Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2023.29586

295 (2023) 133–141
May

Removal of boron from aqueous solution through adsorption process using cationic surfactant (CTAB)-modified kaolin clay

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Received 25 January 2023; Accepted 30 April 2023

ABSTRACT

In the current study, a new type of adsorbent was synthesized by intercalating a cetyltrimethylammonium bromide (CTAB) cationic surfactant- onto the kaolin clay mineral interlayers in order to improve the adsorption process of boron from aqueous solution. Firstly, the pH experiments were carried out by raw and modified kaolin. Due to the relatively low adsorption capacity of the raw kaolin, the modified kaolin was used in further experiments. The effect of CTAB on the adsorption efficiency of kaolin was examined and showed superior adsorption efficiency than pure kaolin due to enhanced electrostatic interaction between adsorbate "pollutants" and adsorbent "the adsorbed cationic surfactant kaolin". Batch experiments were used for the purpose of evaluating the efficiency of boron adsorption. The percent of boron removal was investigated at different parameters including pH values, initial concentration of boron, adsorbent dosage, temperature and contact time. The adsorption capacities for raw kaolin and chemically modified kaolin by CTAB at initial concentration of 1.50 mg/L were 0.89 and 3.89 mg/g, respectively. The effect of pH on the adsorption showed that the maximum adsorption occurred at pH of 2. It was also observed that the equilibrium data followed the Langmuir isotherm adsorption model indicating that the boron is monolayer adsorbed on the surface of CTAB-kaolin composites and the adsorption sites on the surface are uniform. The adsorption kinetics data showed a better fit of pseudo-second-order model than pseudo-first-order model, which implies that the adsorption mechanism more favors electrostatic interaction between boron and CTAB-kaolin. It can be concluded that CTAB-kaolin is considered a favorable adsorbent and cost-effective material available for boron removal from the aqueous solution particularly at low concentrations.

Keywords: Boron removal; CTAB-kaolin; Adsorption; Isotherm; Kinetics

1. Introduction

Boron (B) is considered a non-metallic element naturally presented in combination with oxygen in both surface water and groundwater. The concentration of boron in surface water range commonly from 0.001 to 150 mg/L, naturally in the form of boric acid, and it is not reduced by the conventional treatment of drinking water [1]. Despite the fact that B has long been known to be a necessary nutrient for both plants and animals, new research has associated B intake to acute kidney damage and the possibility of chronic kidney disease. Accordingly, the World Health Organization has

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established a recommended limit for B in drinking water of 2.4 mg/L; however, several regions have enacted tighter standards. Boron has been found to be toxic for specific crops, particularly citrus plants, which needs irrigation water within the range of 0.3–0.5 mg/L [2]. Actually, soluble B can be commonly detected at low and medium concentrations because of the industrial release of B-containing pollutants and wastewater from borosilicate glass, cosmetics, drugs, textiles, paints, wood processing, detergents and insecticides [3].

For the purpose of boron removal from natural water or wastewater, numerous technologies have been developed such as membrane bioreactors, ion-exchange, chemical precipitation and reverse osmosis. These methods are effective for removing B from aquatic environments, but they necessitate expensive equipment, high energy costs, and the generation of unsolicited waste during the treatment process [4]. More significantly, B cannot be easily treated in aquatic environments using traditional purification approaches, because it passes through purification procedures almost unabsorbed or unmodified [5]. Therefore, adsorption technique is considered one of the most favorable methods for boron removal due to its advantages of simple operation, easy design and low cost. According to the adsorption principle, the boron is transmitted from the water to the surface of the adsorbent. There are two types of adsorptions, physisorption and chemisorption. Actually, chemisorption is mostly focused on the creation of covalent or ionic interactions between the boron and functional groups on the surface of the adsorbent, while physisorption is primarily based on van der Waals forces. Due to its high selectivity and lack of sensitivity to background anions and cations, chemisorption technique for boron removal is considered the dominant in practical applications [6]. Consequently, several boron adsorbent materials have been developed, include activated carbon, layered double hydroxides (LDHs), industrial waste materials (such as concrete particles [7]), natural materials (such as eggshells [8]), metal–organic frameworks (MOFs), and porous aromatic frameworks (PAFs), and other novel materials (such as zirconium-chitosan hydrogel beads [9].

It is beneficial to find a low-cost, environmental friendly and effective adsorbent materials for boron removal. Clay minerals are earthy, fine-grained material consist of crystalline materials used as a natural adsorbent of pollutants from aqueous solutions due to their adsorptive characteristics such as high cation exchange capacity, swelling capacity, high specific surface area, and strong adsorption capacity. Among clay types, kaolin displays the ability to purge water contaminants due to its good physical and chemical stability [10]. The adsorption capacity of raw clay is still insufficient for removal of water pollutants below the recommended level. Hence, synthesis of organically modified clay is developed to improve the adsorption capacity. Organo-clays are prepared by intercalation of cationic surfactant onto the interlayers of the clay minerals via ionic exchange between Ca^{2+}, K^{+} and Mg^{2+} in the clay interlayers and the cationic surfactant where the net surface charges of the clay are reversed from negative to positive [11].

Therefore, in this study, we have utilized cetyltrimethylammonium bromide (CTAB) to produce a chemically modified kaolin (CTAB-kaolin) for enhanced removal and efficient adsorption of boron from aqueous solution. The adsorption efficiency of CTAB-kaolin has been inspected at numerous adsorption parameters such as pH values, adsorbent dosages, initial boron concentrations, temperature and contact time. Additionally, the thermodynamics, isotherms and kinetics of boron adsorption have been investigated.

2. Materials and methods

2.1. Preparation of standard solutions

The stock solution of boron (measured as 50 mg/L) was prepared from analytical grade H_3BO_3. Suitable solutions were freshly prepared by using H_3BO_3 stock solution with distilled water before conducting the adsorption experiments.

2.2. Materials

Natural raw kaolin, hydrochloric acid (HCl 33%), sodium hydroxide (NaOH 10%) potassium dichromate ($K_2Cr_2O_7$), silver nitrate ($AgNO_3$) CTAB used for CTAB-kaolin preparation. Distilled water was used through the whole experiments.

2.3. Preparation of adsorbent: cationic surfactant (CTAB) modified kaolin clay

Before modification process, the raw kaolin sample was washed at least three times using distilled water at a (mass: volume) ratio of 1:4 to remove surface contaminants. The kaolin sample then oven dried in a ceramic crucible at 105°C for 6 h. The dried kaolin sample was crushed using a mortar and pestle to get fine particles. To prepare surfactant modified kaolin clay (CTAB-kaolin), 5 g of pulverized kaolin was added to 250 mL of 10, 15 and 20 mmol CTAB solutions. The mixture was agitated for 5 h at 70°C on a table shaker. Then, the CTAB-modified kaolin solution was aged overnight to settle down the CTAB-kaolin. The residues were washed with distilled water several times to remove all bromide from solution. The existence of bromide ions is designated by formation of white precipitate by adding ($AgNO_3$). The obtained residues of CTAB-kaolin was then filtered and oven dried at 105°C for 6 h and crushed using a mortar and pestle to fine powder particles. The experiment was repeated until sufficient adsorbent was produced.

2.4. Characterization of the adsorbent

The Fourier-transform infrared (FTIR) spectra of the raw kaolin and modified CTAB-kaolin was recorded using (FTIR Spectrometer Frontier/TGA 4000-PerkinElmer) and the measurements were performed over 4,000–400 cm^{-1}. X-ray fluorescence (XRF) method was engaged to examine the mineralogical and elemental composition of the kaolin and modified kaolin clay. Furthermore, nitrogen adsorption measurements were used at liquid nitrogen temperature,77 K to determine the surface area and the pore-size distribution of the adsorbents using the Brunauer–Emmett–Teller (BET) equation.

2.5. Experimental procedure – batch adsorption and isotherm study

Adsorption experiments were performed in batch adsorption method. During the experiments different parameters were used such as adsorbent dosage 0.05, 0.075, 0.10, 0.15, 0.20, and 0.25 g, pH 2, 4, 6, 8, 10 and 12, initial boron concentration 1.50, 4.50, 8.50, 12.50, and 16.5 mg/L and temperature of 25°C and 35°C. A mass, 0.05 g of the adsorbent CTAB-kaolin was thoroughly mixed with 50 mL of prepared stock solutions in 100 mL cleaned polythene bottles using a mechanical shaker (Innova 2100 Platform Shaker) for a various programmed time interval at a constant speed of 150 rpm at room temperature (25°C ± 1°C), for a contact time of 60 min and the pH was adjusted by 0.1 M HCL and 0.1 M NaOH. The solution was agitated until equilibrium and then filtered by Whatman Membrane Filter Paper of pore-size 0.45 μm. Finally, the absorbance of residual boron concentration was determined using an inductively coupled plasma-optical emission spectrometry (ICP-OES) (Thermo Scientific iCAP 6300 ICP-OESCID Spectrometer). Only plastic materials were used when the aqueous solutions were collected and stored for the boron analysis because the water samples can be contaminated by borosilicate glass.

The removal (%) and adsorption capacity (mg/g) of CTAB-kaolin were determined by Eqs. (1) and (2), respectively [12].

$$\text{Removal}(\%) = \frac{(A_i - A_t)}{A_i} \times 100 \quad (1)$$

$$q_t = \frac{(C_i - C_e)V}{m} \quad (2)$$

where A_i denotes initial concentration of boron and A_t is absorbance of boron at a time t. q_t is the adsorption capacity (mg/g), C_i indicates the initial boron concentration (ppm), C_e is the equilibrium boron concentration (mg/L) in solution after adsorption process, V is the volume (L) of the aqueous solution and m is the mass (g) of CTAB-kaolin.

2.6. Experimental procedure – kinetic study

To evaluate the effect of contact time and the adsorption kinetics, the contact time at different intervals (10, 15, 30 min, 1, 2 and 3 h) and adsorbent weights (0.1, 0.15, 0.2 and 0.3) g/50 mL were applied for each experiment to enable the system to approach the equilibrium. Different kinetic models, specifically Lagergren's pseudo-first-order and pseudo-second-order, were applied to the experimental data.

The average relative error deviation (ARED) is the minimization of the fractional error distribution through the entire concentration range as shown in Eq. (3) [12].

$$\text{ARED} = \frac{1}{N}\sum \frac{(q_c - q_e)}{q_e} \times 100 \quad (3)$$

where N is the number of experimental data points, q_c denotes the theoretically calculated adsorption capacity at equilibrium (mg/g) and q_e represents the experimental adsorption capacity at equilibrium (mg/g).

2.7. Statistical analysis

The regression model coefficients, that is, probability constants (student's t-test and p values) were used to test effect of different parameters on adsorption capacity. The analysis of boron was implemented in triplicate and the mean values of the results were reported, in addition to standard error.

2.8. Effect of other competitive ions

The influence of competitive ions such as Na^+, Mg^{+2}, Ca^{+2}, Cl^-, NO_3^- and SO_4^{-2} was evaluated at the initial boron concentration of 1.5 mg/L. A mass, 0.1 g CTAB-kaolin was added to 50 mL boric acid solution which contained one of the above ions in the centrifuge tube. Then the concentration of boron in the solution was measured after shaking for a different time periods.

3. Results and discussions

The CTAB was used to make modification for raw kaolin clay throughout coating and intercalation mechanism into the interlayer surface area of the kaolin. Therefore, the surface of kaolin changed to a positive surface charge which enable it to make an electrostatic interaction with the negative charge species of boron [H_3BO_3/$B(OH)_4^-$].

3.1. Performance characterization of adsorbents

3.1.1. FTIR analysis

The FTIR spectra of raw kaolin and CTAB-kaolin is displayed in Fig. 1. For raw kaolin, the absorption bands at 3,605 and 1,752 cm^{-1} are related to –OH stretching vibration in physiosorbed water. The CTAB-kaolin displays a highest absorption band at the region of 3,575 and 3,680 cm^{-1} which corresponds to the O–H stretching bond.

Moreover, the bands at 915 and 1,001 cm^{-1} are associated with the vibration and stretching of Si–O–Si or Si–O–Al. The results are also agreed well with other studies which stated that the characteristic absorption bands at (3,700; 3,670; 3,650 and 3,620) cm^{-1} for modified kaolin by CTAB contributed with a strongest absorption because of the inner connection of OH with Al or O [13–15].

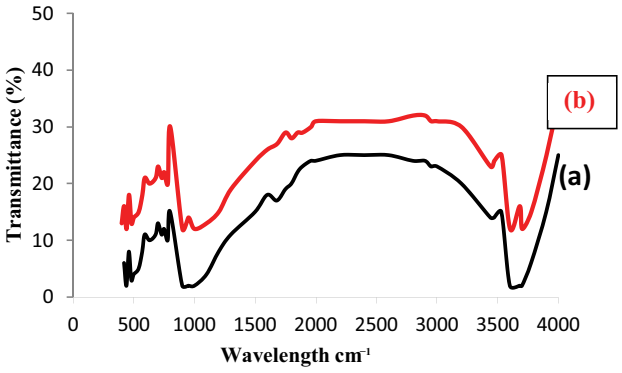

Fig. 1. Fourier-transform infrared spectra of (a) raw kaolin and (b) CTAB-kaolin.

3.1.2. BET analysis

The BET analysis was conducted to find the surface area, pore volume and pore-size distribution of raw kaolin and CTAB-kaolin. Table 1 displays that the total surface area of kaolin clay decreased from 17.97 to 11.96 m^2/g after modification. On the other hand, the intercalated surfactant filled up most of the space in the clay surface leading to increase the pore volume and the pore diameter from 0.041 to 0.052 cc/g and 9.20 to 14.43 nm, respectively.

3.1.3. XRF analysis

The elemental composition of raw kaolin clay and modified kaolin clay by CTAB was determined by XRF analysis as shown in Table 2. The results indicated that SiO_2 and Al_2O_3 are considered the main components of the kaolin clay mineral be around 56.63% and 32.05%, respectively followed by Fe_2O_3 be around 3.57%. These results confirms that this kaolin clay is an aluminosilicate material. In addition, the elemental composition of CTAB-kaolin decreased due to the dilution during intercalation of cationic surfactant interlayers and the percent of SiO_2, Al_2O_3 and Fe_2O_3 decreased to 51.37%, 28.74% and 2.85%, respectively. Ion-exchange happened due to the reaction between the reaming oxides such as MgO, CaO and K_2O and the cationic surfactant led to decrease in their percent.

3.2. Adsorption study of boron

3.2.1. Effect of pH value on boron adsorption process

At what time, the total concentration of boron is lower than 25 mM, boron will be as a form of H_3BO_3 or $B(OH)_4^-$ instead of polyanion. The molecular form of boric acid changes with pH of aqueous, resulting in the change of adsorption capacity. With pH (for pH < 8) increasing, H_3BO_3 converted into the $B(OH)_4^-$ gradually, the tetrahedral structure constructed between poly hydroxyl groups and $B(OH)_4^-$ is much more stable than H_3BO_3. Once pH > 8, with solution alkalinity increasing, the electrostatic repulsion between $B(OH)_4^-$ and negatively charged adsorbent gives rise to the decrease in boron adsorption at high pH. The electrostatic repulsion weakens adsorption, so the stability of adsorbent is reduced and the complexation between boron and ci-diol groups is relatively weak [16–18].

During the experimental tests, it was observed that pH value has a strong influence on the boron speciation and consequently its removal percent and adsorption capacity. Fig. 2 shows the effect of pH on boron removal (%) by chemically modified CTAB-kaolin. The maximum removal (%) of boron is higher at low pH 2. As the pH increases, the surface of kaolin becomes more negatively charged, which reasonably increases the repulsion between $B(OH)_4^-$ and modified kaolin-CTAB. Therefore, the removal (%) efficiency decreases with an increase in pH value.

3.2.2. Effect of adsorbent dosage on boron adsorption process

The adsorbent dosage is considered a significant parameter in adsorption process because it determines the adsorbent capacity for a given initial concentration of a pollutant in the solution. Fig. 3 illustrates the effect of different dosages mass of CTAB-kaolin on adsorption capacity at equilibrium. It was noted that the percentage removal of boron and adsorption capacity increased with an increasing in the adsorbent dosage of CTAB-kaolin and the highest boron adsorption was determined at the dosage of 0.10 g of CTAB-kaolin for boron concentration 1.50–16.50 ppm. This is happened, because the pores of the adsorbent are not get fully used at higher dosages, particularly at lower pollutant's concentration.

3.2.3. Effect of initial boron concentration on the adsorption process

Fig. 4 presents the effect of initial boron concentration on the adsorption capacity of CTAB-kaolin. The initial

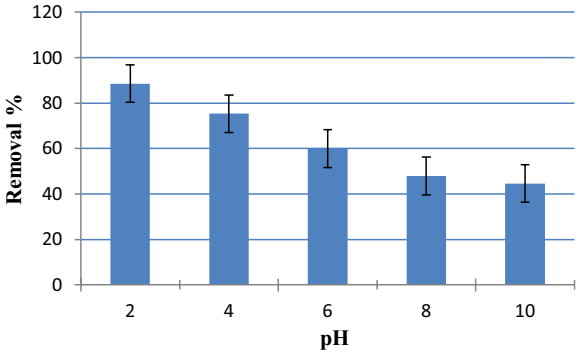

Fig. 2. Effect of pH value on boron removal efficiency of chemically modified CTAB-kaolin (Experimental conditions: solution volume: 50 mL, contact time: 3 h, temperature: 25°C, speed: 150 rpm and adsorbent dosage: 0.1 g).

Table 1
Pore volume, pore-size and surface area of adsorbents

	Surface area (m^2/g)	Pore volume (cc/g)	Pore diameter (nm)
Raw kaolin	17.97	0.041	9.20
CTAB-kaolin	11.96	0.052	14.43

Table 2
Elemental composition of raw kaolin and CTAB-kaolin

	Oxides								
	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	K_2O	TiO_2	P_2O_5	MgO
Raw kaolin (%w/w)	56.63	32.05	3.57	0.016	0.45	0.96	1.16	0.09	0.62
CTAB-kaolin (%w/w)	51.37	28.74	2.85	0.014	0.29	0.41	0.89	0.04	0.26

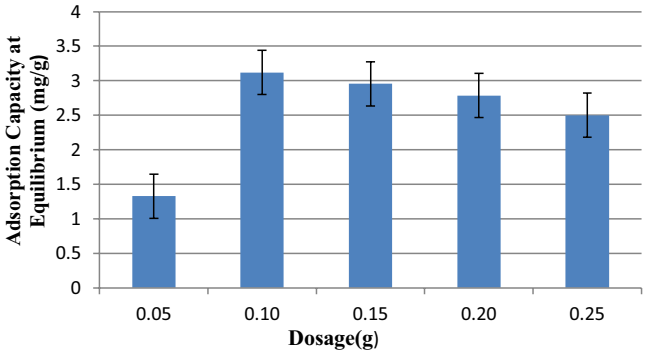

Fig. 3. Effect of adsorbent dosage on boron adsorption of chemically modified CTAB-kaolin (Experimental conditions: solution volume: 50 mL, contact time: 3 h, temperature: 25°C, speed: 150 rpm and pH value: 2).

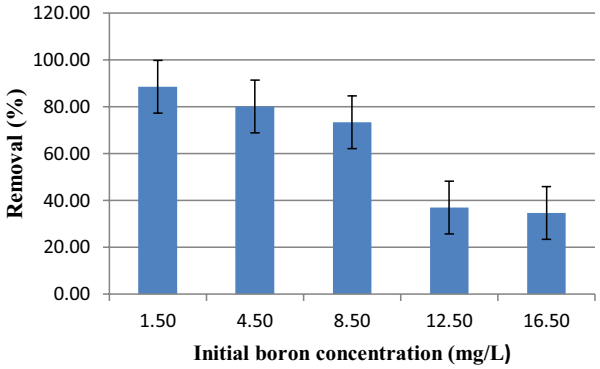

Fig. 4. Effect of initial boron concentration on adsorption of chemically modified CTAB-kaolin (Experimental conditions: solution volume: 50 mL, contact time: 3 h, temperature: 25°C, speed: 150 rpm and pH value: 2).

concentration was varied from 1.50 to 16.50 ppm. According to the results, the removal (%) decreases as the initial concentration of boron increases. This denotes that the adsorption of boron onto CTAB-kaolin is strongly dependent on initial metal ion concentration. At low initial boron concentrations, the available adsorption sites were easily occupied by boron resulting in higher removal efficiencies. Nevertheless, as the initial boron concentration increased, most of the available adsorption sites became occupied, leading to a decrease in the removal efficiency. The results show that the maximum removal efficiency was 88.60% for 1.50 ppm boron concentration.

3.2.4. Effect of contact time on boron adsorption process

Fig. 5 shows the effect of time on boron adsorption. At the beginning of adsorption process, by increasing the adsorption time, the boron concentration decreases rapidly due to high concentration of boron and the large number of active sites of adsorbent, while the decrease trend of boron concentration become slight with the continued increase of time. When the time exceeds 180 min, the concentration of boron does not change, indicating that the adsorption reaches equilibrium. Therefore, the boron adsorption within

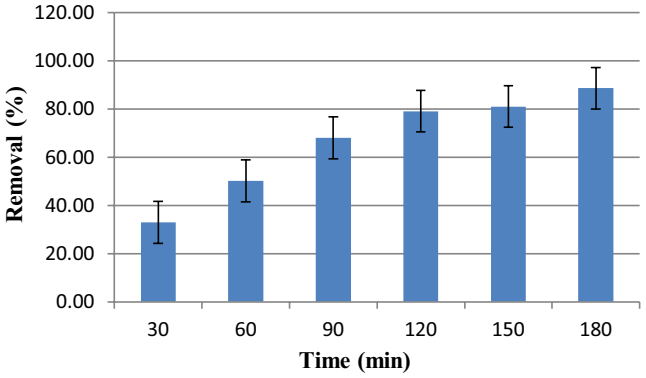

Fig. 5. Effect of contact time on boron adsorption of chemically modified CTAB-kaolin (Experimental conditions: solution volume: 50 mL, contact time: 3 h, temperature: 25°C, speed: 150 rpm, initial boron concentration: 1.5 mg/L and pH value: 2).

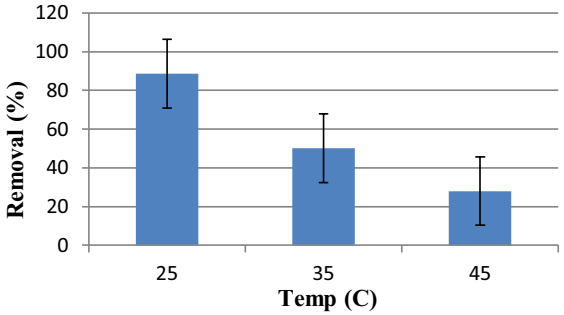

Fig. 6. Effect of contact time on boron adsorption of chemically modified CTAB-kaolin (Experimental conditions: solution volume: 50 mL, contact time: 3 h, dosage: 0.1 g, speed: 150 rpm, initial boron concentration: 1.50 mg/L and pH value: 2).

180 min contact time could be considered as adsorption equilibrium because the total surface coverage of adsorbent was completed and no further adsorption was observed.

3.2.5. Effect of temperature on boron adsorption process

Effect of temperature on boron adsorption onto adsorbent produce either endothermic or exothermic reactions. Boron adsorption onto modified CTAB-kaolin clay was studied at different temperatures 25°C, 35°C and 45°C and other parameters were initial boron concentration 1.50 ppm, adsorbent dosage ratio 0.1 g/50 mL, pH 2 and 150 rpm agitation speed. The results show that boron adsorption onto modified CTAB-kaolin was exothermic nature and the boron removal capacity increased at low temperatures as shown in Fig. 6.

3.2.6. Effect of other competitive ions on boron adsorption process

To evaluate the influence of competitive ions, boron adsorption experiment was conducted in the presence of 10 mg/L of Na^{+}, Mg^{+2}, Ca^{+2}, Cl^{-}, NO_3^{-} and SO_4^{-2}. The results indicated that the presence of Cl^{-}, NO_3^{-}, SO_4^{-2} inhabits the percentage of boron removal which means that these anions

compete with boron species leading to its reduced percentage of removal. Conversely, the presence of Mg^{2+} and Ca^{2+} increased the percentage of boron removal. Accordingly, the summation effect of anions and cations on boron adsorption process was neutral and the CTAB-kaolin is highly appropriate adsorbent.

3.3. Thermodynamic analysis

The thermodynamic analysis of adsorption process is based on temperature to attain the nature of the adsorption process (i.e., spontaneous or unspontaneous/ physical or chemical reaction). In order to confirm the boron adsorption mechanism, the adsorption thermodynamic parameters (ΔG: Gibb's free energy change, ΔH: the enthalpy change and ΔS: the entropy change) can be determined from the Gibb's free energy equations as follows [19,20].

$$\Delta G = -RT\left(\ln K\right) \tag{4}$$

$$\Delta G = \Delta H - T\Delta S \tag{5}$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{6}$$

$$K = \frac{Q_e}{C_e} \tag{7}$$

where ΔG is the free energy change (J/mol), ΔH is the enthalpy change (J/mol), ΔS is the entropy change (J/mol·K) and they are determined from the slope and intercept of plot of ln$K$ against 1/T and apply linear Eq. (6), respectively. While $K = (q_e/C_e)$ is the equilibrium constant (L/g), T is absolute temperature (K) and R is the universal gas constant 8.314 J/mol·K. The Gibb's free energy change of the process was calculated as –0.798, 0.862, and 2.673 kJ/mol for 25°C, 35°C, and 45°C temperatures. The enthalpy of the boron adsorption onto CTAB-kaolin clay was calculated as –52.508 kJ/mol and entropy of the process was calculated as –173.4 J/mol·K. The negative value of enthalpy (ΔH) displayed that the adsorption of boron was exothermic reaction. This means the reaction for adsorption of boron transferred energy into the surroundings. The negative value of Gibb's free energy change (ΔG) at temperature 25°C indicates that the adsorption of boron was spontaneous. The figure fitting to ln(K) vs. (1/T) is given in Fig. 7.

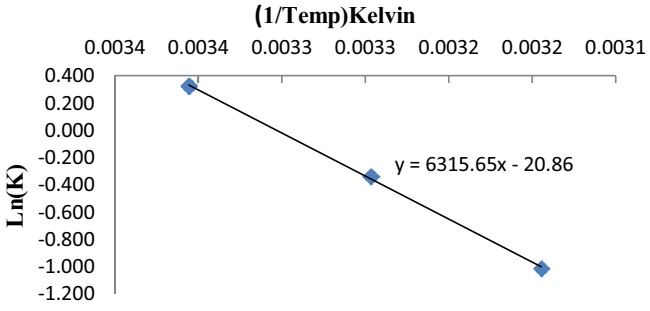

Fig. 7. Thermodynamic analysis of boron adsorption.

3.4. Adsorption isotherm models

The adsorption isotherms express the relationship between the concentration of the adsorbed substance and its enrichment on the surface of adsorbent at a constant temperature. Moreover, adsorption isotherms are used to design the batch adsorption reactors. Two isotherm models were investigated in the present study which is widely determined by the Freundlich isotherm and the Langmuir isotherm. Langmuir isothermal adsorption model is commonly characterized by monolayer adsorption of pollutants, and it is calculated by the linear form of the model as follows [21].

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \tag{8}$$

where C_e is the equilibrium concentration in the liquid phase (mg/L), q_e the amount of adsorbate in the adsorbent at equilibrium (mg/g). $q_{\max}$ is the maximum monolayer converging capacities (mg/g). K_L is the Langmuir isotherm constant (L/mg). The Freundlich isotherm normally describes the multilayer adsorption and it normally describes the physical adsorption and the linear form of the model is calculated as follows [22]:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{9}$$

where q_e the amount of adsorbate in the adsorbent at equilibrium (mg/g), K_f is the Freundlich adsorption constant (mg/g), and C_e is the equilibrium concentration in the liquid phase (mg/L) and 1/n is the heterogeneity coefficient. The value of n refers the type of isotherm. The adsorption will be favorable when 1/n is greater than zero ($0 < 1/n < 1$), the adsorption will be irreversible when 1/n = 1, and the adsorption will be unfavorable when 1/n > 1 [23].

The adsorption isotherm model of boron on CTAB-kaolin is illustrated in Figs. 8 and 9. The correlation coefficient (R^2) of the Langmuir adsorption isotherms curve is 0.987 as shown in Table 1, which showed that the isotherm data is well fitted to the Langmuir model than the Freundlich model (R^2 = 0.605). Therefore, the adsorption of boron onto the CTAB-kaolin describes mostly monolayer adsorption process of boron ions and the maximum monolayer adsorption capacity was theoretically calculated to be 2.37 mg/g. Table 1 shows that the value of 1/n was between zero and one, this means that the adsorption process is favorable.

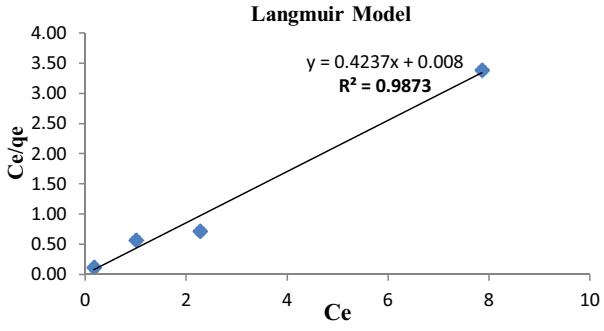

Fig. 8. Langmuir adsorption model of boron adsorption on CTAB-kaolin.

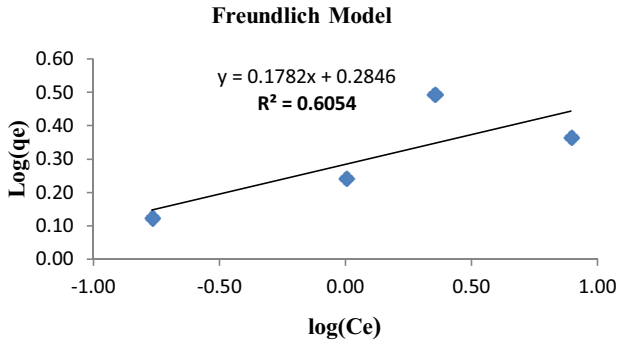

Fig. 9. Freundlich adsorption model of boron adsorption on CTAB-kaolin.

Table 3
Adsorption isotherm parameters for boron adsorption onto CTAB-kaolin

Isotherm models	Parameters		
Langmuir isotherm	q_{max} (mg/g)	K_L (L/mg)	R^2
	2.37	0.02	0.987
Freundlich isotherm	n	K_f (mg^n/(L)$^{1/n}$·g)	R^2
	5.61	1.095	0.605

3.5. Adsorption kinetics models

The adsorption kinetics of boron onto CTAB-kaolin is essential in the batch reactor since the retention time of solution is determined by the kinetics of removal.

The concentration of numerous pollutants in aqueous solution is determined by an empirical equation as a function of time in most kinetic adsorption models. The commonly kinetic models used to fit the experimental data are pseudo-first-order and pseudo-second-order models.

The pseudo-first-order model is commonly used but its application might be uncertain because of the heterogeneity of the sorbent surfaces and diversity of sorption occurrences [24,25].

The linear form of Lagergren's first-order kinetic model is shown in Eq. (6) as follows [26].

$$\log\left(q_e - q_t\right) = \log q_e - \frac{K_1}{2.303}t \tag{10}$$

where K_1 is the rate constant of pseudo-first-order adsorption reaction and q_e indicates the equilibrium amount of boron adsorption.

The pseudo-second-order kinetic model is based on the assumption of determining the rate of chemisorption including valency forces during sharing of electrons between adsorbent and adsorbate [27]. It denotes that adsorption occurs throughout the electrostatic interaction between boron and CTAB-kaolin surface. The linear form of pseudo-second-order kinetic model is shown in Eq. (7) as follows [28]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{11}$$

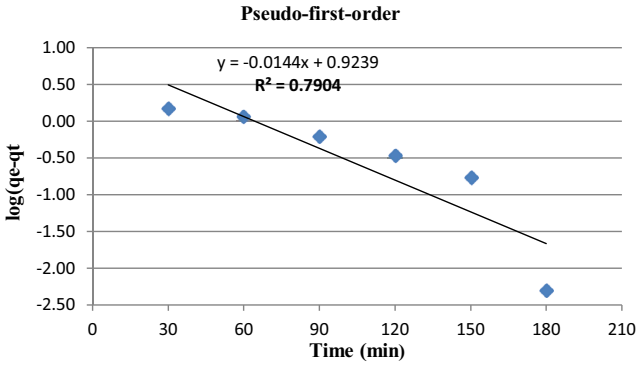

Fig. 10. Pseudo-first-order kinetic curve of boron adsorption onto CTAB-kaolin (Experimental conditions: solution volume: 50 mL, dosage: 0.1 g, speed: 150 rpm, initial boron concentration: 8.50 mg/L and pH value: 2).

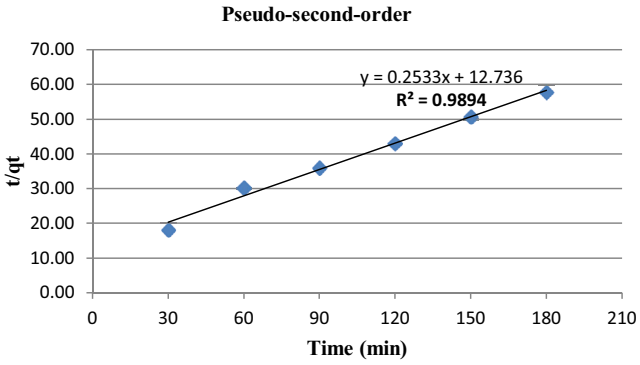

Fig. 11. Pseudo-second-order kinetic curve of boron adsorption onto CTAB-kaolin (Experimental conditions: solution volume: 50 mL, dosage: 0.1 g, speed: 150 rpm, initial boron concentration: 8.50 mg/L and pH value: 2).

where K_2 is the rate constant of pseudo-second-order adsorption reaction.

Figs. 10 and 11 show the adsorption kinetic model plots of $\log(q_e - q_t)$ vs. t and t/q_t vs. t for boron adsorption onto CTAB-kaolin using the experimental parameters, pH value = 2, solution volume = 50 mL, dosage = 0.1 g, speed = 150 rpm, and initial boron concentration was 1.50 mg/L. Table 4 summarizes the final findings of applying the linearized pseudo-first-order and pseudo-second-order kinetic model on the boron adsorption. Among these two adsorption kinetic models, the pseudo-second-order kinetic model is more fitted the experimental data in describing the adsorption kinetics of boron on CTAB-kaolin in terms of the correlation coefficient (R^2 = 0.989), and in terms of the difference between the experimental adsorption capacity which is 3.89 mg/g, and calculated value 3.95 mg/g. This means that the rate control step may be chemisorption. Furthermore, the ARED value was 1.47 demonstrating the appropriateness of the kinetic model.

In contrast, it is noticed in the pseudo-first-order kinetic model, that there is difference between the experimental adsorption capacity and the calculated value 8.39 mg/g; therefore, it could be concluded that the Lagergren's pseudo-first order-model do not fit with the experimental data.

Table 4
Pseudo-first-order and pseudo-second-order kinetic parameters for boron adsorption onto CTAB-kaolin

Kinetics models	Parameters				
Pseudo-first-order	$q_{e,exp}$. (mg/g)	$q_{e,cal.}$ (mg/g)	K_1 (min^{-1})	R^2	ARED
	3.89	8.39	0.033	0.79	115.79
Pseudo-second-order	$q_{e,exp}$. (mg/g)	$q_{e,cal.}$ (mg/g)	K_2 (g/(mg·min))	R^2	ARED
	3.89	3.95	0.005	0.989	1.47

ARED: Average relative error deviation

Table 5
Adsorption isotherms of boron for various adsorbents

Adsorbent	Experimental conditions	Equilibrium[a]/Maximum[b] adsorption capacity	References
Bentonite	C_i = 120 mg/L, pH = 9, time = 24 h, adsorbent dose = 50 g/L, T = 25°C	[b]0.51 mg/g	[29]
Bentonite-$FeCl_3$	C_i = 120 mg/L, pH = 9, time = 24 h, adsorbent dose = 50 g/L, T = 25°C	[b]0.83 mg/g	[29]
Kaolinite	C_i = 120 mg/L, pH = 9, time = 24 h, adsorbent dose = 50 g/L, 25°C	[b]0.60 mg/g	[29]
Kaolinite-$FeCl_3$	C_i = 120 mg/L, pH = 9, time = 24 h, adsorbent dose = 50 g/L, T = 25°C	[b]0.80 mg/g	[29]
Waste calcite	C_i = 120 mg/L, pH = 9, time = 24 h, adsorbent dose = 50 g/L, T = 25°C	[b]1.05 mg/g	[29]
Waste calcite-$FeCl_3$	C_i = 120 mg/L, pH = 9, time = 24 h, adsorbent dose = 50 g/L, T = 25°C	[b]1.60 mg/g	[29]
Zeolite	C_i = 120 mg/L, pH = 9, time = 24 h, adsorbent dose = 50 g/L, T = 25°C	[b]0.53 mg/g	[29]
Zeolite-$FeCl_3$	C_i = 120 mg/L, pH = 9, time = 24 h, adsorbent dose = 50 g/L, T = 25°C	[b]0.76 mg/g	[29]
Magnesite and bentonite clay composite	C_i = 20 mg/L, pH = 11, time = 30 min, adsorbent dose = 2 g/L, T = 26°C	[b]4 mg/g	[30]
Fly ash zeolite	C_i = 50 mg/L, pH = 7, time = 0.5 h, adsorbent dose = 20 g/L, T = 25°C	[a]2.3 mg/g	[31]
F400 + xylitol	C_i = 60 mg/L, pH = 7, time = 4 h, adsorbent dose = 20 g/L, T = 25°C	[a]1.45 mg/g	[32]
F400 + sodium gluconate	C_i = 60 mg/L, pH = 7, time = 4 h, adsorbent dose = 20 g/L, T = 25°C	[a]1.04 mg/g	[32]
Cur-AC	C_i = 1,000 mg/L, pH = 5.5, time = 2 h, adsorbent dose = 40 g/L, T = 25°C	[b]5.0 mg/g	[33]
CWZ-30	C_i = 30 mg/L, pH = 6, time = 2 h, adsorbent dose = 20 g/L, T = 20°C	[a]0.294 mg/g	[34]
CTAB-kaolin	C_i = 8.50 mg/L, pH = 2, time = 3 h, adsorbent dose = 0.1 g/50 mL, T = 25°C	[a]3.12 mg/g	This study

[a]The equilibrium adsorption capacity is the adsorption capacity when the adsorption rate is equal to the desorption rate.
[b]The maximum adsorption capacity is the ideal adsorption capacity that all adsorption sites are filled with adsorbate.

3.6. Comparison with other adsorbents

Table 5 is prepared to compare the boron adsorption capacity achieved in this study with the capacities reported in the literature. It is obvious that CTAB-kaolin produced in this study is considered a competitive adsorbent compared to other adsorbents that have been reported in the literature. This might be happened due to the difference in adopted pH values.

4. Conclusion

In conclusion, natural kaolin clay was efficiently modified through intercalation of CTAB surfactant onto the interlayers by a simple and economical technology.

CTAB-kaolin has ability to separate the boron from aqueous solutions dependent on pH value, initial boron concentration, adsorbent dosage, contact time and temperature. The results of BET analysis displayed that the modification

of clay by CTAB reduced the surface area and increased the pore diameter. It was observed that the highest adsorption capacity was at initial boron concentration 1.5 ppm, pH 2 and adsorbent dosage 0.10 g. The presence of anionic ions Cl^-, NO_3^- and SO_4^{-2} decreased the adsorption capacity while the presence of cationic ions Mg^{+2}, Ca^{+2} increased it. The adsorption thermodynamics models displayed that during adsorption process boron ions were distributed randomly and adsorption process was spontaneous and exothermic. In addition, the isotherm data for boron removal was best described by Langmuir isotherm model indicating that the adsorption occurred onto a monolayer surface. Furthermore, the adsorption kinetics of boron demonstrates that the adsorption process of boron could be complete in 3 h and the adsorption process of boron could be defined by pseudo-second-order kinetic model, indicating that the adsorption process by CTAB-kaolin fits to chemisorption. Therefore, it is inferred that CTAB-kaolin was hopefully used in the process of boron desorption from the aqueous solution particularly at low concentrations, and it confirms that it can be widely used as a cost-effective adsorbent.

Acknowledgements

The authors are kindly acknowledging Reach Education Fund Institution for supporting the study and Institute of Water and Environment in Al-Azhar University for conducting the experimental tests in the IWE Lab.

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