Nitrate removal from aqueous solution by adsorption onto various materials

Neşe Öztürk*, T. Ennil Bektaş

Osmangazi Üniversitesi, Mühendislik-Mimarlık Fakültesi Kimya Mühendisliği Bölümü, 26480 Meşelik, Eskişehir, Turkey

Abstract

In this study sepiolite, sepiolite activated by HCl, slag and powdered activated carbon were used as adsorbent with a particle size was between 71 and 80 μm (200–170 mesh). NaNO$_3$ solution (100 mg/l) was used in batch adsorption experiments for nitrate removal. First kinetic studies were carried out and it was determined that slag was not effective for nitrate removal, then contact time, pH and adsorbent dosage effects on nitrate removal by adsorption were investigated using other adsorbents except slag. The equilibrium time was found to be 30, 45, 5 min for sepiolite, powdered activated carbon and activated sepiolite, respectively. The most effective pH value for nitrate removal was 2 for powdered activated carbon. pH value did not affect nitrate removal significantly for other adsorbents. Adsorbent dosages were varied from 5 to 20 g/l solutions. An increase in adsorbent dosage increased the percent removal of nitrate. A series of isotherm studies were undertaken and the data evaluated for compliance with the Langmuir and Freundlich isotherm models. To investigate the adsorption mechanisms, three simplified kinetic models, i.e., first-, second-order and intraparticle diffusion were tested. Adsorption followed second-order rate kinetics. The correlation coefficients for second order kinetic model are greater than 0.996. Experimental data show that sepiolite activated by HCl was effective for nitrate removal.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Nitrate removal; Adsorption; Sepiolite; Activated sepiolite; Wastewater

1. Introduction

Eskişehir city supplies water from the Porsuk River that polluted by some factories located around Kütahya city and municipal wastewater. Although some factories have wastewater treatment units some of them do not work efficiently. Nitrogen Fertilizer Production Factories are the main polluting sources of the nitrogen forms of concern.

Several nitrogenous compounds, including ammonia, nitrite and nitrate have been frequently present in drinking water and various types of agricultural, domestic and industrial wastewater [1,2]. Nitrate can cause several environmental problems. Nitrates and phosphates can stimulate eutrophication where pollution is caused in waterways by heavy algal growth, as they are both rate-limiting nutrients for the process. Nitrate contaminated water supplies have also been linked outbreaks of infectious disease [3]. Excess nitrate in drinking water may cause methemoglobinaemia also called a blue baby disease, in newborn infants [4,5].

Traditional methods for nitrogen removal from wastewater are biological processes (denitrification, nitrification), chemical processes (breakpoint chlorination, selective ion exchange) and physical operation (ammonia stripping). Other operations or processes are conventional treatment (primary, secondary), biological processes (bacterial assimilation, harvesting of algae, oxidation ponds), chemical processes (chemical coagulation, adsorption), physical operations (ammonia stripping, electrodialysis, filtration, reverse osmosis), land application (irrigation rapid infiltration, overland flow) [6–8].

Adsorption in general, is the process of collecting soluble substances that are in solution on a suitable interface. In the past, the adsorption process has not yet been used extensively in wastewater purification but demands for a better quality of treated wastewater effluent have led to an intensive examination and use of the process of adsorption on activated carbon. Activated carbon is a very expensive adsorbent for

---

* Corresponding author. Tel.: +90 222 2393750/3280;
fax: +90 222 2393613.

E-mail address: nozturk@ogu.edu.tr (N. Öztürk).

Nomenclature

b	Langmuir isotherm constant which related to energy of adsorption (l/mg)
k_1	rate constant of first order adsorption (l/min)
k_2	rate constant of second-order adsorption g/(min mg)
K_f	Freundlich adsorption isotherm constant $(mg/g)(l/mg)^{1/n}$
k_{p2}	rate parameter of intraparticle diffusion model $(mg/g\,min^{1/2})$
n	Freundlich adsorption isotherm constant
q_e	amount of nitrate adsorbed at equilibrium (mg/g)
q_t	amount of nitrate adsorbed at time t (mg/g)
r	particle radius (m)
t	time (min)
C_e	concentration of nitrate solution at equilibrium (mg/l)
D	diffusivity of solute in the particle (m^2/s)
Q_o	monolayer capacity of the adsorbent (mg/g)
R^2	correlation coefficient

---

removal of pollutant so other adsorbents must be investigated [9–12].

Sepiolite is an inexpensive material and most of the world reserves are found in Turkey. Sepiolite, which is a kind of fibrous silicate clay mineral, is formed of tetrahedral and octahedral sheets. The magnesium content provides strength while the hydrogen and oxygen contribute porosity. Sepiolite has three types of active surface centers (i) oxygen atoms (ii) water molecules and (iii) Si–OH groups. The distribution of these sites within the mineral makes the surface. The surface irregularities might cause increase in the number of active sites [13].

Sepiolite is one of the lightest and most porous substances. It is a natural filter. This natural absorptivity causes the tobacco pipes to slowly change color, eventually turning rich brown color filtering tobacco flue. They are made mostly for export.

Sepiolite reserves are mainly located in Eskişehir and Konya. Sepiolite is used as adsorbent, absorbent, catalyst packed material, carrier for methanogenic bacteria in biogas production, insulation material in rocket and light building materials, etc. [14]. The high capacity values were observed for the heavy metal ion removal and wastewater treatment using sepiolite [15].

In adsorption, adsorbent surface area must be large. Surface area can be increased by activation [16]. So sepiolite activated by HCl is used in adsorption experiments. Sabah et al. [17] studied adsorption mechanism of cationic surfactants onto acid and heat activated sepiolites. Adsorption of cobalt from aqueous solutions onto sepiolite and activated sepiolites was studied [18].

In this study nitrate removal from aqueous solutions by adsorption onto selected adsorbents was investigated. Waste sepiolite sources from hand-carving, activated waste sepiolite, slag and powdered activated carbon were used as adsorbent. Toward this aim, the effect of various parameters on the adsorption process has been investigated. The results are presented and discussed in this study.

2. Materials and methods

2.1. Materials

Sepiolite was obtained from hand-carving waste from Eskişehir Margı area. Sepiolite was analyzed in the Eskişehir Cement Factory and Magnesia Factory. Chemical analysis result is 57.51% SiO_2, 27.52% MgO, 0.09% Al_2O_3, 0.03% Fe_2O_3, 0.9% CaO, 0.01% TiO_2, 0.02% Na_2O, 0.01% K_2O, 13.9% ignition loss. Slag was obtained from a textile factory boiler fired Soma coal. The powdered activated carbon was originated from plants. Waste sepiolite (about 10 g) activated with 400 ml 0.75 M acid solution (HCl) in a reactor under reflux condenser at 75 °C for 4 h. All of the adsorbents were dried at 105 °C for 2 h before being used. Particle size of all the adsorbents used in adsorption experiment was between 71 and 80 μm (200–170 mesh).

Surface areas of all of the adsorbents were determined by gas adsorption equipment (NOVA-2200) using N_2 gases at −196 °C. Surface area was determined by the Langmuir method.

$NaNO_3$ solution (100 mg/l) was used in adsorption experiments.

The reagents and salts used in the experiments were reagent-grade Merck products.

2.2. Adsorption studies

Adsorption of nitrate ions onto different adsorbents was studied by batch experiments. A fixed amount of each dry adsorbent (0.5 g) and 50 ml of $NaNO_3$ solution (100 mg/l) was placed in a capped volumetric flask (50 ml) and shaken at 140 rpm using a temperature-controlled water bath (NUVE) with shaker (MEMMERT). Then, the adsorption samples were centrifuged and the nitrate concentration in supernatant was determined.

Nitrate was measured with an ion meter (Consort P 903) using the nitrate electrode (Orion 9707 BN). The ion meter was calibrated using standard nitrate solutions before every analysis. Calibration is performed in a series of standards that prepared freshly from standard nitrate solution (0.1 M NO_3^-: Orion 920706). Ionic strength adjuster solution (Nitrate ISA: Orion 930711) containing $(NH_4)_2SO_4$ was added to all solutions to ensure that the samples and standards have similar ionic strength, proper pH, and to reduce the effect of interfering ions.

For comparison, nitrate was analyzed by diazotization method outlined in the Standard Methods of Examination of Water and Wastewater [19] using spectrophotometer

(Shimadzu UV-120-01). Calibration is performed in a series of standard solution prepared from stock KNO_3 solutions.

Also the analyses were performed in duplicate.

2.3. Kinetic studies

In kinetic studies 50 ml $NaNO_3$ solution (100 mg/l) and 0.5 g adsorbent were used. Batch experiment was repeated at different periods for all adsorbents. $NO_3{}^-$ concentrations in supernatant have been constant after a time period. This period was accepted as equilibrium time for relevant adsorbent.

2.4. pH studies

In order to investigate the effects of pH on nitrate adsorption, the pH of the $NaNO_3$ solutions (100 mg/l) were adjusted to different values (2, 5.5, 7, and 10) by dilute NaOH or HCl solutions. pH was measured by using a pH-meter (Consort P 903). pH adjusted solution and 0.5 g adsorbent were used in batch experiments conducted at the determined equilibrium time. The pH value providing the maximum nitrate removal was determined.

2.5. Adsorbent dosage studies

Adsorption of 100 mg/l of $NaNO_3$ solution by different adsorbent doses (0.25–1.0 g/50 ml) for each adsorbent was carried out at the optimum pH.

2.6. Other ions studies

The effects of presence of sulphate, phosphate and ammonium ion on nitrate adsorption were studied. Tests were conducted in the presence of 100 mg/l of nitrate and 10 mg/l each of sulphate, phosphate and ammonium ions. The K_2SO_4, KH_2PO_4 and NH_4Cl salts were used to obtain the respective anions. Tap water sample (50 ml) was also used in nitrate adsorption studies by using various amount of sepiolite activated by HCl as adsorbent. The adsorbent amount used were 0.05, 0.1, 0.2, 0.3, 0.4 and 0.5 g. The amount of 0.2 g/50 ml tap water was found to be optimum for adsorption of nitrate.

3. Results and discussion

Treatment processes depend on adsorption method are more effective than chemical and biological processes, but at the same time more expensive. So alternative adsorbent must be researched. In this study, sepiolite, sepiolite activated by HCl, slag and powdered activated carbon were used as adsorbent for nitrate removal by adsorption.

Surface areas of sepiolite, sepiolite activated by HCl, slag and powdered activated carbon determined by the Langmuir method using gas adsorption equipment were 516.3, 519.06, 18.13, 866.25 m^2/g, respectively. It is observed that activation were increased the surface area. This is because the proton (H^+) of the acids was replaced by part of the Mg^{2+} ions located in the octahedral sheet during acid activation. Furthermore, more carbonates in sepiolite are partially decomposed leading to new pores and fresh surfaces [14,18].

Nitrate was measured with an ionmeter using nitrate electrode and analyzed using a spectrophotometer according to standard methods [19]. It was observed that the results obtained by both methods were parallel to each other.

Effective parameters, adsorption kinetics and adsorption isotherms were given by the following subtitles for nitrate removal onto different adsorbents.

3.1. Effect of contact time

Effect of contact time on removal of nitrate by several adsorbents is shown in Fig. 1. The values of equilibrium time were found to be 30 min for sepiolite, 45 min for powdered activated carbon and 5 min for activated sepiolite. Nitrate removal was not effective for slag. So slag was not used in the other experiments. It was thought that the metals (Ca^{2+}, Mg^{2+}, etc.) on the surface of slag passed to the solution and
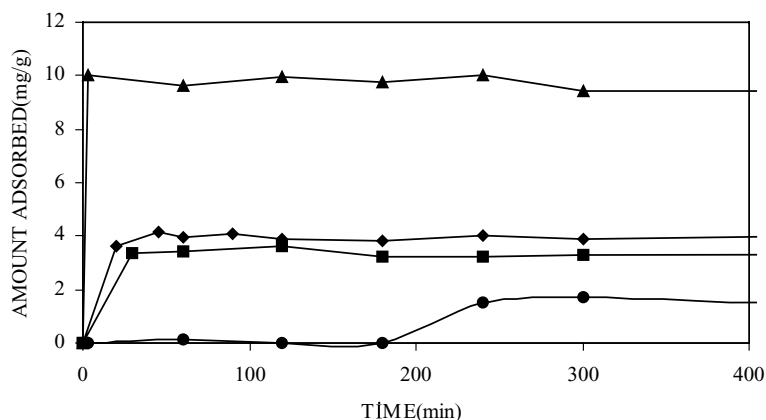

Fig. 1. Effect of contact time on the removal of nitrate by different adsorbents: (◆) activated carbon, (■) sepiolite, (▲) sepiolite activated by HCl, (●) slag.
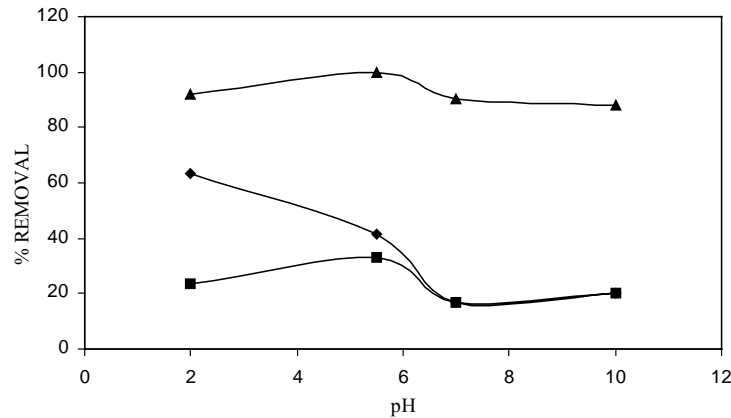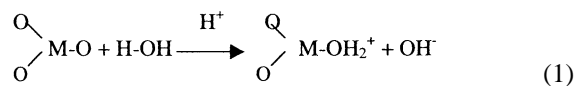
Fig. 2. Effect of pH on the removal of nitrate by different adsorbents: (◆) activated carbon, (■) sepiolite, (▲) sepiolite activated by HCl.

they reacted with nitrate and formed stable compounds. For this reason, these nitrates could not be adsorbed.
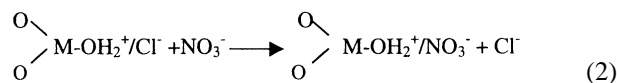
3.2. Effect of pH

The effect of pH on the removal of nitrate is shown in Fig. 2. The most effective pH value for nitrate removal was 2 for powdered activated carbon and pH value did not affect nitrate removal significantly for other adsorbents. For activated carbon, the reason for good removal of nitrate at the lower pH is that the negative charge on the surface is reduced due to the excess of protons in solutions. As a result, the pH of the system decreases and the number of positively charged sites increase. A positively charged surface site on the adsorbent favors the adsorption of the nitrate anions due to electrostatic attraction.

The chief constituents of sepiolite are mainly Si and metal oxides. These oxides form hydroxide complexes in solution and subsequent acidic or basic dissociation of these complexes at the solid solution interface leads to development of a positive or negative charge on the surface. As can be seen from Eq. (1), at acidic pH values, the oxides in solution tends to form an aqua complex to yield a positively charged surface [20].

$$\begin{matrix} O \\ \diagdown \\ \diagup \\ O \end{matrix} M\text{-}O + H\text{-}OH \xrightarrow{H^+} \begin{matrix} O \\ \diagdown \\ \diagup \\ O \end{matrix} M\text{-}OH_2^+ + OH^- \qquad (1)$$

where M: mainly Si and metals.

When hydrochloric acid was used for activation, the positively charged surface would be associated with chloride ions, which would subsequently be exchanged for nitrate anions, as shown in Eq. (2)

$$\begin{matrix} O \\ \diagdown \\ \diagup \\ O \end{matrix} M\text{-}OH_2^+/Cl^- + NO_3^- \longrightarrow \begin{matrix} O \\ \diagdown \\ \diagup \\ O \end{matrix} M\text{-}OH_2^+/NO_3^- + Cl^- \qquad (2)$$

Nitrate adsorption with sepiolite activated by HCl was not affected by pH change and the ion exchange becomes the main mechanism of the nitrate removal.

Initial pH of the aqueous solution has essentially no effect on the nitrate removal by sepiolite and ion exchange resins [2,21,22].

3.3. Adsorption kinetics

In order to examine the controlling mechanisms of adsorption process such as mass transfer and chemical reaction, several kinetic models are used to test the experimental data.

The rate constant of adsorption is determined from the following first-order rate expression given by Lagergreen [23–26]

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (3)$$

where q_e and q_t are the amounts of nitrate adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 (l/min) is the rate constant of first-order adsorption [27].

A second-order equation based on adsorption equilibrium capacity may be expressed in the form

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (4)$$

where k_2 g/(min mg) is the rate constant of second-order adsorption. If the above two equations cannot give definite mechanisms, the intraparticle diffusion model is tested. The fractional approach to equilibrium changes according to a function of $(Dt/r^2)^{1/2}$, where r is the particle radius and D diffusivity of solute within the particle. The initial rates of intraparticle diffusion can be obtained by linearization of the curve $q_t = f(t^{1/2})$ [28–31].

The fit of these models was checked by each linear plot of $\log(q_e - q_t)$ versus t, (t/q_t) versus t and q_t versus $t^{1/2}$, respectively and by comparing to the regression coefficients for each expression. The results show that such first-order rate expression and intraparticle diffusion model is not fully valid for the present systems. Due to low correlation coefficients, figures not shown. For the first order rate expression, the experimental q_e values do not agree with the calculated

Table 1
Values of adsorption rate constants for different adsorbents

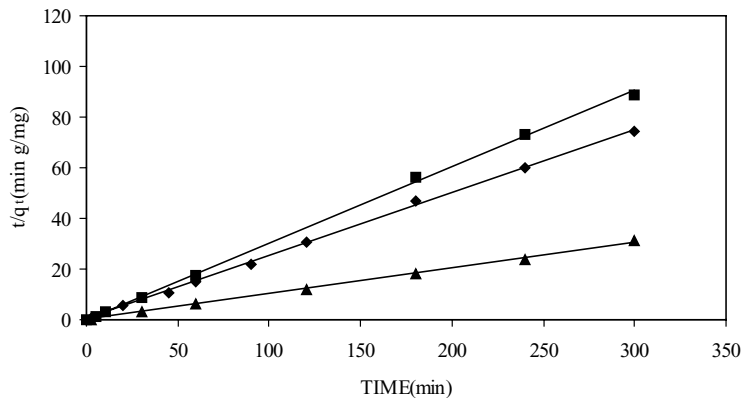| Adsorbent	q_e (exp) (mg/g)	First-order kinetic model			Second-order kinetic model			Intraparticle diffusion model	
		k_1 (l/min)	q_e (cal) (mg/g)	R^2	k_2 (g/(mg min))	q_e (cal) (mg/g)	R^2	$k_{p,2}$ (mg/g min$^{1/2}$)	R^2
Activated carbon	4.14	5.98×10^{-3}	0.67	0.2651	0.28	4.00	0.9991	0.042	0.3303
Sepiolite	3.46	1.61×10^{-3}	0.41	0.2713	11.78	3.32	0.9993	0.018	0.0587
Sepiolite activated by HCl	9.80	4.6×10^{-4}	0.58	0.0190	0.47	9.81	0.9993	0.086	0.1294

Fig. 3. Plots for second-order model for nitrate adsorption by different adsorbents: (◆) activated carbon, (■) sepiolite, (▲) sepiolite activated by HCl.

ones obtained from the linear plots (Table 1). A good agreement of the experimental data with the second-order kinetic model (Fig. 3) was observed for different adsorbents. The correlation coefficients for the second-order kinetic models are greater than 0.996 and the calculated q_e values agree very well with the experimental data (Table 1).

3.4. Effect of adsorbent dosage

Fig. 4 shows the removal of nitrate as a function of adsorbent dosage. In general, increase in adsorbent dosage increased the percent removal of nitrate, which is due to the increase in adsorbent surface area of the adsorbents. It is evident that for the removal of 100 mg/l of NaNO$_3$, removal

percent decreases in the order activated sepiolite, activated carbon and sepiolite, respectively. The results also clearly indicate that the removal efficiency increases up to optimum dosage beyond which the removal efficiency is negligible.

3.5. Adsorption isotherm

The equilibrium adsorption isotherm is of fundamental importance in the design of adsorption system [32]. The Langmuir isotherm is represented by the following equation [33]:

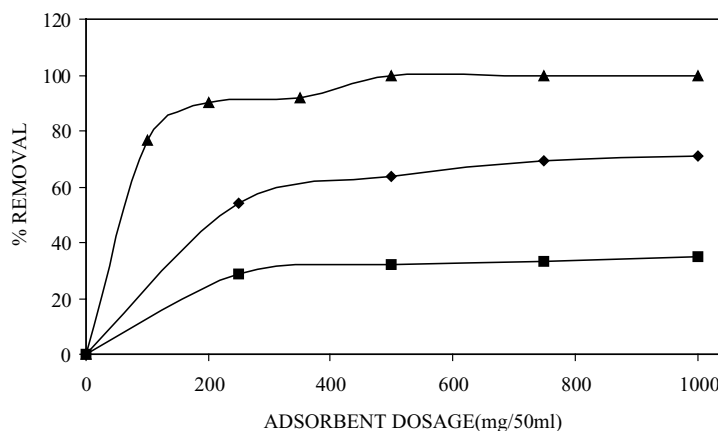$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \tag{5}$$

Fig. 4. Effect of adsorbent dosage on removal of nitrate by different adsorbents: (◆) activated carbon, (■) sepiolite, (▲) sepiolite activated by HCl.

Table 2
Isotherm constants for different adsorbents

Adsorbent	Langmuir			Freundlich		
	Q_o	b	R^2	K_f	n	R^2
Activated carbon	−3.01	−0.017	0.499	2.6×10^{-4}	0.359	0.863
Sepiolite	−0.33	−0.013	0.935	9.16×10^{-17}	0.11	0.917
Sepiolite activated by HCl	38.16	0.239	0.681	2.49	1.133	0.901
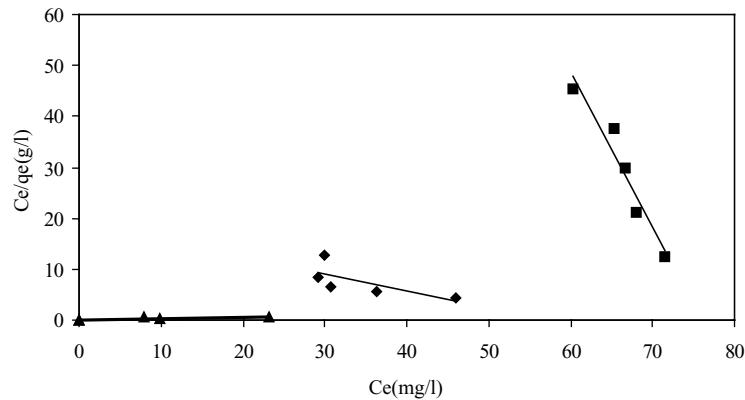
Fig. 5. Langmuir plots for the adsorption of nitrate by different adsorbents: (♦) activated carbon, (■) sepiolite, (▲) sepiolite activated by HCl.

where C_e is the concentration of nitrate solution (mg/l) at equilibrium. Q_o is the monolayer capacity of the adsorbent (mg/g) and b is related to the energy of adsorption (l/mg). A plot of C_e/q_e versus C_e gives b and Q_o if the isotherm follows the Langmuir equation (Fig. 5). Table 2 lists the values of Q_o and b which were calculated from the slope and intercept of the linear plots.

The Freundlich isotherm, which has been successfully applied to many adsorption processes, was also applied for the adsorption of nitrate [34–36]

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{6}$$

where K_f (mg/g)(l/mg)$^{1/n}$ and n are Freundlich adsorption isotherm constants, affecting the adsorption capacity and intensity of adsorption. Linear plots of $\log q_e$ versus

$\log C_e$ show that the adsorption follows Freundlich isotherm (Fig. 6). Values of K_f and n were calculated from the intercept and slope of the plots and are given in Table 2. In general, as the K_f value increases the adsorption capacity of the adsorbent increases. K_f value showed that sepiolite activated by HCl is more effective than other adsorbents (Table 2). According to Treybal [37] it has been shown using mathematical calculations that n were between 1 and 10 representing beneficial adsorption. So sepiolite activated by HCl represents beneficial adsorption.

Negative values for the Langmuir isotherm constants indicate the inadequacy of the isotherm model to explain the adsorption process [38]. The Freundlich model would be applicable. The fit of the data to the Freundlich equation may indicate the heterogeneity of the adsorbent surface.
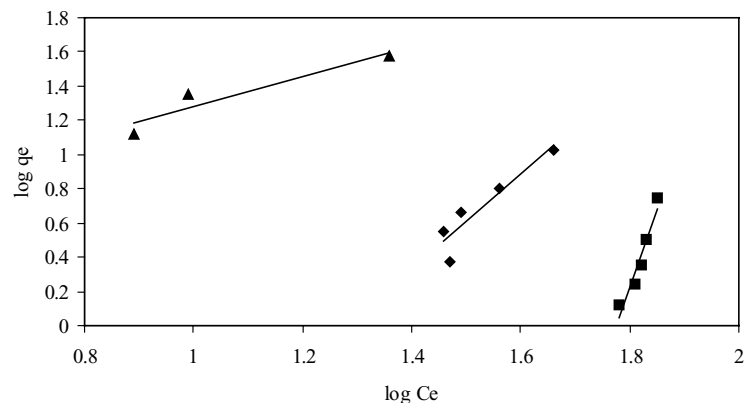

Fig. 6. Freundlich plots for the adsorption of nitrate by different adsorbents: (♦) activated carbon, (■) sepiolite, (▲) sepiolite activated by HCl.
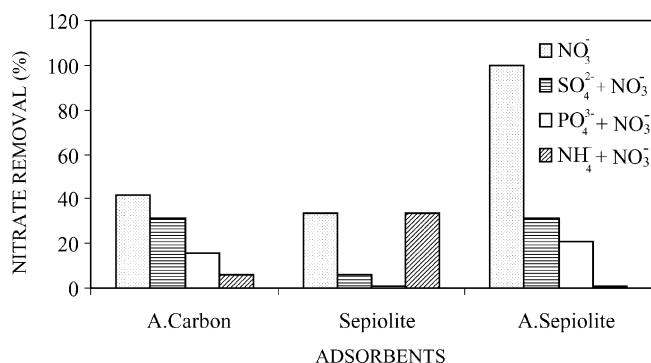
Fig. 7. The effects of presence other ions on nitrate adsorption onto different adsorbents.

3.6. Effect of other ions

In the present study all the tests were done with single ion, i.e. nitrate solutions. However, in real systems several other ions are present which can compete with nitrate. The effects of presence of sulphate, phosphate and ammonium ions on nitrate adsorption were studied. Among several N species, NO_3^- is the most stable and NO_2^- is quickly converted to nitrate so nitrate level of contaminated water is higher than NO_2^- level. Işıklı et al. (1994) evaluated the tap water in view of the levels of nitrate and nitrite in Eskişehir. In the result of analysis, the amount of nitrate was between 6.4 and 11 mg/l and the amount of nitrite was between 0.003 and 0.029 mg/l [39]. So the effect of presence of nitrite ion on nitrate adsorption was not studied. The adsorption abilities of the adsorbents for nitrate removal in the presence of nitrate only and also in the presence of nitrate and the other ions (sulphate, phosphate and ammonium) are shown in Fig. 7. It can be seen that in the presence of 10 mg/l sulphate, 10 mg/l phosphate and 10 mg/l ammonium ions, the nitrate removal decreased from 41.4 to 31.4, 15.9, 5.6% for activated carbon and from 33.4 to 5.6, 0.5, 33.4% for sepiolite and from 100 to 31.4, 21.1, 0.5% for sepiolite activated by HCl, respectively.

Sepiolit activated by HCl was also used as adsorbent for the nitrate removal from tap water including 7.94 mg/l nitrate, and 96.7% nitrate removal was obtained.

4. Conclusions

1. Sepiolite has good adsorption properties due to its channel structure, high surface area and sorption capacities. Experimental data showed that sepiolite activated by HCl was effective for nitrate removal than the other adsorbents and the adsorption rate was very high especially at early stages of the treatment. Since sepiolite is a waste material from hand carving, the treatment method seems to be economic.
2. Equilibrium adsorption data followed Freundlich isotherm for all adsorbents.
3. The maximum removal for nitrate was observed at pH 2 for activated carbon. pH value did not affect nitrate removal significantly for other adsorbents.
4. The increase in adsorbent dosage increased the percent removal of nitrate due to adsorbent surface area increase in adsorbent dosage.
5. For all adsorbents, the second-order equation gives a best fit to the equilibrium data.

References

[1] H.S. Peavy, D.R. Rowe, G. Tchobanoglous, Environmental Engineering, McGraw-Hill Book Company, New York, 1985, p. 696.
[2] S.H. Lin, C.L. Wu, Removal of nitrogenous compounds from aqueous solution by ozonation and ion exchange, Water Res. 30 (8) (1996) 1851.
[3] W.P. Barber, D.C. Stuckey, Nitrogen removal in a modified anaerobic baffled reactor (ABR): 1 denitrification, Water Res. 34 (9) (2000) 2413.
[4] Z. Feleke, Y. Sakakibara, A bio-electrochemical reactor coupled with adsorber for the removal of nitrate and inhibitory pesticide, Water Res. 36 (2002) 3092.
[5] T.V. Arden, The removal of nitrate from potable water supplies, New World Water 1994, (1994) 59.
[6] G. Tchobanoglous, Wastewater Engineering: Treatment Disposal Reuse, second ed., McGraw-Hill Inc., New York, 1979, p. 88.
[7] M. Henze, Nutrient removal from wastewater, New World Water 1995, (1995) 114.
[8] B. Bae, Y. Juang, W. Han, H. Shin, Improved brine recycling during nitrate removal using ion exchange, Water Res. 36 (2002) 3330.
[9] W.J. Weber, Physicochemical Processes For Water Quality Control, Wiley, New York, 1972, p. 638.
[10] W. Eckenfelder, Industrial Water Pollution Control, second ed., McGraw-Hill Inc., New York, 1989, p. 400.
[11] T.E. Bektaş, Master of Science thesis, Investigation of efficiency of sepiolite and other adsorbents for dyestuff and some anions removal, Chemical Engineering Department, Osmangazi University, Turkey, 2000.
[12] K.E. Noll, V. Gounari, W.S. Hou, Adsorption Technology for Air and Water Pollution Control, Lewis Publishers Inc., MI, 1992, p. 347.
[13] S. Balcı, Nature of ammonium ion adsorption by sepiolite: analysis of equilibrium data with several isotherms, Water Res. 38 (2004) 1129.
[14] İ. Kıpçak, Master of Science thesis, Investigation of dissolution kinetics of magnesium from sepiolite in acid medium, Chemical Engineering Department, Osmangazi University, Turkey, 1999.
[15] S. Balcı, Y. Dinçel, Ammonium ion adsorption with sepiolite use of transient uptake method, Chem. Eng. Process. 41 (2002) 79.
[16] H.S. Altundoğan, S. Altundoğan, F. Tümen, M. Bildik, Arsenic adsorption from aqueous solutions by activated red mud, Waste Manage. 22 (2002) 357.

[17] E. Sabah, M. Turan, M.S. Çelik, Adsorption mechanism of cationic surfactants onto acid and heat-activated sepiolites, Water Res. 36 (2002) 3957.

[18] M. Kara, H. Yüzer, E. Sabah, M.S. Çelik, Adsorption of cobalt from aqueous solutions onto sepiolite, Water Res. 37 (2003) 224.

[19] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, 12th ed., American Public Health Association, 1967.

[20] M. Özacar, ı.A. Şengil, Adsorption of reactive dyes on calcined alunite from aqueous solutions, J. Hazard. Mater. B98 (2003) 211.

[21] F. Akkurt, A. Alıcılar, O. Sendil, Removal of nitrate in water by means of adsorption, J. Fac. Eng. Arch. Gazi Univ. 17 (4) (2002) 83.

[22] L. Kınalı, Master of Science thesis, Examination of nitrate removal from drinking water by ion exchange and biological denitrification, Ondokuz Mayıs University, Turkey, 1994.

[23] H.S. Altundoğan, S. Altundoğan, F. Tümen, M. Bildik, Arsenic removal from aqueous solution by adsorption on red mud, Waste Manage. 20 (2000) 761.

[24] F.C. Wu, R.L. Tseng, R.S. Juang, Kinetic modelling of liquid phase adsorption of reactive dyes and metal ions on Chitosan, Water Res. 35 (3) (2001) 613.

[25] C. Namasivayam, R. Radhika, S. Suba, Uptake of dyes by a promising locally available agricultural solid waste: coir pith, Waste Manage. 21 (2001) 381.

[26] C. Namasivayam, D. Kavitha, Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, Dyes Pigments 54 (2002) 47.

[27] R. Sivaraj, C. Namasivayam, K. Kadirvelu, Orange peel as an adsorbent in the removal of Acid Violet 17 (acid dye) from aqueous solutions, Waste Manage. 21 (2001) 105.

[28] C.K. Lee, K.S. Low, L.C. Chung, Removal of some organic dyes by hexane-extracted spent bleaching earth, J. Chem. Tech. Biotechnol. 69 (1997) 93.

[29] T. Viraraghavan, F.M. Alfaro, Adsorption of phenol from wastewater by peat fly ash and bentonite, J. Hazard. Mater. 57 (1998) 59.

[30] F.A. Banat, B.N. Bashir, S. Al-ashen, O. Hayajneh, Adsorption of phenol by bentonite, Environ. Pollut. 107 (2000) 391.

[31] G. Annadurai, R.S. Juang, D.J. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, J. Hazard. Mater. B 92 (2002) 263.

[32] M. Doğan, M. Alkan, Y. Onganer, Adsorption of Methylene Blue from aqueous solution onto perlite, Water, Air, Soil Pollut. 120 (2000) 229.

[33] M.I. Panayotova, Kinetics and thermodynamics of copper ions removal from wastewater by use of zeolite, Waste Manage. 21 (2001) 671.

[34] B. Al Duri, Adsorption Modeling and Mass Transfer, CRC Press Inc., New York, 1996, pp.133–173.

[35] S. Rengaraj, S.H. Moon, R. Sivabalan, B. Arabindoo, V. Murugeson, Agricultural solid waste for removal of organics: adsorption of phenol from water and wastewater by palm seed coat activated carbon, Waste Manage. 22 (2002) 543.

[36] V.K. Gupta, C. K Jain, I. Ali, S. Chandra, S. Agarwal, Removal of lindane and malathion from wastewater using bagasse fly ash a sugar industry waste, Water Res. 36 (2002) 2483.

[37] R.E. Treybal, Mass Transfer Operations, third ed., McGraw-Hill Inc., New York, 1981.

[38] K.R. Ramakrishna, T. Viraraghavan, Dye removal using low cost adsorbents, Water Sci. Tech. 36 (2-3) (1997) 189.

[39] B. Işıklı, C. Kalyoncu, S. Metintaş, S. Etiz, Evaluation of nitrate and nitrite content of Eskişehir potable water, OGU Tıp Fakültesi Dergisi. 16 (1) (1994) 27.