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Removal of boron from waste waters using HDTMA-modified zeolites

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ABSTRACT

In this study, boron removal is implemented by adsorption process using modified natural zeolite. Due to natural zeolites have no affinity for anions, Hexadecyltrimethylamine (HDTMA) was used to modifiy natural zeolites. Experiments were run in both batch and column systems. Batch studies were performed to investigate the effects of various experimental parameters, such as optimum HDTMA loading level, adsorbent dose, initial concentration and pH, on the removal of boron. It is found that removal of boron increases while adsorbent dose and initial concentration increase at the optimum pH level 8.5 and HDTMA loading level 100%. Equilibrium isotherms of batch system were also analyzed by Langmuir and Freundlich isotherm models. Freundlich isoterm model represents the sorption process very well for batch system. Effect of bed height, flow rate and initial concentration on boron removal were investigated in column experiments. All the solutions that were used for the column system were adjusted optimum pH level 8.5. As a result of these experiments, removal of boron increases with increasing bed height and decreases with increasing flow rate and initial concentration. Thomas and BDST models were used for column system analyzing. Thomas and BDST models are well agree with experimental data.

Keywords: Boron; Adsorption; HDTMA-zeolite; Modelling

1. Introduction

Boron has a number of minerals, in nature, mostly calcium and/or sodium borates, such as colemanite, ulexite and tinkal [1]. Boron is widely distributed in the environment, occurring naturally or from anthropogenic contamination, mainly under the form of boric acid or borate salts. Even if it is an important micronutrient for plants, animals and humans, the range between deficiency and excess is narrow [2]. The acceptable daily intake is 0.3 mg boron kg^{-1} d^{-1}, which is well above the normal exposure levels [3]. WHO recommends a limit of 0.3 mg boron l^{-1} for drinking water. In European Union, its recommend content for drinkink water is 1 mg l^{-1} [4].

It is a variety of an application including various boron fertilizers, insecticides, corrosion inhibitors in anti-freeze formulations for motor vehicles and other cooling systems, buffers in pharmaceutical and dyestuff production, and the use of boron compounds for moderators in nuclear reactors where anthropogenic water-soluble boron compounds are discharged to an aqueous environment [5,6].

The main processes for removal of boron that have been studied are: precipitation–coagulation, adsorption on oxides, adsorption on active carbon or cellulose, ion exchange with basic exchangers, solvent extraction after complexation, membrane filtration, and reverse osmosis processes [7,8].

Zeolites are hydrated aluminosilicate materials having cagelike structures with internal and external surface areas of up to several hundred square meters per gram

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and cation exchange capacities of up to several meq/kg. At least 41 types of natural zeolites are known to exist, and many others have been synthesized. Both natural and synthetic zeolites are used in industry as adsorbents, soil modifiers, ion exchangers, and molecular sieves [9]. Natural zeolites possess permanent negative charges in their crystal structures, making them suitable for modification using cationic surfactants. Recent studies on the properties of surfactant-modified zeolite indicate that it is an effective sorbent for multiple types of contaminants. Surfactant modified zeolite can remove organic compounds and oxyanions from water. Partitioning is responsible for organic sorption by surfactant-modified zeolite while transition metal cation sorption is generally uneffected. While the sorption of oxyanions by surfactant-modified zeolite was attributed to anion exchange on the positively charged surfactant bilayer, the sorption of hydrophobic organic contaminants was due to partitioning of the organics into the organic phase created by the surfactant tail groups [10,11]. The positively charge head groups are balanced by anionic counterions (A−) which make surfactant-modified natural zeolites a potential sorptive media to sorb anionic contaminants such as arsenate, chromate, antimonate oxyanions via ion exchange mechanism [12–15].

In this study boron removal is implemented by adsorption process using modified natural zeolite. For modifying studies Hexadecyltrimethylamine (HDTMA) was used. Experiments were run in both batch and column systems. Studies were performed in batch system to investigate the effect of various experimental parameters, such as adsorbent dosage, initial solution concentration and pH on the removal of boron. In the column experiments, effect of bed height, flow rate and initial solution concentration on boron removal were investigated. Equilibrium isotherms of batch system were also analyzed by Langmuir and Freundlich isotherm models while Thomas and BDST models were used for column system analyzing.

2. Experimental

2.1. Zeolite

Natural zeolite (clinoptilolite) samples used in the experiments were obtained from Manisa-Gördes of Turkey. The Gördes zeolite has following properties: an external cation exchange capacity (ECEC) of 6.57 meq/100 g, total cation exchange capacity (CEC) of 58.93 meq/100 g which were determined by using Ming and Dixon method [16] and the grain size ranging from 0.5 to 1.5 mm.

Prior to the treatment with HDTMA, the zeolite was converted to its homoionic Na-zeolite form. To prepare homoionic Na-zeolite, 30 g of zeolite was mixed with 500 ml 1 M NaCl solution. After 24 h end-over-end shaking, the zeolite suspension was filtered and fresh 500 ml 1 M NaCl solution was added on the solid phase. This procedure was repeated three times, followed by a threefold washing with 500 ml distilled water. The solid phase was dried at room temperature.

2.2. Preparation of surfactant modified zeolite and determination of optimum HDTMA loading level

Hexadecyl trimethyl ammonium bromide (HDTMA-Br) (purity 99%) supplied by Fluka was used for modifying the surface of zeolite. 30 g of zeolite and 600 ml solution with varying amounts of HDTMA-Br (HDTMA loading levels ranging from 0 to 300% of ECEC of zeolite) were put into 1000 ml bottles and shaken for 24 h. The HDTMA-zeolite suspensions were filtered and the solid phase was dried at the room temperature overnight.

The boron solutions used in the experiments were prepared synthetically. 1000 mg/l boron stock solution was prepared by adding 5.72 g H_3BO_3 in 1000 ml distilled water. To determine the optimum loading level of HDTMA on zeolite for boron removal, 1 g of HDTMA-zeolite, which was prepared as mentioned above, was suspended in 50 ml 10 mg/l boron solutions and shaken 24 h end-over-end, then supernatants were filtered by using 0.45 µm syringe filters. Initial and final boron concentrations were analyzed by atomic absorption spectroscopy (Ati Solar Unicam 929 AA Spectrometer). Sorbed boron was calculated as the difference between initial and final boron concentrations in solution.

2.3. Batch experiments

In batch experiments, effects of pH, amount of adsorbent and initial solution concentration on boron removal were studied. HDTMA-zeolite, which was used in the whole experiments, was prepared by using optimum HDTMA loading level. To obtain the effect of pH and optimum pH level, 1 g of HDTMA-zeolite were suspended in 50 ml 10 mg/l boron solutions and pH of the solutions were adjusted ranging from 2 to 12. The solutions were shaken 24 h and analyzed for boron concentration in the solution. To investigate the effect of amount of adsorbent and initial solution concentration on removal of boron, adsorbent dosage was varied between 0.1–10 g, initial solution concentration was varied between 10–40 mg/l and pH of the solutions were adjusted at optimum pH level. All the samples were shaken 24 h end-over-end, then supernatants were filtered by using 0.45 µm syringe filters and analyzed by atomic spectroscopy to determine final boron concentration in solution.

2.4. Column experiments

The laboratory-scale experimental set-up consists of HDTMA-zeolite which was prepared by using optimum HDTMA loading level, fixed bed column, boron solution tank and peristaltic pump. The cylindrical plexiglass column has an internal diameter of 1.9 cm and height of 20 cm. The partical size of clinoptilolite was about 0.5–1.5 mm. The pH of boron solution was adjusted to optimum pH level which was determined in batch studies.

Boron solution which was prepared by appropriate dilution of the stock solution was pumped through the column at desired flow rate by a peristaltic pump. Samples were collected from the exit of the column at different time intervals until the saturation of the bed ($c/c_o = 1$) occurred and analysed for boron concentration. Experiments were performed to determine the effects of bed height, flow rate and initial solution concentration on boron removal. The sorption performance of the column was tested at various bed heights (5–10 cm), flow rates (4–16 ml/min) and initial concentrations (40–80 mg/l). Amounts of the adsorbed boron were calculated from the difference between influent and effluent concentrations.

3. Results and discussion

3.1. Optimum HDTMA loading levels

The HDTMA loading levels in a range of 0–300% ECEC were studied to investigate their effect on the removal of boron. Fig. 1 shows the sorption of boron on zeolite pretreated with HDTMA solutions of different concentrations. At low concentrations, HDTMA forms a monolayer on the zeolite surface with the hydrofobic ends of the molecules reaching out in the solution. Increasing in the concentration causes a second HDTMA layer formation on the zeolite surface. This bilayer presents positively charged functional groups towards the solution which can serve as sorption sites for anions. The most effective removal of boron occurs at an HDTMA loading level of 100% ECEC and thus it was chosen as optimum value in the parametric experiments.

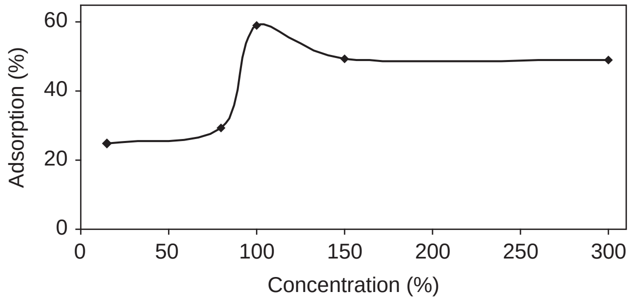

Fig. 1. Adsorption-concentration graph of HDTMA.

3.2. Batch experiments

3.2.1. Effect of pH on boron removal

Fig. 2 shows the change of the removal efficiency of boron by HDTMA-zeolite at pH values of 2–12 and a given initial boron solution of 10 mg/l. The removal efficiency is at the highest level at pH 8.5.

3.2.2. Effect of adsorbent dosage

To investigate the effect of adsorbent dosage on boron removal, HDTMA-zeolite amounts were changed between 0.1–10 g while the solution concentration and pH were held constant at 10 mg/l and 8.5, respectively. The effect of adsorbent dosage on boron removal is shown in Fig. 3. This figure shows that removal of boron increases with the increase in adsorbent dosage. The boron removal efficiencies varied from 3 to 44% for HDTMA-zeolite. An increase in adsorption with the adsorbent dosage can be attributed to greater surface area and availability of more adsorption sites.

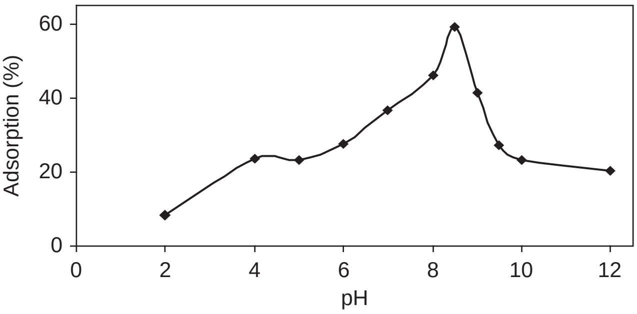

Fig. 2. Adsorption-pH graph.

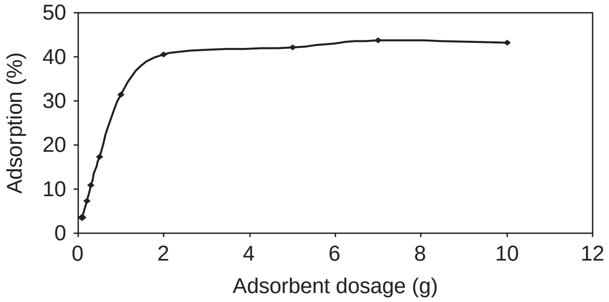

Fig. 3. Adsorption (%)-adsorbent dosage graph.

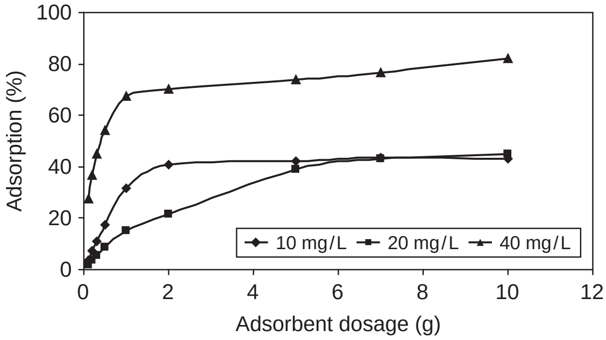

Fig. 4. Adsorption-adsorbent dosage graph for 10, 20 and 40 mg/l initial solution concentrations.

3.2.3. *Effect of initial solution concentration*

The experiments were studied at three initial concentrations (10, 20 and 40 mg/l) while the solution pH was kept as 8.5. The experiments were also repeated as changing the adsorbent dosage between 0.1 and 10 g. As shown in Fig. 4 the adsorption of boron on HDTMA-zeolite increases as the initial concentration increases. Increasing the initial boron concentration would increase the mass transfer driving force. This would result in higher boron adsorption.

3.2.4. *Adsorption isotherms*

In the present study, the sorption of boron by HDTMA-zeolite was analyzed by Langmuir and Freundlich isotherm models.

A basic assumption of the Langmuir theory is that the sorption takes place at specific homogenous sites in the sorbent. Moreover, when a site is occupied by a solute, no further sorption can take place at this site [17]. The Langmuir adsorption isotherm can be written as shown below:

$$q_e = \frac{Q^o b c_e}{1 + b c_e}$$

where q_e is the amount adsorbed at equilibrium (mg/g), c_e is the equilibrium concentration (mg/l), Q^o is the amount of adsorbate on per gram of adsorbent (mg/g) which is needed to occur a monolayer on the adsorbent, b is a constant related to adsorption energy (l/mg).

This equation can be rearranged to the following linear form:

$$\frac{1}{q_e} = \frac{1}{Q^o} + \frac{1}{bQ^o} \times \frac{1}{c_e}$$

Fig. 5 shows the graph of $1/q_e$ versus $1/c_e$ gives a straight line with slope $1/Q^o$ and intercepts $1/bQ^o$.

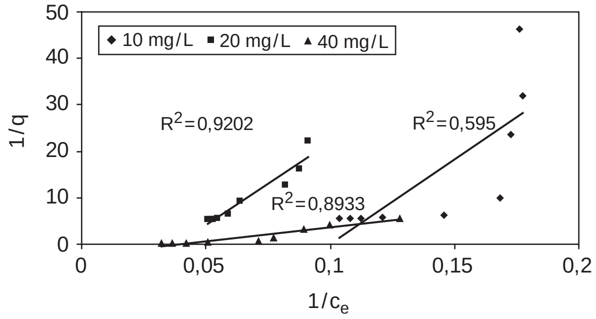

Fig. 5. Langmuir isotherm graph.

The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution. This experimental model can be applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption. The Freundlich adsorption isotherm can be written as shown below:

$$q_e = K_F \times c_e^{1/n}$$

Here, K_F is a constant related to adsorption capacity, $1/n$ is a constant related to adsorption intensity.

This equation can be rearranged to the following linear form:

$$\log q_e = \log K_F + \frac{1}{n} \log c_e$$

Fig. 6 shows the graph of log q_e versus log c_e gives a straight line with slope $1/n$ and intercepts log K_F.

The Langmuir and Freundlich parameters for adsorption of boron onto HDTMA-zeolite are shown in Table 1.

According to Table 1, Freundlich model is more suitable than the Langmuir model for the representation of the adsorption data, as reflected by higher correlation coefficients (R^2) in all cases.

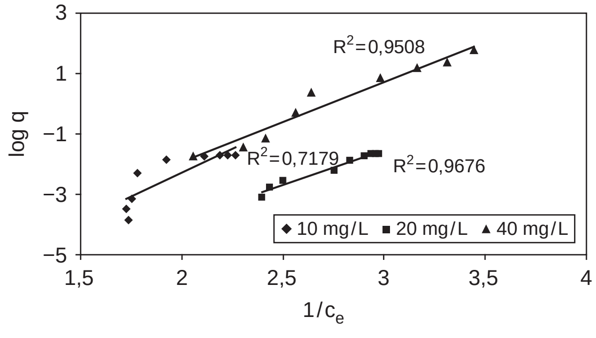

Fig. 6. Freundlich isotherm graph.

Table 1
Langmuir and Freundlich parameters (Q^0, b, K_F,n)

10 mg/l		20 mg/l		40 mg/l	
Langmuir	Freundlich	Langmuir	Freundlich	Langmuir	Freundlich
$Q^0 = 0.002745$ $R^2 = 0.59$	$K_F = 0.000169$ $R^2 = 0.739$	$Q^0 = 0.002802$ $R^2 = 0.9202$	$K_F = 0.000184$ $R^2 = 0.9676$	$Q^0 = 0.016799$ $R^2 = 0.8933$	$K_F = 0.000743$ $R^2 = 0.9508$

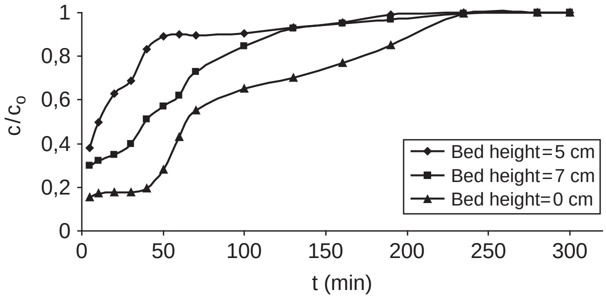

Fig. 7. Breakthrough curves for 5, 7 and 10 cm bed heights.

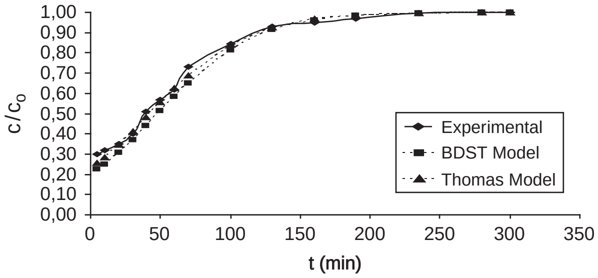

Fig. 8. Breakthrough curves after modelling of experimental data.

3.3. Column experiments

3.3.1. Effect of bed height

The sorption performance of HDTMA-zeolite was tested at various bed heights (5–10 cm) at 4 ml/min flow rate and 40 mg/l initial solution concentration. The column studies were run by using HDTMA loading level of 100% of ECEC.

The breakthrough curves in Fig. 7 show that the breakthrough time and exhaustion time increase with increasing of the bed height. The breakthrough times for 5, 7 and 10 cm bed heights are 10, 30 and 40 min, respectively. The higher bed height the longer service time can be explained with increasing of the binding sites on the adsorbent. Fig. 8 shows the results of the Thomas and BDST model applications. Boron adsorption capacity increases with increasing bed height for both models.

Table 2 shows the predicted parameters of BDST and Thomas models. The lower bed depth gets saturated earlier than higher bed depth.

As shown in Table 2, N_o for HDTMA-modified zeolite increases with increasing bed height. As the bed depth increases, the residence time of the fluid inside the column increases, allowing the adsorbate molecules to diffuse deeper inside the adsorbent. Therefore, the bed capacity will change with service time. For the Thomas model it can be seen that the values of Thomas rate

Table 2
Parameters predicted from the BDST and Thomas models of HDTMA-modified zeolite at different bed heights

Model	C_o (mg/l)	h (cm)	Q (ml/min)	U (cm/min)	K (ml/mg*min)	N_o (mg/l)	R^2
BDST Model	42.34	5	4	1.41	0.649	32	0.88
	40.94	7	4	1.41	0.701	349	0.98
	41.20	10	4	1.41	0.693	473	0.93

Model	C_o (mg/l)	h (cm)	Q (ml/min)	W (mg)	q_{total} (mg)	Y (%)	k_{Th} (ml/mg*min)	q_{oexp} (mg/g)	q_{ocal} (mg/g)	R^2
Thomas Model	42.34	5	4	32	5	15	0.649	0.40	0.04	0.88
	40.94	7	4	38	9	23	0.701	0.49	0.38	0.98
	41.20	10	4	15	13	86	0.819	0.54	0.44	0.93

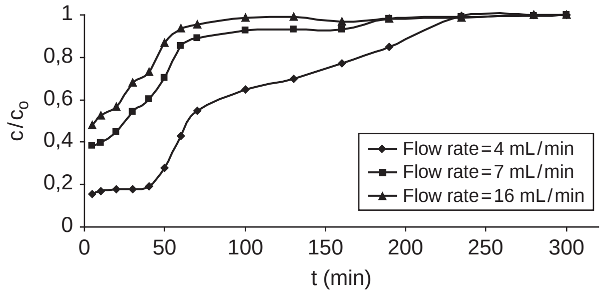

Fig. 9. Breakthrough curves for 4, 7 and 16 ml/min flow rates.

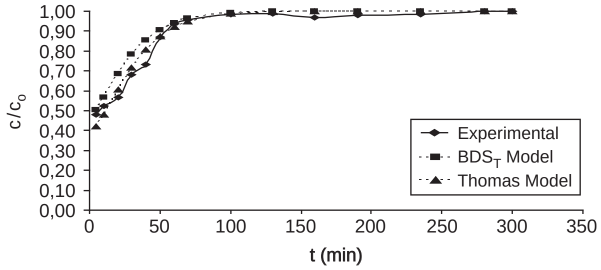

Fig. 10. Breakthrough curves after modelling of experimental data.

constant (k_{Th}) and bed capacity (q_o) increase with increasing of the bed height. Inspection of each lines indicated that they were all fits with regression coefficients (R^2) ranging from 0.88–0.98.

3.3.2. *Effect of flow rate*

The effect of flow rate on boron sorption by HDTMA-zeolite was studied by varying the flow rate from 4 to 16 ml/min, while the bed height and initial solution concentration were held constant at 10 cm and 40 mg/l. Fig. 9 shows the results of the boron adsorption at different flow rates.

The breakthrough curves in Fig. 9 show that the breakthrough time and exhaustion time decrease with increasing of the flow rate. The breakthrough times for 4, 7 and 16 ml/min flow rates are 40, 20 and 10 min, respectively. When the flow rate increases, the residence time of the solute in the column decreases which causes the boron solution to leave the column before equilibrium occurs.

Fig. 10 shows the results of the Thomas and BDST model applications. Sorption data correlate well with both of the models and this was proved by the values obtained of R_2 0.93–0.96.

Table 3 shows the predicted parameters of BDST and Thomas models. As shown in Table 3, adsorption capacity of the column (N_o) for both of the adsorbents decreases with increasing flow rate. It can be seen that the removal efficiency of boron (Y) decreases with increasing flow rate. At low flow rates, sorption of boron increased due to the long retention time in the column, which resulted in higher removal of boron in fixed-bed column. With the flow rate increased, the value of k_{Th} increased with the same inlet concentration.

3.3.3. *Effect of initial solution concentration*

The effect of initial solution concentration was investigated by using 40 and 80 mg/l initial solution concentrations. The bed height and flow rate were kept constant as 10 cm and 4 ml/min, respectively.

Fig. 11 shows that breakthrough time decreases with increasing initial solution concentration. The breakthrough times for 40 and 80 mg/l solution concentrations are 40 and 10 min, respectively.

Fig. 12 shows the results of the Thomas and BDST model applications. The results of models are well agree with the experimental data.

Table 3
Parameters predicted from the BDST and Thomas models of HDTMA-modified zeolite at different flow rates

Model	C_o (mg/l)	h (cm)	Q (ml/min)	U (cm/min)	K (ml/mg*min)	N_o (mg/l)	R^2
BDST Model	41.20	10	4	1.41	0.693	473	0.93
	41.32	10	7	2.47	0.864	222	0.95
	43.60	10	16	5.64	1.153	282	0.96

Model	C_o (mg/l)	h (cm)	Q (ml/min)	W (mg)	q_{total} (mg)	Y (%)	k_{Th} (ml/mg*min)	q_{oexp} (mg/g)	q_{ocal} (mg/g)	R^2
Thomas Model	41.20	10	4	15	13	86	0.819	0.54	0.44	0.93
	41.32	10	7	68	11	16	0.864	0.47	0.27	0.95
	43.60	10	16	133	17	13	1.153	0.71	0.34	0.96

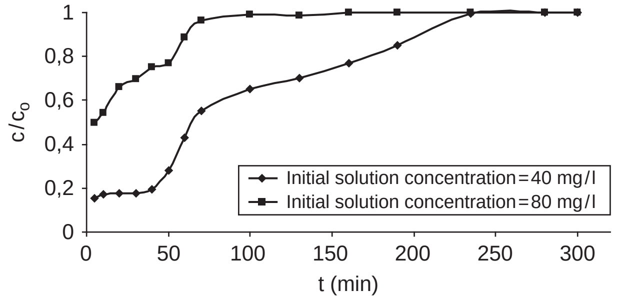

Fig. 11. Breakthrough curves for 40 and 80 mg/l initial solution concentrations.

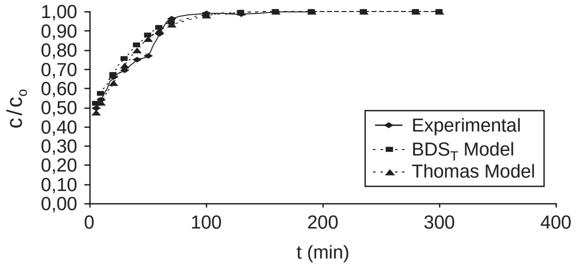

Fig. 12. Breakthrough curves after modelling of experimental data.

Table 4
Parameters predicted from the BDST model of HDTMA-modified zeolite at different feed concentrations

Model	C_o (mg/l)	h (cm)	Q (ml/min)	U (cm/min)	K (ml/mg*min)	N_o (mg/l)	R^2
BDST Model	41.20	10	4	1.41	0.693	473	0.93
	85.60	10	4	1.41	0.492	91	0.97

Model	C_o (mg/l)	h (cm)	Q (ml/min)	W (mg)	q_{total} (mg)	Y (%)	k_{Th} (ml/mg*min)	q_{oexp} (mg/g)	q_{ocal} (mg/g)	R^2
Thomas Model	41.20	10	4	15	13	86	0.819	0.54	0.44	0.93
	85.60	10	4	55	7	13	0.492	0.30	0.11	0.97

The results of the application of BDST and Thomas models are shown in Table 4 for HDTMA modified-zeolite. It can be seen that the adsorption capacity of the column (N_o) decreases with increasing feed concentration for HDTMA modified-zeolite. Also, the value of k_{Th} decreases with increasing feed concentration.

4. Conclusions

It is known that natural zeolite has no affinity for borat anions in aqueous solutions. In the present study, the surface of natural zeolite was modified to enhance the boron capability. The clinoptilolite type natural zeolite was modified by HDTMA and used as a novel adsorbent for boron removal. For this purpose, boron removal from aqueous solution by using HDTMA-zeolite was investigated in batch and column systems. The optimum HDTMA loading level was found as 100% of ECEC, at which HDTMA-zeolite showed the best performance for the removal of boron. In batch experiments, removal of boron increased with increasing in adsorbent dosage and initial concentration.The optimum pH was found as 8.5 for removal of boron by using HDTMA-zeolite. Sorption of boron from solution onto zeolite surface is fitted well by the Freundlich isotherm. The column studies showed that decrease in the flow rate and in the initial solution concentration caused extension of the breakth rough time, whereas the reduction of the bed height resulted in the decrease of the removal efficiency. Thomas and BDST models were both capable of adequately describing the column sorption. To show the availability of the sorption process, the experiments should also be performed by using original waste water.

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