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EFFICIENT NITRATE ADSORPTION FROM WATER BY ALUMINUM POWDER. KINETIC, EQUILIBRIUM AND INFLUENCE OF ANION COMPETITION STUDIES

The feasibility of aluminum powder (with particle size of 75–150 μm) for nitrate removal from aqueous solutions has been investigated. Adsorption was examined in function of initial nitrate concentration, contact time, pH and influence of other interfering anions. Maximum nitrate removal occurred at equilibrium pH of 10. The kinetics of adsorption of nitrate ions was discussed based on three kinetic models, namely: the pseudo-first order, the pseudo-second order and the intraparticle diffusion model. The experimental data fitted the pseudo-second order kinetic model very well; the rate constant was 4×10^{-4} g/ (mg·min) at the concentration of NO_3^- of 100 mg/dm^3. The adsorption data followed both Langmuir ($R^2 = 0.808$) and Freundlich ($R^2 = 0.865$) isotherms probably due to the real heterogeneous nature of the surface sites involved in the nitrate uptake. The maximum sorption capacity of aluminum powder for nitrate adsorption was found to be ca. 45.2 mg/g at room temperature. The results indicate that aluminum powder is an interesting alternative for nitrate removal from the water.

1. INTRODUCTION

The concentration of nitrates (NO_3^-) in surface waters and especially in ground waters has increased in many locations in the world [1]. Among the inorganic anions, ni-

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trate is a great concern for groundwater pollution [2]. Sources of nitrate pollution include agriculture runoff, animal waste, septic systems, atmospheric deposition, disposal of untreated sanitary and industrial wastes in unsafe manner, as well as industrial processes [3]. Increased level of nitrates in drinking water can cause methemoglobinemia also called a blue-baby syndrome. Outbreaks of infectious disease have been related to nitrate contaminated water [4]. It can also cause increased risk of cancer incidence due to the formation of nitrosamines [5]. According to World Health Organization (WHO) guidelines, the maximum permissible level for nitrate is 10 mg N/dm^3 or 50 mg, therefore, reducing the nitrate concentration in drinking water is necessary [6].

Conventional methods used for nitrate removal consist of ion exchange, reverse osmosis, electrodialysis, biological denitrification, and use of reductive metals. Physicochemical processes such as ion exchange, reverse osmosis, and electrodialysis have high operational costs. Furthermore, in the above mentioned processes generated concentrates or brines are troublesome and hard to dispose [7]. Biological denitrification process requires consistent monitoring and provision of organic substrate. Biological processes are slow in pace and are partly incomplete compared to chemical processes [8]. Sorption is generally accepted as one of the most efficient methods of nitrate removal, mainly due to convenience, ease of operation and simplicity of design. Numerous adsorbents were used for nitrate removal from water and wastewater [9]. Of these, meal oxides are excellent sorbents for anions removal from aqueous solutions because they posses positive charge and adsorbed anions with negative charge strongly [10]. Aluminum oxides are a significant fraction of the Earth's crust and nitrates could be strongly adsorbed onto various aluminum-containing mineral surfaces [11].

Therefore, in the present study, the sorption feasibility of aluminum powder has been assessed for nitrate removal from aqueous solution. The nitrate removal studies were conducted under various experimental conditions, such as pH, equilibrium time, initial nitrate concentrations, and major co-existing anion. The data from the experiments were fitted with different kinetic and isotherm models to identify the adsorption mechanism.

2. MATERIALS AND METHODS

Materials and reagents. Aluminum powder (purity of 99%, particle size of 75–150 μm) was purchased from Kimia Sanat Company (Tehran, Iran) and used without any treatment. A stock solution of 1000 mg NO_3^-/dm^3 (KNO_3 salt (Merck, Germany) in deionized water) was used to prepare the sorbate solutions at the concentrations of 50, 100, 200, and 300 mg NO_3^-/dm^3 by appropriate dilution. pH was adjusted to the required values (from 5 to 11) using HCl and NaOH. The concentration of residual nitrate ions was determined spectrophotometrically according to the Standard Methods [12] using a UV-visible spectrophotometer (Lambda 25, Perkin-Elmer Inc., USA).

Adsorption methods. Batch experiments were carried out to determine the adsorption characteristics of aluminium powder towards nitrates. The adsorbent dose was fixed at 1 g/dm^3. The rate of adsorption of nitrates was studied at various time intervals (1–60 min). For kinetic studies, 250 cm^3 of solutions of 50 and 100 mg $\mathrm{NO_3^-/dm^3}$ were adjusted to pH of 10. The adsorbent dose was 2 g/dm^3 and solutions were kept in a shaker at 150 rpm and room temperature. The amount of nitrate adsorbed at equilibrium q_e was calculated from:

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

where C_0 is the initial concentration of nitrate (mg/dm^3), C_e is the equilibrium nitrate concentration in solution (mg/dm^3), m is the weight of adsorbent used (g) and V is the volume of nitrate solution (dm^3).

The equilibrium experimental data were fitted with Langmuir and Freundlich isotherm models to describe the interaction between nitrate molecules and the adsorbent surfaces 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:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{2}$$

- Freundlich:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{3}$$

where, C_e (mg/dm^3) is the equilibrium concentration of the adsorbate in the solution, q_e (mg/g) is the amount of nitrate adsorbed on adsorbent at equilibrium, where Q_0 is the amount of nitrate adsorbed at complete monolayer (mg/g) and b is the Langmuir constant related to the binding site (dm^3/mg). A linear plot of C_e/q_e versus C_e gives Q_0 and b from the slope and intercept in Langmuir isotherm model. K_F [(mg/g)·(dm^3/g)$^{-1/n}$] and n are the Freundlich constants related to the adsorption capacity and intensity, respectively. Linear plots of logq_e versus logC_e give the values of K_F and n from the slope and intercept in Freundlich isotherm model.

The essential characteristics of the Langmuir isotherm commonly known as the 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/dm^3). 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 ($R_L = 0$) [13].

Effect of competing anions on adsorption. The effects of different co-existing ions (chloride and sulphate) on nitrate adsorption were investigated by performing nitrate adsorption under a fixed nitrate concentration (100 mg NO_3^-/dm^3), initial competing anion concentrations of 100–300 mg/dm^3, sorbent dosage of 2 g/dm^3, contact time of 60 min and initial pH of 10. The NaCl and K_2SO_4 salts were used to obtain chloride and sulfate anions, respectively. Concentrations of chloride and sulfate in the feed and equilibrium solutions were analyzed by ion chromatograph (metrohm 850, switzerland).

3. RESULTS AND DISCUSSION

3.1. EFFECT OF pH

pH is an important parameter influencing the sorption process at the water-adsorbent interfaces. The adsorption of nitrate ions on aluminum powder is strongly pH dependent (Fig. 1).

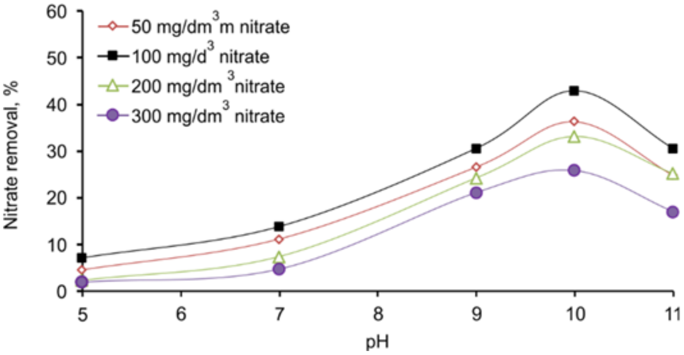

Fig. 1. Dependences of nitrate removal by aluminum powder on pH; aluminum powder dose 2 g/dm^3, contact time 60 min

The adsorption of nitrate increased upon increasing pH, reaching a maximum at initial pH 10, and then decreased with further increase in pH. Initially, as pH increased from 5 to 10, the nitrate sorption also increased due to the fact that the surface of aluminum powder became positively charged and attracted negative nitrate anions. The decrease in sorption capacity at pH higher than 10 may be due to the competition for the active sites by OH^- ions and the electrostatic repulsion of anionic nitrate by the negatively charged surface [10, 14]. According to Leyva Ramos [15] at pH value above 4, aluminum precipitates as Al (OH) and at pH below 4, the predominant species is the Al^{3+} ion. However, at higher pH nitrate ions adsorb to Al (OH) precipitates and swept from solution. The interaction between nitrate ions and aluminum powder as a metal oxide could be modeled in two step ligand exchange reactions as follows [16]:

$$\mathrm{MOH} + \mathrm{H}^+ \rightleftharpoons \mathrm{MOH}_2^+ \tag{5}$$

$$\mathrm{MOH}_2^+ + \mathrm{NO}_3^- \rightleftharpoons \mathrm{MOH}_2\text{–}\mathrm{NO}_3 \ (\text{or } \mathrm{MNO}_3 + \mathrm{H}_2\mathrm{O}) \tag{6}$$

where M presents a metal ion (here, Al).

3.2. EFFECT OF CONTACT TIME AND INITIAL NITRATE CONCENTRATION

The nitrate removal increased with increasing reaction time (Fig. 2). It can be seen that, the adsorption process consisted of two steps; an initial rapid step whereby adsorption was fast followed by second slower step whereby equilibrium uptake was achieved.

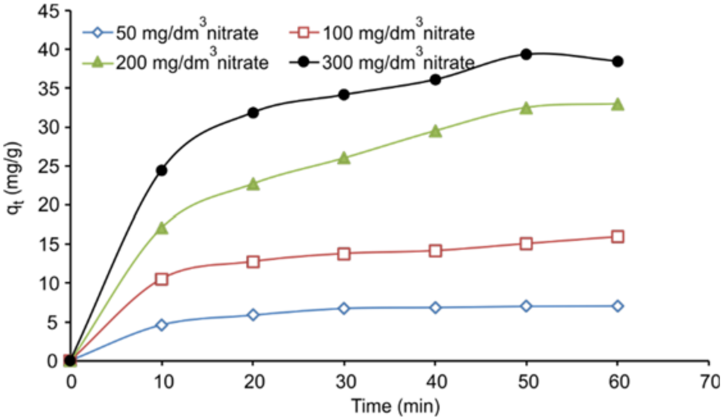

Fig. 2. Effect of contact time on nitrate uptake by adsorbent; aluminum powder dose 2 g/dm^3, pH 10

The beginning rapid step (during the first 15 min of adsorption) was due to the availability of adsorption sites for the uptake of nitrate. The second slower process was due to the quick exhaustion of the adsorption sites [17]. The agitation time for two initial nitrate concentrations studied showed that after 60 min, the nitrate uptake remained almost constant, beyond which there was almost no increase in q_t. This implies that the adsorption reached an equilibrium state and optimum agitation time was fixed at 60 min. Also, nitrate uptake by aluminum powder increased when the initial nitrate concentration increased from 50 to 100 mg $\mathrm{NO_3^-/dm^3}$. This phenomenon is due to the increase in the driving force of the concentration gradient when initial concentration of nitrate is increased. This behavior is common in batch reactor when one of the initial adsorbate concentration or adsorbent dose is fixed and the other one is varying [18].

3.3. KINETIC MODELING

The kinetics of nitrate sorption on aluminum powder was analyzed using two common kinetic models, pseudo-first order [19] and pseudo-second order [20] to identify the dynamics of the solute adsorption process. Also, to determine whether intraparticle diffusion was the rate limiting step for nitrate adsorption onto aluminum powder, the experimental data were fitted to the intraparticle diffusion model [21]:

- pseudo-first order equation

$$\log\left(q_e - q_t\right) = \log q_e - \frac{k_1 t}{2.303} \tag{7}$$

- pseudo-second order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

- intraparticle diffusion model:

$$q_t = k_{id} t^{0.5} + C \tag{9}$$

where q_e and q_t are the sorption capacities (mg/g) at equilibrium and at any time t, respectively, k_1 is the rate constant of pseudo-first order (min^{-1}), k_2 is the pseudo-second order rate constant (mg/(g·min)), k_{id} is the intraparticle diffusion rate constant (g/(mg·min$^{-0.5}$) and C is the intercept. The experimental data in Fig. 2 were fitted linearly by using Eqs. (8)–(10), as shown in Figs. 3a–c. The kinetic parameters obtained are summarized in Table 1. It can be seen that the calculated correlation coefficients (R^2) are closer to the unity for the pseudo-second order kinetic model compared with that two other models. In addition, the theoretical q_e calculated from the pseudo-second order kinetic model agreed well to the experimental equilibrium amount of absorbed nitrate ($q_{e\,(\mathrm{exp})}$). Therefore, pseudo-second order model can be used to favorably explain the nitrate sorption on aluminum powder. This also implies that the adsorption of nitrate onto aluminum powder is mostly controlled by the chemisorption possibly due to exchange or sharing of electrons between cation groups of aluminum and anion groups of nitrate [22].

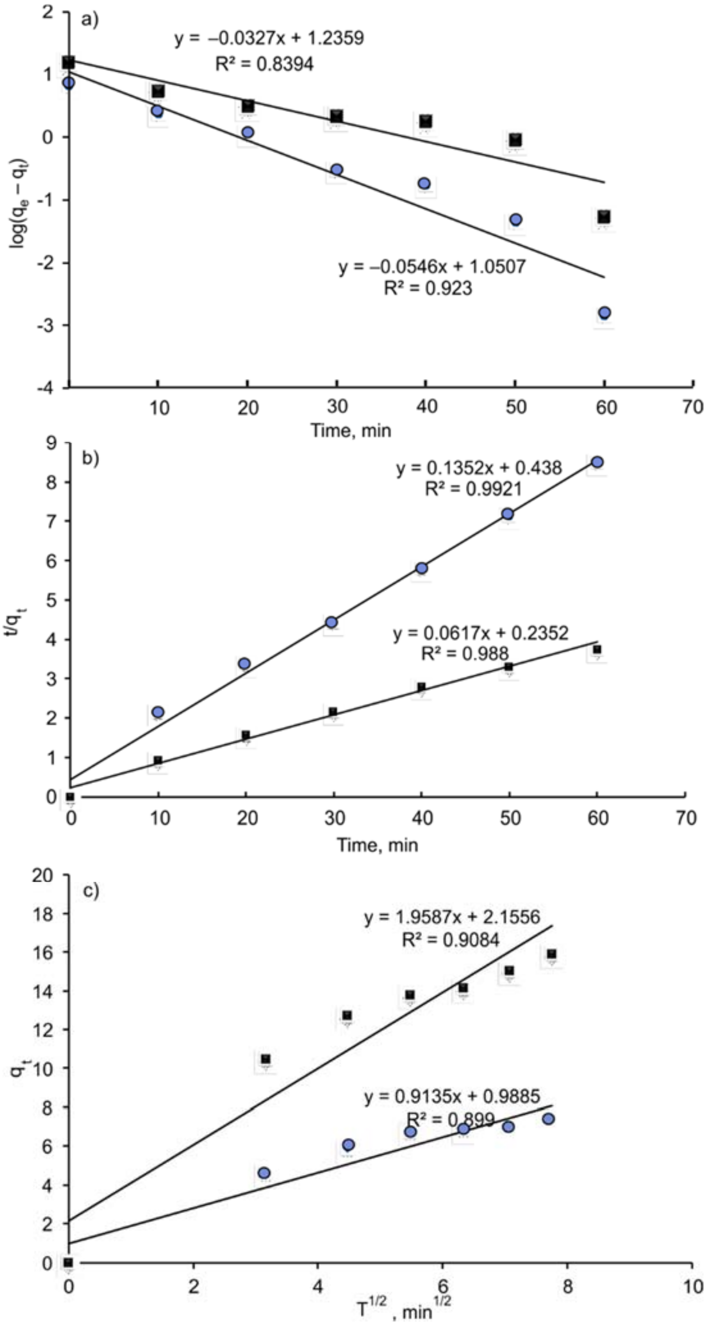

Fig. 3. Plots for adsorption kinetic models of nitrate ions on aluminum powder: a) pseudo-first order, b) pseudo-second order, c) intraparticle diffusion models circles – 50 mg/dm^3 of nitrate, squares – 100 mg/dm^3 of nitrate

As shown in Fig. 3c, the plots of q_t versus $t^{1/2}$ did not pass through the origin (0, 0) and this deviation might be contribute to the disagreement between the mass transfer rate in the initial and final stages of adsorption. This indicated that the adsorption is not the rate-limiting step and might be controlled by a variety of adsorption mechanisms [22, 23].

Table 1

Pseudo-first order, pseudo-second order and intraparticle diffusion models for nitrate adsorption onto aluminum powder (pH = 10, room temperature)

Pseudo-first order kinetic model					
C_0 [mg NO$_3^-$/dm^3]	q_e (exp) [mg/g]	q_e (theor) [mg/g]	k_1 [1/min]		R^2
50	7.09	16.81	0.135		0.923
100	16	18.34	0.076		0.839
Pseudo-second order model					
C_0 [mg NO$_3^-$/dm^3]	q_e (exp) [mg/g]	q_e (theor) [mg/g]	k_2 [mg/ (mg·min)]		R^2
50	7.09	7.38	0.010		0.992
100	16	16.46	0.004		0.998
Intraparticle diffusion model					
C_0 [mg NO$_3^-$/dm^3]	q_e (exp) [mg/g]	q_e (theor) [mg/g]	k_{id} [mg/ (g·min$^{0.5}$)]	C [mg/g]	R^2
50	7.09	7.43	0.523	3.38	0.899
100	16	15.95	1.107	7.35	0.908

3.4. ADSORPTION ISOTHERMS

The analysis of the isotherms data is an important step in the study of adsorption systems. Isotherm models can be used to design the process at a constant temperature and pH. When an adsorbent and nitrate species solution are contacted, the concentration of the nitrate on the aluminum powder will increase until a dynamic equilibrium is reached, at which point there is a well distribution of nitrate species between the solid and liquid phases [13, 24]. The isotherm constants were calculated and presented in Table 2. The straight-line plots of logq_e against logC_e for the Freundlich model and C_e/q_e against C_e for the Langmuir model are presented in Figs. 4a, b.

Table 2

Langmuir and Freundlich constants for the adsorption of nitrate on aluminum powder at constant temperature

Langmuir constants				Freundlich constants		
Q_0 [mg/g]	b	R_L	R^2	n	K_F [(mg/g)·(dm^3/g)$^{-1/n}$	R^2
45.2	0.006	0.33	0.808	1.46	0.75	0.865

The adsorption isotherms obtained for nitrate ion uptake by aluminum powder were found to follow at a satisfactory extent both the Freundlich ($R^2 = 0.865$) and Langmuir ($R^2 = 0.808$) predictions. The R^2 value for the Freundlich isotherm is little higher than that of the Langmuir isotherm, which indicates that the adsorption of nitrate ions on aluminum powder is more consistent with the Freundlich model.

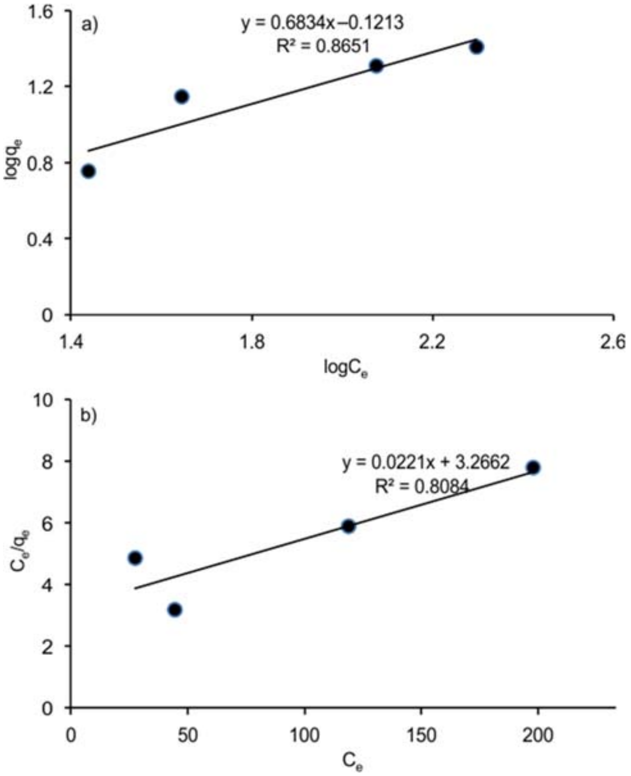

Fig. 4. Freundlich (a) and Langmuir (b) isotherms of nitrate sorption on aluminum powder

This may be due to more heterogeneous distribution of active sites of adsorption on aluminum powder surface and multilayer adsorption. However, the sorption of nitrate on the aluminum powder is complex, involving more than one mechanism, such as ion exchange, surface complexation, and electrostatic attraction. The maximum adsorption capacity, Q_0, was 45.2 mg/g calculated from the Langmuir plot. This value indicated that the adsorbent had a high capacity to remove nitrate ions. At 300 mg NO_3^-/dm^3 nitrate, R_L was calculated to be 0.33; thus, adsorption is favorable. The n value was higher than 1 which indicated that the adsorption intensity is favorable at higher concentrations. These observations were in agreement with the work reported earlier with the other adsorbents for nitrate removal [16]. In recent years, various adsorbents such as carbon-based sorbents, natural sorbents, agricultural wastes, industrial wastes, biosorbents and miscellaneous adsorbents (e.g., cement paste, layered double hydroxide and mesoporous silica) were used for the removal of nitrate from water. The adsorption capacity of the aluminum powder was compared with other adsorbents of NO_3^- that were reported in literature and presented in Table 3.

Table 3

Adsorption capacities and other parameters for the removal of nitrate by various sorbents

Adsorbent	Adsorption capacity [mg/g]	Concentration range [mg/dm^3]	Contact time	Temperature [°C]	pH	Reference
Carbon nanotubes	25[a]	–	60 min	25	<5.0	[25]
Bamboo powder charcoal	1.25	0–10	120 h	10	–	[26]
Iron modified pumice	10–21	50-100	50 min	ambient	5	[27]
Commercial activated carbon	1.22	0–25	10 min	15	–	[28]
Ammonium-functionalized mesostructured silica	46.0	100–700	60 min	5	<8.0	[29]
Aluminum powder	45.2	50-300	60 min	ambient	10.0	this study

[a] Concentration of carbon nanotubes in mmol/g.

3.5. CONCENTRATION OF ALUMINUM RESIDUAL IN SOLUTION

Accumulation of aluminum in human has been reported to be associated with dementia, Parkinson's disease, and Alzheimer's disease. The release of aluminum ion into the solution can occur through the reaction with nitrate ions.

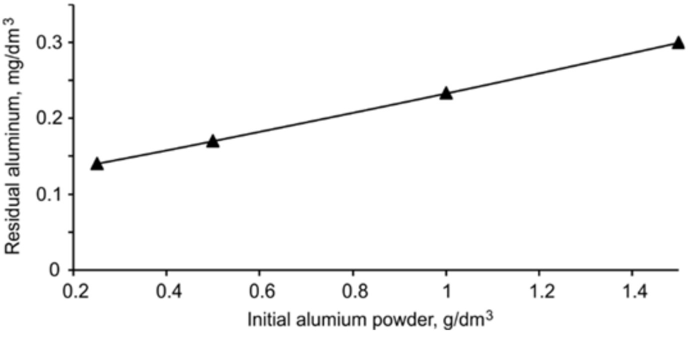

Fig. 5. Aluminum residual at equilibrium in solution;
nitrate concentration 100 mg/dm^3, time 60 min and pH 10

Figure 5 illustrates aluminum residual as a waste by-product after equilibrium adsorption treatment process for initial nitrate concentration of 100 mg NO_3^-/dm^3. It can be seen that increase initial aluminum dose from 0.25 to 1.5 g/dm^3 results in 0.3 mg/dm^3 of aluminum residual which a little exceeds the WHO guideline (from 0.1 to 0.2 mg/dm^3) [30].

3.6. EFFECT OF COMPETING ANIONS

The nitrate adsorption was not significantly influenced by the presence of competing anions at selected concentration (Fig. 6). Anions co-existing in the nitrate solutions possibly limit the nitrate removal efficiency.

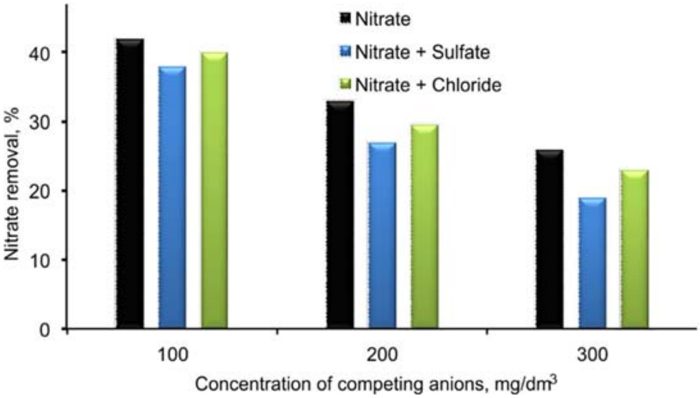

Fig. 6. Effect of various concentrations of competing anions on nitrate sorption on aluminum powder; dose 2 g/dm^3, nitrate concentration 100 mg/dm^3, time 60 min and pH 10

In the presence of sulfate, the percentage removal of nitrate reached 19, 27 and 38% at 100, 200 and 300 mg SO_4^{2-}/dm^3, respectively, while in the case of chloride, the percentage values of removal of nitrate were 23, 29 and 40% at 100, 200 and 300 mg Cl$^-$/dm^3, respectively. Sulfate had higher influence on nitrate adsorption than chloride. Previous research [31] indicated that Cl$^-$ formed outer-sphere surface complexes, while SO_4^{2-} formed both outer-sphere and inner-sphere surface complexes. Therefore, this outer and inner-spherically sorbing chloride and sulfate anions can interfere with the sorption of nitrate where the sorption competition occurred for the limited amount of sorption sites on aluminum powder.

4. CONCLUSIONS

Aluminum oxide which is abundant in the environment showed strong adsorption and high capacity for nitrate ions. The sorption of nitrate onto aluminum powder was found to be strongly pH dependent with maximum nitrate removal occurring at pH 10. The equilibrium time for removal of nitrate was found to be 60 min. Kinetic analyses indicate that the sorption process followed pseudo-second order kinetics under the selected concentration range (50–100 mg NO_3^-/dm^3). Though the equilibrium data were successfully modeled by both the Langmuir and Freundlich models, data were fitted better to the Freundlich model, indicating surface heterogeneity and multilayer adsorption. It was found that, the aluminum residual in water were lower than the standard level of 0.2 mg/dm^3 for adsorbent dose used in this study. Nitrate sorption was influenced to somewhat by the presence of competing anions, chloride and sulfate, which interfere with the sorption of nitrate on the aluminum powder.

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