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Isotherm and kinetic studies on the adsorption of nitrate onto nanoalumina and iron-modified pumice

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ABSTRACT

The use of nanoalumina and iron-modified pumice (IMP) as adsorbents for removal of nitrate from aqueous solution was investigated. Adsorption experiments were carried out as a function of the pH, contact time, and concentration of nitrate. Both adsorbents were effective for the nitrate removal in a pH range of 4–6, and optimum removal of nitrate ions occurred in a pH 5.0. The adsorption of nitrate on both adsorbents reached equilibrium within 50 min. Nitrate sorption kinetics was well fitted by pseudo-second-order model. The maximum nitrate uptake capacities for nanoalumina and IMP were found to be 70.8 and 86.7 mg g^{-1}, respectively. The kinetic results showed that the nitrate sorption to nanoalumina and IMP followed pseudo-second-order kinetics with a correlation coefficient greater than 0.99. The equilibrium data for both the adsorbents for nitrate removal were fitted to Langmuir and Freundlich isotherms, but the experimental data were found to be little better fitted by the Langmuir model. These results indicate that nanoalumina and IMP are interesting alternatives for nitrate removal from the aqueous solution.

Keywords: Nanoalumina; Iron-modified Pumice; Nitrate removal; Adsorption isotherms; Kinetics

1. Introduction

Nitrate contamination in surface and groundwater is a controversial issue due to its harmful effects [1,2]. Nitrate is one of the most important factors affecting the water quality [3]. The most common sources of nitrate in water resources are fertilizers, septic tank effluents, biodegradation of nitro-organic compounds, discharge of raw wastewater, production of explosives, and pharmaceuticals. High concentrations of nitrate in drinking water cause health problems, such as cyanosis among children and cancer due to formation of nitrosamine [4–6]. Based on WHO's guidelines the maximum concentration of nitrogen in drinking water is 10 mg L^{-1} (or 50 mg L^{-1} in terms of nitrate) [7].

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Studies on the removal of nitrate from aqueous solutions by different methods have been reported in a number of publications. These include ion exchange [8], electrolysis [9], biological denitrification [10], reverse osmosis [11], and adsorption [12]. Physicochemical treatment processes such as ion exchange, reverse osmosis, and electrodialysis require high maintenance and operation costs; they also produce sludge, which is difficult to handle [13]. Biological denitrification needs high maintaining and an operational consideration at their optimum conditions. Also, the problems of contamination by dead bacteria have to be solved to make sure that such processes have enough safety for utilization in drinking water treatment [14,15]. Adsorption is another effective method for nitrate removal because of its interesting features, including low costs, easy design, and operation. Different adsorbents have been used for nitrate removal [16]. In recent years, nanotechnology has become one of the most interesting technologies for water treatment. Nanoparticles have some advantages like high specific surface area and reactivity, *in situ* production, and high capability for water treatment purposes [17]. Pumice is a light and porous volcanic tuff made in volcanic activity. Pumice has been used in different applications such as adsorbent, media, or catalyst [18]. Also In addition, it can be used as the adsorbent for removal of oil and fats [19] Strontium, Cesium [20], Phosphorous [21], Copper, and Nickel [22].

In this study, we investigated the adsorption efficiency of nanoalumina and IMP for nitrate. The effects of pH, initial nitrate concentration, and contact time on nitrate adsorption by both adsorbents were examined using batch experiments.

2. Materials and methods

2.1. Materials and reagents

Nanoalumina (γ-Al_2O_3) was purchased from Kimia Sanat Company (Tehran, Iran) and used without any treatment. Nanoaluminum oxide with a purity of 99.9%, aluminum powder with a purity of 99%, and a mesh size of 200–100 mesh were used. Pumice was obtained from Eastern Azerbaijan province, Iran. The chemical composition of the tested pumice samples was as follows (wt. %): SiO_2—74.00; Al_2O_3—13.72; K_2O—4.66; Na_2O—3.65; Fe_2O_3—1.98; CaO—1.16; MgO—0.32; and Others—1.05. The weight percent of Si, Al, Fe, and K were found to be 71.84, 15.43, 7.12, and 5.61, respectively. The naked Pumice particles had a mean diameter of 126 nm. The full physicochemical characteristics of the tested pumice samples are presented elsewhere [23]. A stock solution of 1,000 mg L^{-1} of NO_3 was prepared by KNO_3 salt (Merk) in deionized water and was used to prepare the sorbate solution at concentration of 50, 100, 200, and 300 mg L^{-1} by appropriate dilution. The pH of the solution was adjusted to the required value using HCl and NaOH. Nitrate ion concentration was determined using atomic absorption spectrophotometer (Perkin-Elmer Lambda 25 UV/Vis Spectrometer, Perkin-Elmer, Norwalk, CT, USA). Jar test and pH meter (Metrohm 827) apparatus were used to agitate the solutions and adjust the pH, respectively.

2.2. Preparation of pumice

For increasing pumice porosity and removing its impurities, the adsorbent was soaked in HCl (0.1 N) for 24 h. Next, it was rinsed with deionized double distilled water till the pH of rinse water became 7. The adsorbent was then incubated at 100˚C for 24 h [24]. Afterward, for improving adsorption capability of pumice particles, they were soaked in ferric nitrate (Fe $(NO_3)\cdot 9H_2O$). In order to increase ferrous sorption on Pumice, 20 g of it was added to 180 ml of NaOH (2 M) at 80˚C for 48 h. At the end of the treatment, the mixture was filtered, washed thoroughly, and dried for further use.

2.3. Adsorption methods

Batch experiment was carried out to measure the adsorption characteristics of nitrate by the nanoalumina and IMP. Key variables were the adsorbent dose, the initial nitrate concentration (50–300 mg L^{-1}), pH (4–11), and contact time. The nanoalumina (0.25 g) and IMP (0.5 g) were added to 250 ml of synthetic nitrate solutions of varying initial concentration (50–300 mg L^{-1}). The samples were shaken in Jar test at 160 rpm for various times to determine the equilibrium time at room temperature. After shaking, the mixture was filtered and residual nitrate concentration in the solution was determined spectrophotometrically at 220 and 275 nm using a UV–vis spectrophotometer. The amount of nitrate sorbed (q_e in mg g^{-1}) was calculated as follows:

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

where q_e is the amount of nitrate sorbed by nano alumina and IMP (mg g^{-1}), C_0 is the initial concentration of nitrate (mg L^{-1}), C_e is the equilibrium nitrate concentration in solution (mg L^{-1}), m is the mass of adsorbent used (g), and V is the volume of nitrate solution (L). The equilibrium experimental data were fitted with Langmuir and Freundlich isotherm models to describe the interaction between nitrate molecules and the surface's adsorbents [25], as well as to analyze the distribution type of nitrate in the liquid and solid phases. Identifying the best-fit isotherm is critical for optimizing the adsorption process design. Linear forms of Langmuir and Freundlich isotherm models are as follows:

- Langmuir : $$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_m C_e} \tag{2}$$
- Freundlich : $$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3}$$

where C_e (mg L^{-1}) is the equilibrium concentration of the adsorbent in the solution, q_e (mg g^{-1}) is the amount of adsorbed nitrate on adsorbents at equilibrium, q_m is the amount of nitrate adsorbed at complete monolayer (mg g^{-1}), b is the Langmuir constant related to the binding site (L mg^{-1}) and k_F [(mg g^{-1}) $(L/g)^{-1/n}$], and n are the Freundlich constants that are related to the adsorption capacity and intensity, respectively. When C_e/q_e is plotted vs. C_e a straight line with slope q_e and intercepts b is obtained.

The essential characteristics of the Langmuir isotherm commonly known as separation factor or equilibrium parameter (R_L) can be defined as:

$$R_L = \frac{1}{1 + bC_0} \tag{4}$$

where b is the Langmuir constant and C_0 is the highest initial concentration of NO_3 ions (mg L^{-1}). The value of R_L indicates adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) [26].

3. Results and discussion

3.1. Effect of contact time and initial nitrate concentration

The sorption of nitrate on nanoalumina was investigated as a function of contact time (1–80 min) at two different initial nitrate concentrations (50 and 100 mg L^{-1}). It can be seen (Fig. 1) that the adsorption of nitrate on both adsorbents increased with time. Both adsorbents exhibited an initial rapid uptake of nitrate followed by a slower removal rate that gradually reached an equilibrium condition. A similar trend of fast kinetics was also observed onto nanoscale aluminum oxide hydroxide during fluoride [27] and nitrate [17] sorption.

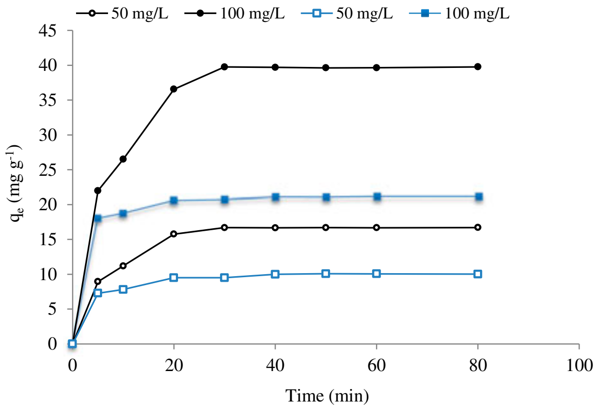

Fig. 1. Effect of contact time on the removal of nitrate by nanoalumina (●) and IMP (■).

The maximum nitrate removals by nanoalumina and IMP were achieved within the first 30 and 20 min, respectively. The values of equilibrium time were found to be 50 min for both adsorbents. There was no significant change in nitrate uptake by nanoalumina and IMP in the following 80 min. However, IMP is more efficient at shorter contact times.

3.2. Effect of solution pH

pH is an important parameter influencing the characteristic and charge of the sorbent's surface. It can be seen (Fig. 2) that the adsorption of nitrate on adsorbents is strongly pH dependent. The removal efficiency increased with increasing pH, reaching a maximum at initial pH 5, and then decreased with

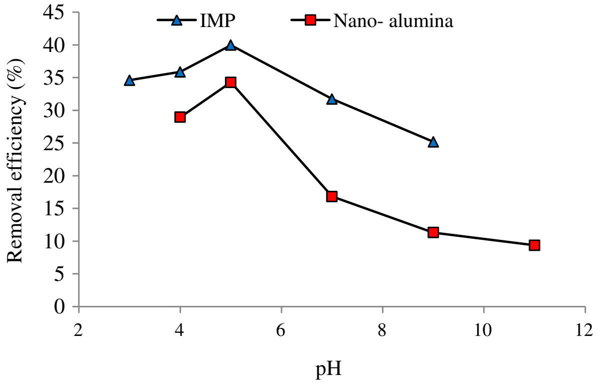

Fig. 2. Effect of pH on nitrate sorption on nanoalumin and IMP (temperature = 20°C, contact time = 30 min, sorbent dose = nanoalumin (0.25 gL^{-1}), IMP (0.5 gL^{-1}), and NO_3 concentration = 50 mgL^{-1}).

Table 1
Comparison of pseudo-first-order and pseudo-second-order model's parameters, calculated $q_{e(theor)}$, and experimental $q_{e(exp)}$ values for different initial fluoride concentrations

			Pseudo-first-order model			Pseudo-second-order model		
Adsorbent	C_0 (mg L^{-1})	$q_{e(exp)}$ (mg g^{-1})	$q_{e(theor)}$	K_1 (min^{-1})	R^2	$q_{e(theor)}$	K_2 (g mg^{-1} min^{-1})	R^2
Nanoalumina	50	16.7	17.90	0.169	0.808	18.84	0.0099	0.993
	100	39.63	59.32	0.186	0.59	44.64	0.0042	0.999
IMP	50	10.08	7.50	0.118	0.91	10.63	0.032	0.998
	100	21.09	8.60	0.148	0.454	21.60	0.040	0.993

further increase in pH. The reason for increasing efficiency in lower pHs might be due to increasing H^+ ions, decreasing OH^- ions in the solution, and increasing amount of positive ions on the surface of the sorbent. Our results suggest that weak acidic environment (pH 4–6) was the optimal pH range for the removal of nitrate by both adsorbents. However, a sharp decline in nitrate adsorption occurred at higher pH that may be due to electrostatic repulsion of anionic nitrate by the negatively charged adsorbents surface. The decrease in sorption capacity at $pH > 5$ can be due to the competition for the active sites by OH^- ions and the electrostatic repulsion of anionic nitrate by the negatively charged surface of nanoalumina and IMP. Different pH_{pzc} (pH point of zero charge) values ranging from 5 to 9 for aluminum based oxides/hydroxide [17,28,29] and 6–7 for pumice [30,31] are reported in the literature. When $pH < pH_{zpc}$, the surface of the sorbent has got more positive charge which causes the electrostatic attraction between positively charged surface ions and nitrate ions [31]. Because pH values of soil and groundwater were generally between 5 and 9 [32,33], therefore these adsorbents could be used for removal of nitrate effectively.

3.3. Kinetic modeling

In this study, the kinetic data of the nitrate were analyzed using the Lagergren first-order [34] and pseudo-second-order [35] rate equations. These equations have been used widely for estimation of adsorption rates and leads to suitable rate expressions characteristic of possible reaction mechanisms. The best-fit model was selected based on the agreement between experimental ($q_{e(exp)}$) and theoretical ($q_{e(theor)}$) uptake values and linear correlation coefficient (R^2) values.

The linear form of pseudo-first-order equation of Lagergren is generally expressed as

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{5}$$

where q_e and q_t are the sorption capacity at equilibrium (mg g^{-1}) and any time t, respectively, and k_1 is the rate constant of pseudo-first-order (min^{-1}).

The liner form of pseudo-second-order equation is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

The initial sorption rate, h (mg g^{-1} min^{-1}) can be calculated from following equation.

$$h = k_2 q_e^2 \tag{7}$$

where k_2 is the pseudo-second-order rate constant (mg g^{-1} min^{-1}). This model is based on the adsorbate

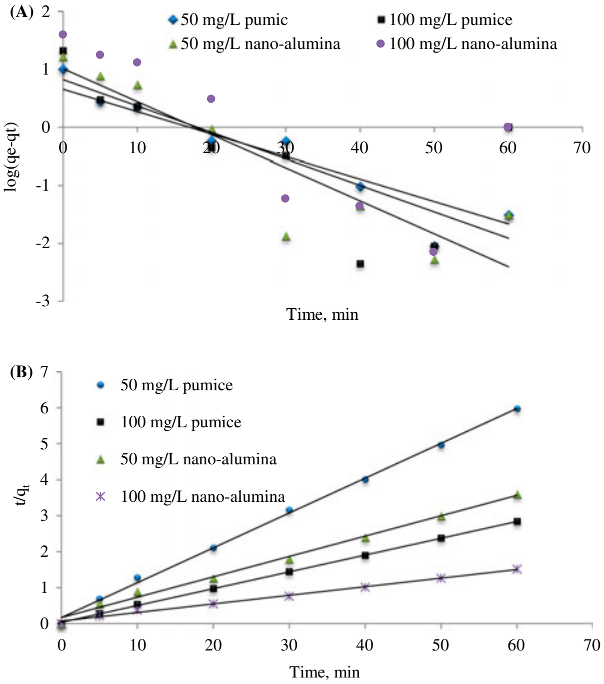

Fig. 3. Kinetic plots for nitrate adsorption (A) pseudo-first-order (B) pseudo-second-order.

quantity on the adsorbent. The calculated kinetic parameters for nitrate adsorbed by nanoalumina and IMP are shown in Table 1 and Fig. 3. For both adsorbents, the regression coefficients of the pseudo-second-order model ($r^2 > 0.99$) were greater than that of the pseudo-first-order model.

The values $q_{e(\text{theor})}$ obtained by pseudo-second-order model were found to be in good agreement with ($q_{e(\text{exp})}$) and can be used to favorably explain the nitrate sorption on nanoalumina and IMP. This suggested that the overall rate-limiting step for the adsorption of nitrate was controlled by chemical process such as the formation of a complex between functional groups of nanoalumina, and IMP, and NO_3^- groups [36]. The results also show that with increasing dose of adsorbents, the initial sorption rate, *h*, increase.

3.4. Adsorption isotherms

In order to investigate the sorption capacity of nanoalumina and IMP for nitrate, the equilibrium sorption of nitrate was studied as a function of nitrate concentration and the sorption isotherms are shown in Fig. 4. The q_e values increased with increasing of nitrate concentration (C_e) on both IMP and nanoalumina. Table 2 showed the q_m and b values for the Langmuir isotherm, the K_F and n values for the Freundlich isotherm, and the regression coefficients (r^2) obtained from the linear regression equation between the values of $1/q_e$ and $1/C_e$, and log q_e and log C_e, respectively. The high regression coefficients for the Langmuir and Freundlich isotherms ($r^2 > 0.95$) for the both adsorbents indicated that the two models were well fit with the experimental data. But Langmuir model ($r^2 = 0.988$)

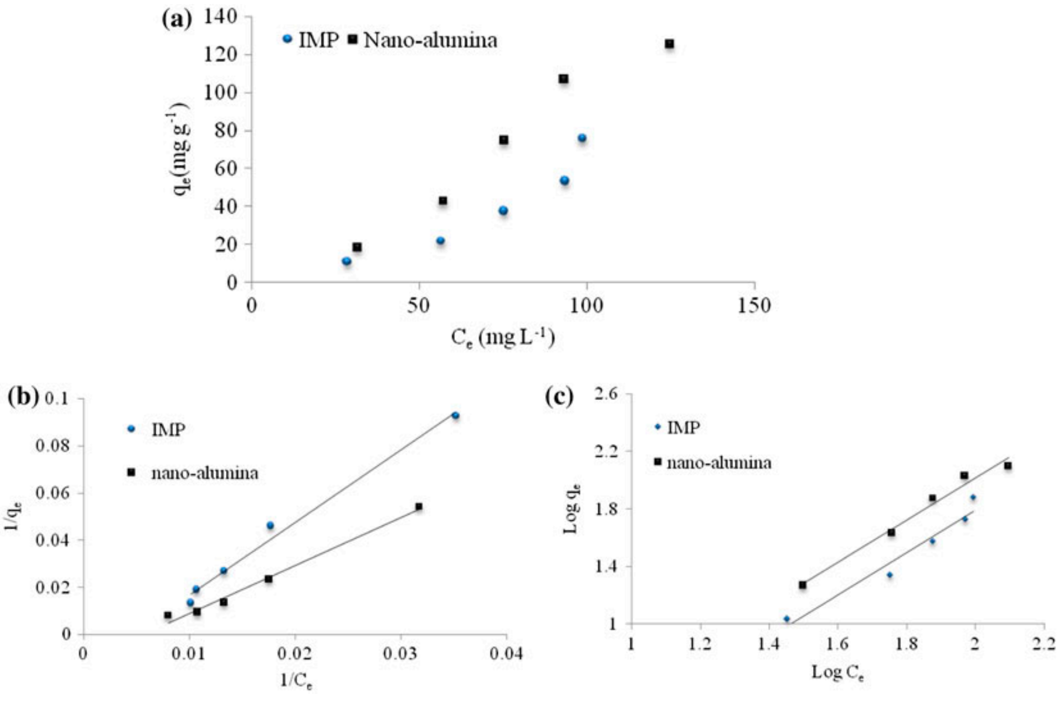

Fig. 4. (a) The adsorption of nitrate on the IMP and nanoalumina, (b) Langmuir, and (c) Freundlich isotherm of nitrate sorption on nanoalumina and IMP. pH 5; contact time, 60 min; IMP dose 0.5 g L^{-1}; and nanoalumina dose 0.25 g L^{-1}.

Table 2
Langmuir and Freundlich constants for the adsorption of nitrate on nanoalumina and IMP at constant temperature

	Langmuir constants				Freundlich constants		
Adsorbent	q_m (mg g^{-1})	b	R_L	R^2	n	K_F (mg g^{-1})(L g^{-1})$^{-1/n}$	R^2
Nanoalumina	86.70	0.004	0.41	0.988	0.679	0.117	0.979
IMP	70.79	0.005	0.46	0.988	0.679	0.070	0.952

Table 3
Comparison of adsorption capacities of nitrate with other adsorbents

Adsorbent	q_m (mg g^{-1})	Experimental conditions	References
Nanoalumina	5.48	pH 4.4 25 ± 2˚C	[17]
Bamboo powder charcoal	1.25	10˚C	[14]
cross-linked and quaternized Chinese reed	7.55	pH 5.8 10˚C	[42]
Halloysite	0.54	pH 5.4 Room temperature	[43]
Untreated coconut granular activated carbon	1.7	pH 5.5 25˚C	[44]
Sepiolite	3.46	pH 5 25˚C	[12]
Sepiolite activated by HCl	9.80	pH 5 25˚C	[12]
Activated carbon	4–9.8	pH 5 25˚C	[12]

yields a little better fit than the Freundlich model. Our result is agreed with the adsorption of Cr(VI) on aluminum magnesium mixed hydroxide [37], the adsorption of fluoride on nanoalumina [27], and fluoride adsorption onto functionalize pumice [38]. Overall, the experimental data fitted well with the Langmuir isotherm model adsorption represent that the sites are homogeneous, adsorption happens chemically, and the monolayer adsorption at equilibrium is occured [39,40].

The maximum adsorption capacity of nitrate from Langmuir model for IMP and nanoalumina was 70.9 and 86.7 mg g^{-1}, respectively. The R_L values of the nanoalumina and IMP were found to be between 0.41 and 0.46 for nitrate concentrations of 50–300 mg L^{-1}, respectively. The observed R_L values indicate favorable adsorption of nitrate on both adsorbents ($0 < R_L < 1$).

After equilibrium adsorption treatment process, the aluminum residual as a waste by product was less than (data not shown) EPA standard (0.2 mg L^{-1}) for drinking water. Direct comparison of IMP and nanoalumina with other adsorbent materials is difficult, owing to the different applied experimental conditions. In the present study, IMP and nanoalumina have been compared with other adsorbents based on their maximum adsorption capacity for NO_3 and shown in Table 3. It can be observed that the both adsorbents compare well with the other adsorbents listed in Table 3. Different adsorbents have various capacities. This could be primarily due to the activation process as well as the pore development due to the basic morphology of the raw material [41]. However, IMP can be considered to be viable adsorbent for the removal of NO_3 from aqueous solutions.

4. Conclusion

In present study, nitrate adsorptions on IMP and nanoalumina were examined. Nitrate removal efficiency increased by increasing contact time. The sorption of nitrate on both adsorbents was found to be strongly pH dependent with maximum nitrate removal occurring at pH 5. Kinetic analyses indicate that the sorption process followed pseudo-second-order kinetics under the selected concentration range. Adsorption modeling showed that the nitrate removal by IMP and nanoalumina followed Langmuir isotherm model. The saturated adsorption capacities (q_m) of the NO_3 by IMP and nanoalumina were 70.8 and 86.7 mg g^{-1}, respectively. Results showed that both adsorbents have great ability to adsorb nitrate from aqueous solutions.

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