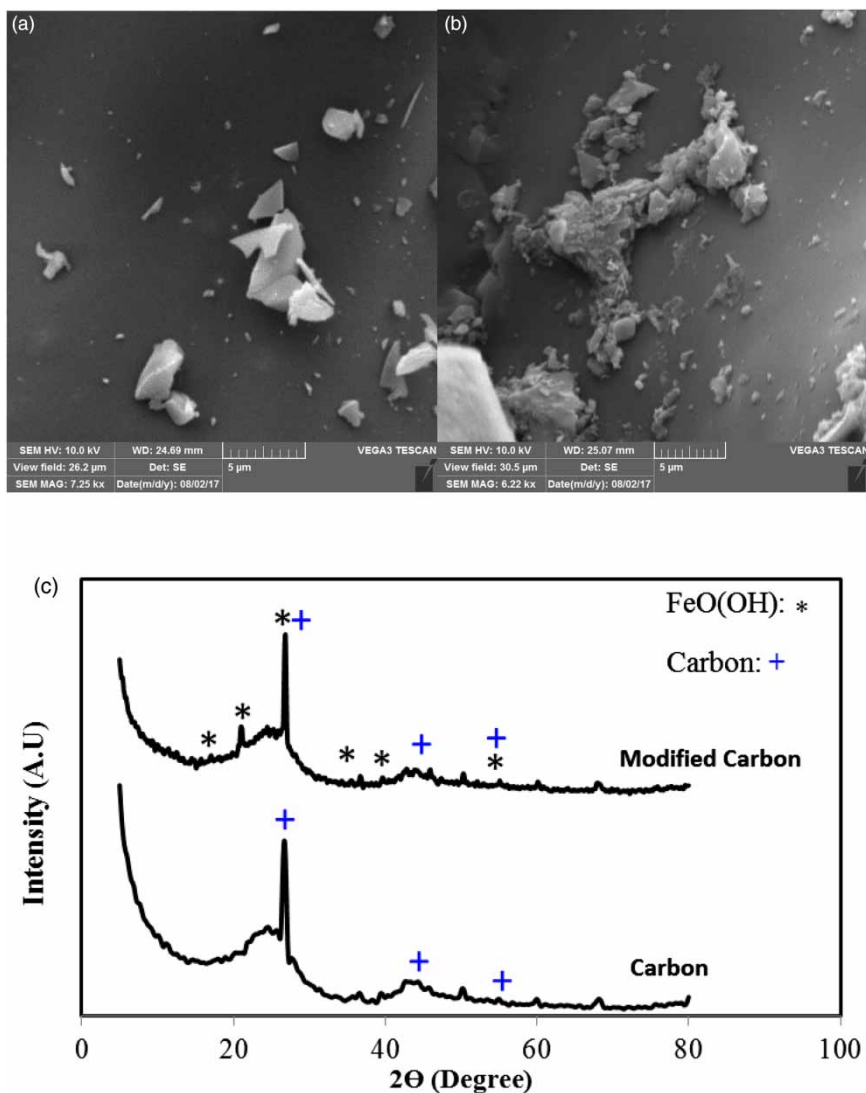


Figure 1 | SEM images of (a) AC and (b) AC-Fe³⁺; (c) XRD images of AC and AC-Fe³⁺.

have acted as appropriate substrates for the generation of iron crystals and the formation of these iron crystals has resulted in production of an adsorbent with higher adsorption capacity. Therefore, treatment of activated carbon with FeCl₃ increases the adsorption surface of activated carbon and provides more active sites for the adsorption of nitrate anions (Hu *et al.* 2015). Also, to analyze AC and AC-Fe³⁺ by XRD, the samples were powdered. Their XRD patterns are exhibited in Figure 1(c). As can be seen, the XRD pattern of AC-Fe³⁺ contains some main peaks that refer to goethite (FeO(OH)) crystal structure. The presence of the iron crystal phase can enhance the adsorption of nitrate ions from water.

Effect of pH

The results of pH effect on the removal of nitrate are displayed in Figure 2. As can be observed, the highest amount of adsorption by AC can be achieved when pH = 3 and decrease of pH increases nitrate adsorption by AC. The reason can be attributed to the increased number of positive charges on the activated carbon. In this state, nitrate anions can adsorb on activated carbon more noticeably due to electrostatic bonding. Furthermore, the results demonstrate that the highest removal of nitrate by AC-Fe³⁺, i.e. 95.4%, is related to pH = 7.

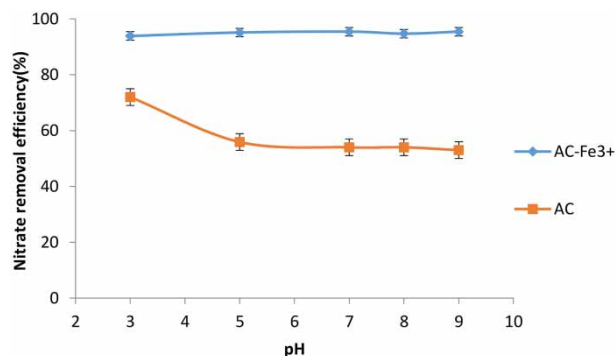


Figure 2 | Effect of pH on removal of nitrate using AC and AC-Fe³⁺ (1.5 g adsorbent in 50 mL, 100 mg L⁻¹ nitrate and 45 min contact time).

The efficiency of nitrate removal by AC-Fe³⁺ was obtained as over 93%, at all studied pH values.

Therefore, the efficiency of nitrate removal by AC-Fe³⁺ does not change significantly over the pH range of 3 to 9 and it can be concluded that AC-Fe³⁺ can remove nitrate from water over a broad range of pH, unlike AC. This finding is consistent with the results reported by other researchers. Mazarji *et al.* (2017) evaluated the removal of nitrate from water using modified granules of activated carbon and showed that when the pH of the nitrate solution changes, nitrate adsorption by the modified activated carbon alters negligibly but maximum adsorption occurs at a pH of 5. Insignificant change of nitrate removal efficiency at various pH values can illustrate the efficiency of this method for different types of surface and ground water with acidic and basic conditions. In further investigations, the pH value of 7 was used as the optimum pH.

Effect of contact time

The performance of AC and AC-Fe³⁺ in the removal of 100 mg L⁻¹ and 200 mg L⁻¹ nitrate at different contact times is depicted in Figure 3. Based on this figure, as the contact time prolongs from 5 to 45 min, the removal efficiency of AC-Fe³⁺ increases from 72.6% to 85.7% and 76.6% to 92.9% for 100 and 200 mg L⁻¹ nitrate solutions, respectively.

Also, for AC, increasing the contact time from 15 to 300 min enhances removal efficiency from 46.4% to 65% and from 32% to 83.6% for 100 and 200 mg L⁻¹ nitrate concentrations, respectively. This finding shows that AC-Fe³⁺ can give a higher efficiency in a shorter contact time, compared with AC, so that AC-Fe³⁺ can adsorb about 75% of

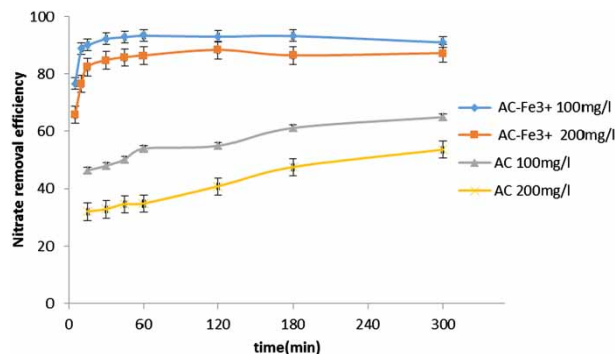


Figure 3 | Effect of contact time on removal of nitrate by AC and AC-Fe³⁺ using 1 g adsorbent in 50 mL, 100 and 200 mg L⁻¹ nitrate and pH = 7.

nitrate in the first 5 min of contact. According to Figure 3, efficiency of nitrate removal increases with contact time but efficiency is highest in the first 15 min interval of contact and, then, it increases with a less steep slope up to 30 min. After 30 min contact time, the amount of adsorbed nitrate remains almost the same. In the first 15 min, since the adsorbent has more free space to adsorb nitrate and more active sites are accessible, collision of the pollutant ions with active sites of the adsorbent is more probable. In such conditions, the ions have more chances to attach to the adsorption sites and, consequently, the removal efficiency increases (Azhdarpoor *et al.* 2015). After 45 min, the adsorption sites of AC-Fe³⁺ saturate and adsorption does not proceed further. Our findings are in line with Bhatnagar *et al.* (2010) who studied removal of 10 and 20 mg L⁻¹ nitrate from water using 1 g of nano-alumina and reported that nitrate removal improves with increase of contact time. They also stated that nitrate adsorption is fast at the beginning and, then, the adsorption rate decreases. In their study, maximum nitrate elimination occurred in the first 15 min. Therefore, 45 min contact time was considered as the equilibration time for further experiments.

Effect of adsorbent dosage on nitrate removal

Figure 4 displays the amount of nitrate removed by different dosages of AC and AC-Fe³⁺ (0.5 to 4 g). With respect to this figure, increasing the dosage of AC from 0.5 to 4.0 g promotes nitrate removal from 33.4% to 69.0%. However, in the case of AC-Fe³⁺, incrementing the adsorbent dosage from 0.5 to 4.0 g increases nitrate removal from 82.6% to 96.9%. This 2.5-times adsorption increase, i.e. the ratio of AC-Fe³⁺ to AC

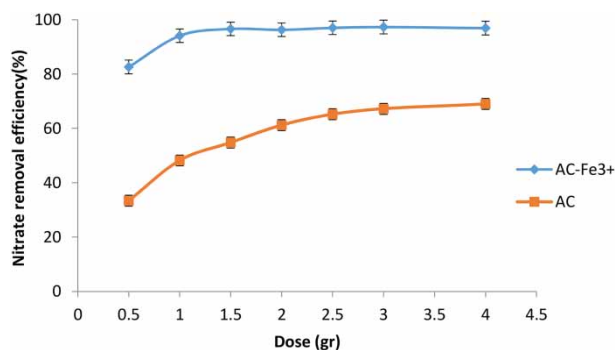


Figure 4 | Effect of adsorbent dosage on removal of nitrate by AC and AC-Fe³⁺ using 100 mg L⁻¹ nitrate, 45 min contact time.

adsorption efficiency, is a direct outcome of the increased number of accessible sites and adsorption surface (Rao & Rehman 2010). Therefore, it can be observed that removal efficiency reaches its maximum value by increasing the dosage of AC-Fe³⁺ from 0.5 to 1.5 g and further increase of its dosage does not have any significant effect on the elimination of nitrate ions. The reason can be attributed to the presence of unsaturated sites at high dosages of activated carbon and reduction of nitrate quantity. Consequently, the optimum amount of 1.5 g AC-Fe³⁺ was used in further investigations.

Effect of initial concentration of nitrate and adsorption isotherm

The results related to the effect of initial nitrate concentration are presented in Figure 5. According to the presented results, efficiencies of nitrate removal by AC and AC-Fe³⁺ are 50% and 98% using 50 mg L⁻¹ nitrate, respectively. When initial concentration of nitrate is increased to 300 mg L⁻¹, efficiencies of nitrate removal by AC and AC-Fe³⁺ reduce to 35% and 88%, respectively. Also, nitrate adsorption capacity increases from 1.63 to 8.75 mg.g⁻¹ for AC-Fe³⁺ and from 1.09 to 3.46 mg.g⁻¹ for AC with an increase of nitrate concentration from 50 to 300 mg L⁻¹. The observed difference in adsorption behavior can be explained by referring to the fact that there are equal accessible surfaces at the beginning of the adsorption process. In other words, higher concentrations of nitrate result in increased numbers of collisions between nitrate ions and AC-Fe³⁺, more nitrate anions surrender the active adsorption sites and, therefore, the adsorption process advances more noticeably (Ye et al. 2010). However, thereafter, restriction of available adsorption surface decreases the

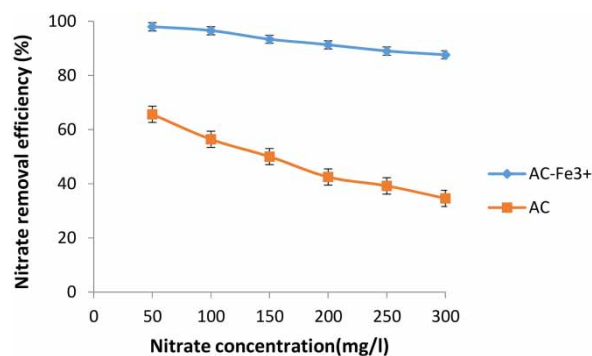


Figure 5 | Effect of initial concentration on removal of nitrate by AC and AC-Fe³⁺ using 1.5 g adsorbent in 50 mL, 45 min contact time and pH = 7.

removal efficiency for higher nitrate concentrations. Also, when nitrate concentration increases from 50 to 300 mg L⁻¹, removal efficiency decreases from 98% to 88% since the nitrate adsorption sites on the adsorbent can adsorb a definite amount of nitrate.

Hafshejani et al. (2016) studied the removal of nitrate from aqueous solutions by modified coal of sugarcane residues and noticed that increasing the initial concentration of nitrate from 1 to 80 mg L⁻¹ increases nitrate adsorption capacity from 0.5 to 23.7 mg.g⁻¹ while further increase in nitrate concentration from 80 to 100 mg.g⁻¹ has no influence on nitrate adsorption. They ascribed this phenomenon to the number of accessible active adsorption sites on the modified adsorbent.

There are different isotherms to evaluate equilibrium properties of adsorption, e.g. Langmuir and Freundlich (Kholghi et al. 2013). In the Langmuir model, it is assumed that the adsorbate interacts with a limited number of adsorption sites homogeneously and adsorption is restricted to a monolayer on the surface (Kholghi et al. 2013). On the other hand, the empirical relationship of Freundlich is based on multilayer adsorption on inhomogeneous surfaces and inhomogeneous distribution of energy throughout the active adsorption sites (Chatterjee & Woo 2009). In this study, the equilibrium data were fitted into the Freundlich and Langmuir isotherm models and 0.91 and 0.928 regression coefficients (R^2) were obtained for these models, respectively. Therefore, the experimental results indicate that the data collected for the adsorption of nitrate on the surface of AC-Fe³⁺ are more consistent with the Langmuir adsorption model, relative to the Freundlich model. According to the experimental data, the process of

adsorption involves monolayer adsorption on the surface. Also, the maximum amount of adsorbed nitrate is 28.9 mg per each gram of adsorbent through this model and the R_L coefficient, which should lie between 0 and 1, is about 0.2 and demonstrates desirable nitrate adsorption.

CONCLUSION

Modified activated carbon can provide a high efficiency of nitrate ion removal at 30 min contact time. At this contact period, the efficiency of 1 g of modified activated carbon is 2.5 and 2.0 times higher than unmodified activated carbon in the removal of 200 and 100 mg L⁻¹ nitrate, respectively. Improved efficiency of nitrate removal is due to increased positive charge and micro-pores on the surface of modified activated carbon with respect to unmodified activated carbon. Optimum conditions of nitrate removal were determined as 1 g adsorbent, 45 min reaction equilibration time and pH of 7. Nitrate adsorption capacity of modified activated carbon was found to be independent of the pH of the starting nitrate solution, which indicates the chemical stability and environmental adaptation of the adsorbent.

ACKNOWLEDGEMENT

This research was carried out as a Master's thesis sponsored by Shiraz University of Medical Sciences (khosrozadeh-10935).

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