
Volume 17, issue 4
April 2010
ISSN 1350-4177
ELSEVIER
Ultrasonics
SONOCHEMISTRY
Available online at www.sciencedirect.com
ScienceDirect
http://www.elsevier.com/locate/ultsonch

Ultrasonics Sonochemistry 17 (2010) 711–717

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultsonch

Sorption studies of nitrate ion by a modified beet residue in the presence and absence of ultrasound

Mahdi Karimi, Mohammad H. Entezari *, Mahmood Chamsaz

Department of Chemistry, Ferdowsi University of Mashhad, 91775 Mashhad, Iran

A R T I C L E I N F O

Article history:
Received 3 August 2009
Received in revised form 1 December 2009
Accepted 1 December 2009
Available online 6 December 2009

Keywords:
Modified beet residue
Adsorption
Desorption
Ultrasound

A B S T R A C T

Kinetic and thermodynamic studies were carried out for the adsorption of nitrate ion from aqueous solutions onto modified beet residue and for desorption from the sorbent to the solution in batch experiments. The beet residue was modified by epichlorohydrin in the presence of pyridine. The experiments were conducted in the presence and absence of ultrasound. The removal of this ion was examined by varying experimental conditions such as the amount of sorbent, contact time, concentration, and temperature. It was found that more than 90% of nitrate ion was removed in less than 2 min from the solution. Results indicate that the adsorption of nitrate in the presence of ultrasound was higher at lower temperature (10 °C) and it was lower at higher temperatures with respect to the control method (without ultrasound). In the case of desorption study, the amount of desorption was higher in the presence of ultrasound than its absence at different applied temperatures. The Langmuir isotherm model fits adequately the experimental data for adsorption and desorption studies. In point of kinetics, the second-order kinetic model describes the sorption process for this ion. The thermodynamic parameters such as $\Delta G°$, $\Delta H°$, and $\Delta S°$ were determined for the sorption of NO_3^- from the temperature dependence of the sorption process.

1. Introduction

Water is an undeniable fact in the species life. Whereas water submerge more earth surface but only about 2.66% of the total global water resources (groundwater, lakes and rivers, polar ice and glaciers) are fresh water [1].

Diminution of the water quality can be attributed to water pollutions or contaminations. Water pollution is generally defined as any physical, chemical, or biological alteration in water quality that has a negative impact on living organisms. On the other hand, pollution can be defined as the transfer of any substance to the environment [2].

Nitrate is one of the water pollution which creates through irregular use of the fertilizers in a relatively small land area. Nitrate is nontoxic in the concentrations lower than 50 mg L^{-1} but above this concentration it is toxic. This pollutant can be fatal for infants under 6 months of age. Nitrate through the convert to nitrite reacts with the hemoglobin in blood and converts the hemoglobin into methaemoglobin which does not carry oxygen to cell tissues. This phenomenon results in a bluish color of infant's skin so called methaemoglobinemia or the blue baby syndrome [3,4].

Nitrate ions can be removed by different methods such as chemical reduction [5–7], biological denitrification [8], and physical adsorption. The sorption process is an easy method and finding a cheap sorbent with high capacity of removal is very important. In general, adsorption is a process of collecting soluble substances from solution to a suitable interface [9,10]. Different materials can be used for the nitrate adsorption such as ion-exchange resins (Amberlite IRA 900, Duolite A 126, Amberlite IRA 996, Purolite A 520 E, Amberlite IRN-78, etc.) [4,11,12], sepiolite and activated sepiolite by HCl [9], activated carbon [3], bamboo powder charcoal [13], amine-modified coconut coir [14], modified wheat residue [15,16], and modified rice hull [16]. All these materials have great external surfaces and have a capacity for nitrate extraction from water. External surface is the main property of adsorbent materials because adsorption is an interface process between water and solid material.

Ultrasound has numerous applications and the major phenomenon responsible is cavitation (formation, growth, and implosive collapse of the bubbles). The collapse of the cavity near the solid boundary is asymmetric and produces high-speed jets of liquid. These jets hit the surface with strong forces. This process causes severe damage at the point of impact, produces newly exposed, and highly reactive surfaces. Ultrasonic waves reduce the thickness of liquid films attached to the solid phase, enhance the mass transfer, and facilitate the diffusion of adsorbate species through the interface [17–19].

Ultrasonic waves also promote desorption of adsorbed species from the sorbent. The cavitation bubbles and the associated

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* Corresponding author.
E-mail address: moh_entezari@yahoo.com (M.H. Entezari).

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doi:10.1016/j.ultsonch.2009.12.002

micro-disturbances near the surface are responsible for that. An important factor of ultrasound on the enhancement of desorption is the thermal effect which is due to ultrasonic energy dissipation. As desorption is an endothermic process and diffusion is faster at higher temperatures, desorption can be enhanced by introducing energy to the process [20–27].

The aim of this study is to use a cheap sorbent such as beet residue and its modification for the fast and efficient removal of nitrate anion from aqueous solution. Kinetics and thermodynamics of the sorption process were studied completely. Another important parameter in this work was the repeatedly use of the sorbent for the removal which is important in applicability of this method in the large scale.

2. Materials and methods

2.1. Materials

All chemicals and reagents used for experiments and analyses were of analytical grades. Stock solution of NO_3^- (2000 mg L^{-1}) was prepared from $NaNO_3$ in de-ionized water. This solution was diluted as required to obtain the standard solutions.

The solid waste of sugar beet was prepared from the regional sugar industries and it was treated for the removal of nitrate anion.

2.2. Preparation of sorbent

The solid waste of sugar beet was washed with distilled water to remove soluble impurities. Then, the sample was dried in an electric oven for 24 h at 150 °C. Five grams of the prepared sample were treated with epichlorohydrin and diethylamine in the presence of pyridine. For the sorbent containing cellulose as a starting material, pyridine was added to the solution to accelerate the wetting rate and extension of the cellulose polymer. Epichlorohydrin attached to the cellulose in alkaline conditions has been demonstrated to be the most likely sites for the attachment of bioactive agents such as amines and imines groups [15].

The size of the prepared particles was measured by MALVERN ZS-NANO and it was in the range of 1.7–4.1 μm with an average size of 3.5 μm. The prepared sorbent has a density of 1.16 g mL^{-1}.

2.3. Apparatus

The ultrasonic irradiation was carried out with equipment operating at 20 kHz (Branson Digital Sonifier, Model W-450D). The acoustic power was set at 25% position (33 W cm^{-2}, it was measured by calorimetric method) and the tip diameter of the horn was 1.1 cm. The reactor was a double cylindrical jacket and the temperature was controlled by circulating water through the cylindrical jacket. Experiments without ultrasound (control method) were performed in a batch reactor with stirring at 300 rpm.

The concentration of nitrate ion was determined by UV spectrophotometry (Agilent 8453) at a wavelength of 200 nm. The LOD of measurement method based on $3s_b$ was 1.3×10^{-2} and the RSD of the method was 0.48 %.

2.4. Procedure

2.4.1. Adsorption

Batch experiments for both methods were conducted by adding various amounts of treated sample to 50 mL of nitrate aqueous solution with concentration about 100 mg L^{-1} at constant temperature. The optimum amount of sorbent was 0.05 g. The obtained data were used to calculate the equilibrium uptake capacity of nitrate ion according to the following equation:

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

where q_e (mg g^{-1}) is the sorption amount of nitrate ion in the sorbent phase at equilibrium, C_0 and C_e are the initial and equilibrium concentrations of nitrate ion (mg L^{-1}) in the aqueous solution, V is the volume of solution (L), and m is the weight of sorbent (g) in the mixture.

2.4.2. Desorption

The nitrate ion loaded on the adsorbent can easily be desorbed under suitable conditions and then used for another removal of nitrate ion from an aqueous solution. Desorption of the adsorbed nitrate ion was done by immersing the loaded solid phase into 50 mL of NaOH solution with concentration in the range of 0–0.05 M for various times of sonication and without sonication. The quantity of desorbed nitrate ion was determined by measuring the amount of nitrate in the solution after the desorption process.

Isotherms, kinetic and thermodynamic functions for adsorption and desorption were found by considering different variables. The important selected variables such as contact time, temperature, presence and absence of ultrasound were the same for both adsorption and desorption but, the concentration of NaOH was a variable only for the case of desorption.

3. Results and discussion

3.1. Kinetic studies

3.1.1. Influence of the amount of sorbent

The amount of sorbent was varied in the range of 0.02–0.15 g for the removal of NO_3^- from aqueous solution by the sorption process, in the presence and in the absence of ultrasound. In these series of experiments the concentration of NO_3^- in solution were fixed at 90 mg L^{-1}, and the contact time was 5 min. As it is shown in Fig. 1, by increasing the mass of sorbent the amount of removal was increased. The enhancement of sorption with higher amount of sorbent can be attributed to the increased surface area of sorbent and availability of more sorption sites. According to Fig. 1, the concentration of nitrate ion almost reaches zero after 5 min in both methods. For all amounts of sorbent, sorption was slightly more effective in the absence than in the presence of ultrasound. This is due to the cavitation bubbles which set free a lot of energy during the collapse of the cavity [19,22,23]. The turbulent flow and shock waves produced by intense ultrasound can facilitate the

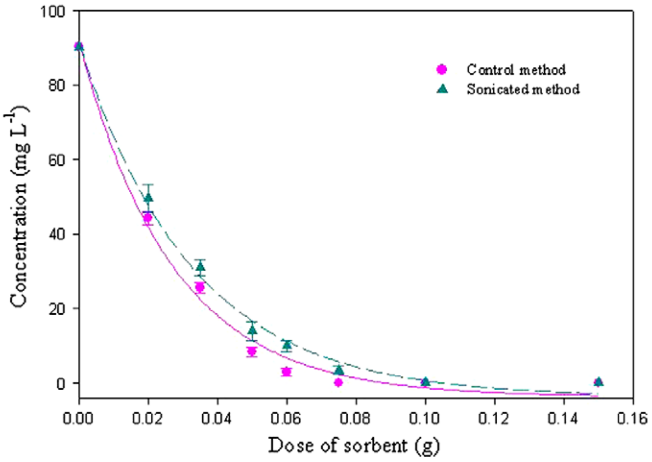

Fig. 1. Effect of amount of sorbent on the removal of nitrate ion (stirring speed: 300 rpm; initial concentration: 90 mg L^{-1}; temperature: 25 °C; time: 5 min).

desorption process and lead to lower amount of sorption. Based on this work, the proper amount of sorbent for the removal of nitrate anion was selected at 0.05 g.

3.1.2. Influence of contact time and temperature

The removal of nitrate ion from aqueous solutions is presented as a function of time at different temperatures (10–50 °C) in Fig. 2. The initial concentration was 88 mg L^{-1} and the removal of nitrate ion was higher in the absence of ultrasound than its presence especially at higher temperatures. As it is shown in Fig. 2, the amount of sorption of nitrate ion increased rapidly in initial times (30 s) and then reached equilibrium. In the presence of ultrasound, desorption was observed at longer time of sonication and it is not shown in the Fig. 2. The fast initial removal indicates a high interaction of treated sorbent with nitrate ion. The sorption capacity of sorbent decreased with increasing the temperature. This means that the sorption is an exothermic process and that is the reason for reaching a higher sorption at lower temperatures. In both methods, the nitrate was almost completely removed in 3 min at low temperature (10 °C) and the removal rate was higher in initial times under sonication than control method.

Ultrasound promotes desorption of adsorbed species from the sorbent. The rate of desorption increases with increasing the temperature [20–23]. Desorption is an endothermic process and it is promoted by the collapse of the bubbles if it occurs in the vicinity of the sorbent surface. After such a cavitation event, the active places for adsorption are available again.

3.1.3. Kinetic model

The sorption data were analyzed in terms of pseudo-first-order and pseudo-second-order kinetic models. The correlation coefficients for the second-order kinetic model were higher than first-order for nitrate ion removal from aqueous solution in the presence and absence of ultrasound. The pseudo second-order equation is generally expressed as follows:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \qquad (2)$$

where q_e and q_t are the amounts of nitrate ion sorbed onto the sorbent (mg g^{-1}) at equilibrium and time t, respectively and k_2 is the rate constant. Integrating Eq. (2) and applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, gives:

$$\frac{1}{(q_e - q_t)^2} = \frac{1}{q_e} + k_2 t \qquad (3)$$

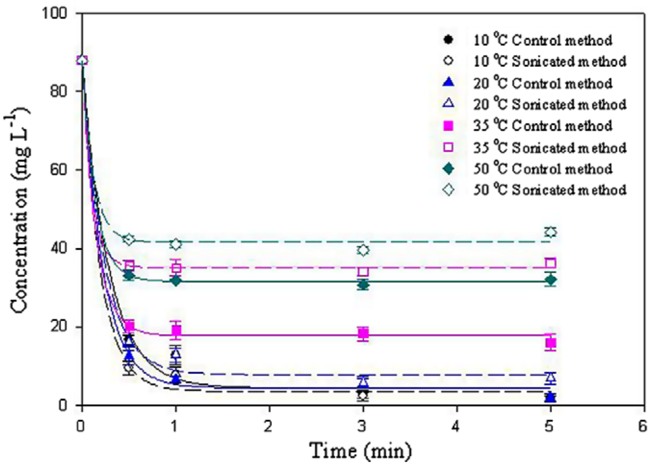

Fig. 2. Effect of contact time and temperature on the sorption of nitrate ion (stirring speed: 300 rpm; amount of sorbent: 0.05 g; initial concentration: 88 mg L^{-1}).

Eq. (3) can be rearranged to obtain a linear form:

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

The constants can be determined experimentally by plotting t/q_t versus time [28–30]. From the slope and the intercept of the plot, the rate constant of sorption (k, g mg^{-1} min^{-1}) and the amount of adsorbed species at equilibrium (q_e, mg g^{-1}) can be determined. Table 1 summarizes the results and shows a good agreement between experimental and calculated values of q_e. In control method, the rate constant was increased with increasing the temperature which is related to the higher collision frequency of sorbate to the sorbent sites at higher temperatures. But in the case of ultrasound, the highest rate constant was observed at 35 °C. This could be explained by the optimization of the cavitation process at this temperature for the solution under applied conditions.

3.2. Adsorption equilibrium studies

3.2.1. Isotherm

The experimental data were applied to four sorption models such as Langmuir, Freundlich, Temkin and Redlich-Peterson. The Langmuir model was fitted properly with high-correlation coefficients (R_{sqr}) in the applied range of initial concentrations (105, 163, 222, 299 mg L^{-1}) in comparison with other sorption models. The linear form of Langmuir isotherm is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \qquad (5)$$

where q_e is the amount of solute adsorbed per unit weight of sorbent at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of solute in the bulk solution (mg L^{-1}), q_{max} corresponds to complete coverage of available sites or the maximum amount of nitrate ion adsorbed per unit weight of sorbent (mg g^{-1}), and b (L mg^{-1}) is the equilibrium adsorption constant [31,32].

The Langmuir constants, b and q_{max} can be derived from plotting C_e/q_e versus C_e. As it is shown in Table 2, the maximum capacity was higher in control method than in the presence of ultrasound. This behavior could be explained by the acoustic cavitation (formation, growth, and collapse of the cavity). The critical conditions produced during the cavitation can reduce the sorbed species from the sorbent and lead to the lower amount of q_{max}.

3.2.2. Influence of temperature

Table 2 shows that the value of q_{max} which represents the monolayer saturation at equilibrium decreased with increasing the temperature in both methods. The value of b represents the affinity of the sorbate to the sorbent. This affinity decreased with increasing the temperature in both methods too which is an indication that the sorption process is exothermic. The R_{sqr} values indicate that the Langmuir model is a proper model for this sorption at different temperatures.

3.3. Thermodynamic functions

According to the Eq. (6), it is possible to calculate the standard Gibbs free energy changes for the sorption process at different temperatures

$$\Delta G^{\circ} = -RT \ln b \qquad (6)$$

The standard enthalpy and entropy changes of sorption can be determined through the slope and intercept of the line produced by drawing ln b versus $1/T$ (Van't Hoff equation). The thermodynamic values are shown in Table 3. The negative values of the stan-

Table 1
Kinetic parameters of sorption in the presence and absence of ultrasound at different temperatures.

	Control method				Sonicated method			
t (°C)	10	20	35	50	10	20	35	50
q_e (exp) (mg g^{-1})	85.90	86.90	71.89	57.12	86.16	82.08	53.81	48.40
q_e (cal) (mg g^{-1})	87.72	86.21	71.43	56.82	86.96	82.64	54.04	48.78
% Dev	2.12	0.79	0.64	0.52	0.01	0.01	0.45	0.78
k (g mg^{-1} mm^{-1})	0.09	0.17	0.49	1.03	0.19	0.15	1.14	0.52
R_{sqr}	0.9987	0.9994	0.9997	0.9998	0.9996	0.9994	0.9999	0.9999

Table 2
Isotherm parameters for the adsorption of nitrate ion onto modified sugar beet refuse in the presence and absence of ultrasound.

	Classical method				Sonicated method			
t (°C)	10	20	35	50	10	20	35	50
q_m (mg g^{-1})	86.21	85.41	80.64	72.46	81.30	79.36	76.92	62.11
b (L mg^{-1})	0.690	0.629	0.358	0.226	0.577	0.430	0.204	0.154
R_{sqr}	0.9944	0.9790	0.9934	0.9885	0.9932	0.9981	0.9820	0.9944

dard Gibbs free energy at various temperatures indicate the spontaneous nature of the sorption of NO_3^- from the solution by the sorbent in the presence and absence of ultrasound. The negative value of the standard enthalpy indicates the exothermic nature of the sorption. The different values of standard enthalpy in the presence and absence of ultrasound might be related to the new active sites of sorption produced by the ultrasound through the change in the particle size. The value of standard entropy changes reflects the randomness at the solid/liquid interface with respect to the solution during the sorption of nitrate ion on the sorbent. The reason for the positive and negative values of the standard entropy changes in control and sonicated methods can be explained by the following equation:

$$\Delta S^{\circ}_{sys} = \Delta S^{\circ}_{sorbent} + \Delta S^{\circ}_{sorbate} \tag{7}$$

The value of $\Delta S^{\circ}_{sorbate}$ is negative for both methods which are due to the lower freedom of adsorbed species with respect to the species in the solution. $\Delta S^{\circ}_{sorbent}$ can be positive or negative in the presence of ultrasound. In the case of sonication, if the particles are divided to smaller particles and lead to a good dispersion, $\Delta S^{\circ}_{sorbent}$ should be increased and it will be positive. In another way, if sonication leads to aggregation, $\Delta S^{\circ}_{sorbent}$ will be negative. In the latter case, the standard entropy changes for the sorption must be negative.

3.4. Desorption studies

3.4.1. Influence of NaOH concentration

In this part, sodium hydroxide solution was used as a reagent for desorption of nitrate anion from the sorbent. Desorption was carried out by soaking the sorbent in 0–0.05 M NaOH aqueous solution for various times in the presence and absence of ultrasound (Fig. 3). The quantity of desorbed NO_3^- was determined by measuring the amounts of NO_3^- released to the solution. This sorbent not only possesses high adsorption capacity, but it also has a good desorption property which significantly reduces the overall needs to the sorbent.

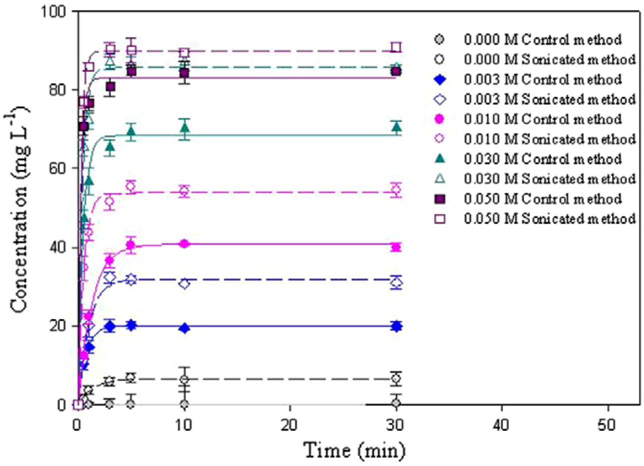

Fig. 3. Effect of contact time and concentration of NaOH on desorption of nitrate ion (amount of nitrate adsorbed on adsorbent: 94 mg L^{-1}; stirring speed: 300 rpm; amount of inactive sorbent: 0.05 g; temperature: 20 °C).

3.4.2. Influence of ultrasound

In control method, desorption is not observed in de-ionized water as a medium. But, ultrasound shows a positive effect on desorption (Fig. 3). The effect of ultrasound on desorption of nitrate ion from prepared sorbent could be ascribed to both the thermal and non-thermal effects of the ultrasonic field. The latter one is more effective [24,26]. The non-thermal effects are due to high-speed microjets (microstreaming) and high-pressure shock waves produced by acoustic cavitation that enhance mass transport and

Table 3
Thermodynamic parameters for the adsorption of nitrate ion.

	Control method			Sonicated method		
t (°C)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1})	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1})
10	−25.10	−22.44	10.27	−24.68	−26.49	−6.32
20	−25.76			−24.84		
35	−25.64			−24.20		
50	−25.65			−24.62		

bond breaking, leading to more nitrate ions released in the regenerating solution [20,25,27].

Sodium hydroxide solution as a medium can facilitate desorption in the presence and absence of ultrasound. It might be related to the ion exchange. Nearly 90% of the adsorbed nitrate ions were desorbed from the modified sorbent by using 50 mL 0.03 M NaOH under sonication process. As it is shown in Fig. 3, ultrasound promotes desorption of adsorbed species from the sorbent.

3.4.3. Influence of temperature

According to the Fig. 4, the rate and the yield of desorption increases with increasing the temperature (10–50 °C) in the presence and absence of ultrasound. The difference between these two methods is higher at lower temperature than higher one. This could be related to the higher critical conditions produced at lower temperature under ultrasound than higher temperature. Desorption is an endothermic process and therefore it is promoted by the collapse of the bubbles if it occurs in the vicinity of the sorbent surface. At low temperature, the collapse of the cavity is harsher than high temperature. This leads to more difference in the amount of desorption at low temperature between control and sonicated methods than high temperature.

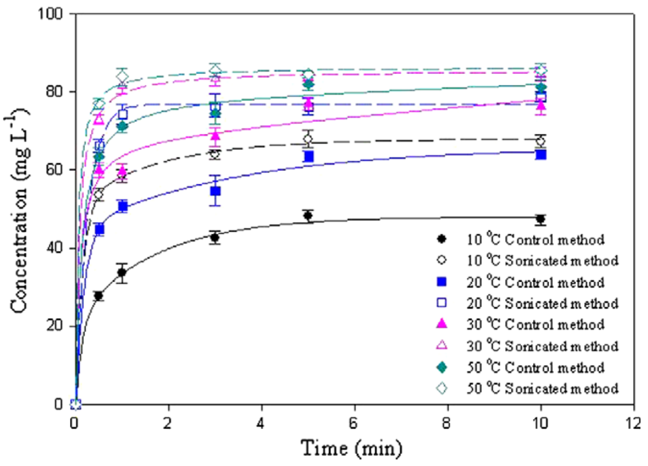

Fig. 4. Effect of contact time and temperature on desorption of nitrate ion (stirring speed: 300 rpm; amount of inactive sorbent: 0.05 g; amount of nitrate adsorbed on sorbent: 95 mg L^{-1}).

3.4.4. Isotherm, kinetic model and thermodynamic parameters

Among different isotherm models applied for desorption, Langmuir model was fitted properly with experimental data. Table 4 shows the isotherm constants for this model.

The data related to the desorption process at different temperatures were analyzed and confirmed that desorption was followed the pseudo-second-order kinetic model the same as adsorption. Table 5 demonstrates the kinetic parameters of this model for desorption process. The rate constants are higher for desorption in the presence of ultrasound than in its absence. This behavior could be explained by the cavitation process which facilitates desorption of species from the surface of the sorbent.

The thermodynamic parameters such as $\Delta G°$, $\Delta H°$, and $\Delta S°$ were also determined for desorption of NO_3^- from the temperature dependence of the desorption process (Table 6). As it is shown desorption process is endothermic and therefore, desorption enhances by introducing energy to the process through increase of temperature or applying ultrasound [20–23].

3.5. Reusability of the sorbent

In order to demonstrate the reusability of the sorbent, the adsorption–desorption cycle was repeated five times for modified

Table 4
Isotherm parameters for the desorption of nitrate ion from modified sugar beet refuse in the presence and absence of ultrasound (time: 10 min; NaOH concentration: 0.03 mol L^{-1}; amount of inactive sorbent: 0.05 g; concentration range: 40–100 mg L^{-1}).

	Classical method				Sonicated method			
t (°C)	10	20	30	50	10	20	30	50
q_m (mg g^{-1})	56.50	68.03	78.12	90.09	68.96	78.74	82.64	97.74
b (L mg^{-1})	0.0749	0.0970	0.105	0.258	0.104	0.168	0.292	0.386
R_{sqr}	0.9964	0.9928	0.9952	0.9920	0.9944	0.9854	0.9797	0.9874

Table 5
Kinetic parameters of desorption in the presence and absence of ultrasound at different temperatures.

	Control method				Sonicated method			
t (°C)	10	20	30	50	10	20	30	50
q_e (exp) (mg g^{-1})	48.10	64.08	77.02	81.98	67.93	78.68	84.46	85.56
q_e (cal) (mg g^{-1})	49.75	63.69	75.76	81.97	68.49	78.74	85.47	86.21
% Dev	3.43	0.61	1.64	0.01	0.82	0.08	1.20	0.76
k (g mg^{-1} mm^{-1})	0.047	0.070	0.083	0.083	0.101	0.147	0.152	0.224
R_{sqr}	0.9971	0.9956	0.9936	0.9986	0.9994	0.9995	0.9995	0.9996

Table 6
Thermodynamic parameters for desorption of nitrate ion.

	Control method			Sonicated method		
t (°C)	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol^{-1})	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol^{-1})
10	−19.88	22.58	149.3	−20.65	25.63	164.2
20	−21.21			−22.55		
30	−22.13			−24.71		
50	−26.01			−27.09		

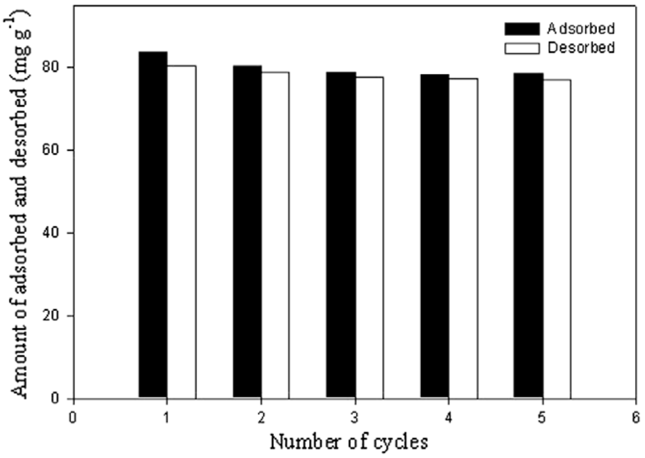

Fig. 5. Reusability of sorbent for the removal of nitrate ion (stirring speed: 300 rpm; initial concentration: 96 mg L^{-1}; temperature: 25 °C; time of adsorption: 5 min; time of desorption: 10 min; concentration of NaOH: 0.1 M; amount of sorbent: 0.05 g).

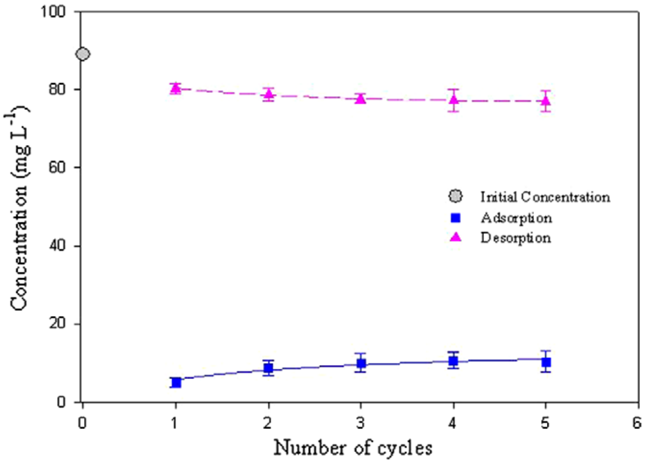

Fig. 6. Adsorption–desorption cycles (stirring speed: 300 rpm; initial concentration: 96 mg L^{-1}; temperature: 25 °C; time of adsorption: 5 min; time of desorption: 10 min; concentration of NaOH: 0.1 M; amount of sorbent: 0.05 g).

sugar beet refuse. Adsorption and desorption experiments were performed in the control method. The adsorption and desorption capacities was approximately the same even after five runs (Figs. 5 and 6).

4. Conclusion

The sugar beet refuse was modified by epichlorohydrin and diethylamine in the presence of pyridine. Kinetics and thermodynamics of sorption were investigated in batch experiments in the presence and absence of ultrasound. The fast removal at the beginning indicates a high interaction of treated sorbent with nitrate anion. The results obtained by the kinetic studies show a good agreement between experimental and calculated values of q_e.

The experimental data were fitted very well with Langmuir model better than the other models. The values of q_{max} and b were decreased with increasing the temperature in both methods. The thermodynamic functions of sorption were calculated from the isotherm constants at different temperatures.

In this case, ultrasound was more effective in desorption than adsorption. Sodium hydroxide solution as a medium facilitates desorption in the presence and absence of ultrasound. Nearly 90% of the adsorbed nitrate ions were desorbed from the modified sorbent under sonication.

In point of kinetics, adsorption and desorption followed pseudo-second-order model. In point of thermodynamics, adsorption and desorption under applying conditions were spontaneous and they were exothermic and endothermic respectively. The most important point is that the adsorption and desorption capacities did not noticeably change even after five runs. In addition, the modified sorbent has great adsorbing and desorbing capacities regarding to the sorbate.

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