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Utilization of fly ash zeolite for boron removal from aqueous solution

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ABSTRACT

A novel zeolite synthesized from fly ash was characterized and studied for the removal of boric acid from aqueous solution. The adsorption behavior of fly ash zeolite (FAZ) for boron was investigated using a batch system and the influence of pH, temperature, adsorption time, initial boron concentration and adsorbent dose on the removal of boron was studied. The results showed that the adsorption was dependent on the pH of the solution and was maximal at around pH 7. The removal of boron increased while the adsorbent dose increased and the temperature decreased. The adsorption equilibrium was achieved after 2 h. The experimental data were fitted better using the Freundlich isotherm than the Langmuir, and Dubinin–Radushkevich models. The boron adsorption capacity and percentage removal from the solution containing 50 mg B L^{-1} amounted to 2.3 mg g^{-1} and 93%, respectively, while pH 7, adsorption time = 0.5 h, and adsorbent dose = 20 g L^{-1}. The thermodynamic calculations indicated the spontaneous and exothermic nature of the adsorption process. The kinetic studies revealed the physisorption as a dominating mechanism of boron removal using FAZ. The pseudo-second-order model adequately described the boron adsorption on FAZ.

Keywords: Boron removal; Fly ash zeolite; Adsorption isotherms; Kinetics; Thermodynamics

1. Introduction

Boron is widely distributed in the environment, and its compounds penetrate into the surface and underground waters as well as sea and ocean waters, which might result in its excessive concentration in natural water reservoirs. Its concentration in natural waters is diversified and ranges from 0.007 to 5 mg L^{-1} in freshwaters to approx. 4 mg L^{-1} in seawaters [1].

Boron is an essential plant nutrient, however, excessive amounts of this element can be harmful for the normal growth of plants, and for animal reproductability. During the production of boron compounds and its applications, many of these are introduced into the environment in the form of waste. Furthermore, there is little difference between boron deficiency and its toxicity levels [2]. A very low boron content is required in irrigation water for certain metabolic activities, but if its concentration is only slightly higher, plant growth can exhibit the effects of boron poisoning, which are yellowish spots on the leaves and fruit, resulting in accelerated decay, and ultimately plant death [3]. Referring to Nable et al. [4] safe concentrations of boron in irrigation water are 0.3 mg L^{-1} for

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sensitive plants, 1–2 mg L^{-1} for semi tolerant plants, and 2–4 mg L^{-1} for tolerant plants. Boron is not classified as an element indispensable to human life, but one which favorably affects human function. Excessive amounts of boron in drinking water and food could potentially poison and damage the central nervous system, skin, digestive system, mucous membranes, liver and kidneys. The natural boron amount taken in by an adult human being is 0.3–20 mg per day (1–3 on average) [3], while the toxic intake is estimated to be 4 g per day [5]. Due to this the boron concentration, in both drinking water, and wastewaters discarded into the environment, is strongly limited according to WHO and European Union regulations. The maximum boron level in drinking water was set at 2.4 mg L^{-1} (Drinking-Water Quality Committee regulations published in 2011) and at 1 mg L^{-1} in the case of wastewaters discarded into the environment (Polish government regulation).

Consequently, the removal of boron from water and wastewater systems becomes important. A number of methods have been studied, such as coagulation, co-precipitation and electrocoagulation [6–8], ion exchange using boron-selective resins [9–11], solvent extraction [12,13], membrane technologies [14–16], and adsorption on activated carbon [17–20]. Among them, the use of boron-selective resins is the most efficient, but not economically viable because of high regeneration costs and expensiveness of resins [21,22]. As a result, developing adsorbents with a high adsorption capacity and relatively low expenses has become a top priority to facilitate the use of adsorption processes for oxoborate removal. In literature currently available, many adsorbents such as fly ashes (FAs) [23,24], modified clays, and zeolites [25,26] and some inorganic materials [27–29], such as oxides, and hydroxides including layered double hydroxides [30,31] were used for boron removal from aqueous solutions. For high concentration of boron dissolved in water, hydrated oxides of some metals like Mg, Fe, Ce, and Al can effectively remove boron [18,29,32,33].

An interesting solution seems to be the use of FA as a sorbent for many toxic substances, e.g. heavy metals, harmful anions, and organic toxins [34–36]. Some sorts of FA also show high affinity to boron dissolved in an aqueous solution. The reduction of boron concentration in waste water with the percentages of boron removal by all types of FA was observed at a minimum of 70% [37]. Studies also showed that pH levels of the boron solution and particle sizes of ash, strongly affect the boron removal efficiency of FA. In the present study, [38] the removal of boron from seawater using low cost methods: three FAs as adsorbents and ferric chloride was studied. It was considered that fruit (date seed) based ash had a remarkably higher efficiency of boron removal (71%) than power plants FA, pine tree FA, and coagulants. The optimum removal efficiency was achieved with the date seeds ash at pH 7 and liquid to solid ratio, $l/s = 5$. According to [24], 94% of boron can be removed using FA from a thermal power plant. Others [39] proposed for boron removal from ceramic wastewater using palm oil mill boiler (POMB) bottom ash and flocculant. POMB bottom ash with particle size larger than 2 mm is a suitable adsorbent where boron is removed up to 80% under the optimum conditions (pH 8.0, dosage = 40 g bottom ash per 300 mL wastewater, and residence time = 1 h). Öztürk and Kavak calculated batch adsorbent capacity of 250–400 μm particle size FA (from a textile plant where Soma coals were used) as 20.9 mg g^{-1} [40]. The results presented in paper [41] show that the selected FA materials (after combustion of the lignite coal) are very effective in boron removal to the extent that the rejection ratio of boron can reach 95% of the initial boron content under certain optimal conditions (pH 9, $l/s = 110$, and reaction time > 6 h). Polowczyk et al. [42] assessed the efficiency of FA agglomerates (from brown coal and a biomass burning power plant) with respect to boron removal from aqueous solutions. The maximum adsorption capacity achieved for FA agglomerates was 6.9 mg g^{-1} for 0.0025 (g mL^{-1}) adsorbent-to-solute ratio. For 100 mg L^{-1} boron solution, the maximum removal was about 90% for 0.75 adsorbent-to-solute ratio.

In the present study, we synthesized a zeolite from FA—a product of brown coal combustion from conventional furnaces. Following this, synthesized fly ash zeolite (FAZ) was used for the first time to remove boric acid from water. The influence of the boron concentration, time, temperature, and dosage of the new zeolite on boron adsorption in the batch system has been examined. This is a lab-scale study to check whether synthesized FAZ may be useful and affective for boron removal.

2. Experimental section

2.1. Materials

A basic standard solution of boron in the form of borax ($Na_2B_4O_7{\cdot}10H_2O$)—1 g B L^{-1}; sodium hydroxide solution—2 and 0.1 mol L^{-1}, hydrochloric acid solution—1 mol L^{-1}, sodium chloride, and ammonia aq. 38% (w/w). All reagents were analytically pure and supplied by POCh situated in Gliwice (Poland). FAZ—an adsorbent used in the present study—was recovered in our own laboratory.

2.2. Apparatus and laboratory equipment

A spectrophotometer ICP-OES Varian 710 (VARIAN), a scanning electron microscope Hitachi S-3400 N (Hitachi High-Technologies, Thermo Noran), ASAP 2020 automatic adsorption/chemisorption analyzer (Micromeritics), X-ray diffractometer (Seifert XRD-3003 TT), Labmate volume pippettes (PZ HTL, Warsaw), a WU-4 universal shaker (PREMED, Warsaw), a WPE 120 electronic balance (Radwag, Radom), an analytical balance WPA 60/C (Radwag, Radom), a test-tube centrifuge MPW–350 (MPW Med. Instruments), a drier Promed KBC G-100/250 (MPW Med. Instruments), a MILL-547 shaker with heating bath (AJL ELEKTRONIC), and pH-meter Basic 20+(CRISON); laboratory glassware and small equipment: conical flasks with ground glass joint, measuring flasks, beakers, and chemical funnels.

2.3. Preparation and analysis of FAZ

FA used for synthesis was a result of energetic combustion of brown coal in the power plant. Chemical composition of FA determined by XRF method was delivered together with samples of FA (see Table 1).

FA was treated by the hydrothermal method without additional pre-treatment, i.e. without fractionation of ash, after-burning and magnetisation. Hydrothermal treatment was carried out in a drier in a polypropylene vessel which contained 100-mL of 2 mol L^{-1} of NaOH, 10 g of FA, and 1 g of NaCl and periodically stirred (40 rpm) at about 100℃ for 24 h. The composition was then washed eight times with deionized water and dried at 100℃ for 6 h [43]. Scanning electron microscopy (SEM) image, Brunauer–Emmett–Teller (BET), and X-ray diffraction (XRD) analysis of reaction product were performed to determine the zeolitic structures resulting from the synthesis.

2.4. Methods

A series of the batch-mode sorption studies are conducted to evaluate the effects of the initial boron concentration, pH level, temperature, time, and adsorbent dose on boron adsorption. The experiments were carried out with 0.1–5 g of adsorbent and 50 mL of boron solution of concentration 5–200 mg B L^{-1} in the pH range of 4.0–12.5 at 25, 50, and 75℃ temperature for 2–240 min in 250 mL conical flask with a ground glass joint. The boron solution and adsorbent were shaken at 120 rpm mixing rate in a mechanical shaker. At the end of the experiment, the suspension was centrifuged and filtered through medium paper filters. The filtrate was analyzed for boron concentration by the ICP-OES method. Each sorption experiment was repeated three times in order to have average values.

2.5. Adsorption isotherms

The boron sorption (q) per unit mass of adsorbent (mg g^{-1}) was calculated from the experimental data in each sample according to Eq. (1):

$$q = \frac{c_0 - c}{m} V_0 \tag{1}$$

where c_0 is the initial concentration of boron in the solution (mg L^{-1}), c is the equilibrium concentration of boron in the solution (mg L^{-1}), V_0 is the volume of the solution (L)and m is the mass of the sorbent (g).

The Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherms [44,45] were checked for the sorption of boron on the FAZ used in the present study. The Langmuir model assumes that the adsorption occurs in surface sites where the energy is equal in each size. The Langmuir equation is given by Eq. (2):

$$q = q_m \frac{B \cdot c}{1 + B \cdot c} \tag{2}$$

where q_m and B are the Langmuir parameters, q_m is the adsorption capacity (mg g^{-1}), expressed as the maximum amount of boron that can be adsorbed by the adsorbent as a monolayer, and B is an equilibrium constant that corresponds to the adsorption energy (L mg^{-1}).

The Freundlich model allows for several kinds of adsorption sites in the solid, each having a different energy of adsorption. The Freundlich model is usually

Table 1
Chemical composition and BET analysis of FA

Component (%)								BET surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Average pore size (nm)
SiO_2	Fe_2O_3	CaO	MgO	SO_3	Free CaO	Al_2O_3	P_2O_5			
34.1	4.06	11.7	1.71	5.36	13.8	25.2	0.22	7.858	0.159	2.235

applied to the adsorption processes on heterogenous surfaces. The Freundlich isotherm is represented by Eq. (3):

$$q = Kc^{1/n} \tag{3}$$

where the parameters K (mg g^{-1}) and n correspond to the relative adsorption capacity and the adsorption intensity of the adsorbent, respectively.

Both Langmuir and Freundlich data fitting was done by linearization of Eqs. (2) and (3) as shown by Eqs. (4) and (5), respectively:

$$\frac{1}{q} = \frac{1}{q_m \cdot B \cdot c} + \frac{1}{q_m} \tag{4}$$

$$\log q = \log K + 1/n \log c \tag{5}$$

Plotting $1/q$ vs. $1/c$ gives a curve with an inclination $1/q_m$ and intersection $1/B{\cdot}q_m$. Plotting log q vs. log c results in a straight line with an inclination $1/n$ and intersection log K.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L which is defined by Eq. (6):

$$R_L = \frac{1}{1 + Bc_0} \tag{6}$$

According to Hall et al. [46], the parameter R_L indicates the shape of the isotherm accordingly: $R_L > 1$, unfavorable; $R_L = 1$, linear; $0 < R_L < 1$, favorable; and $R_L = 0$, irreversible. Similarly, the effectiveness of using the Freundlich equation to describe the adsorption can be assessed by the constant, n. If $1 < n < 10$, the Freundlich equation is adequate for use [47].

In order to explain the adsorption type, equilibrium data were applied to the D–R isotherm. The D–R isotherm is given by the general Eq. (7):

$$q = x_m \exp -(k\varepsilon^2) \tag{7}$$

where ε is the Polanyi potential, which is equal to RT ln $(1 + 1/c)$, x_m is the adsorption capacity (mol g^{-1}) k is a constant related to the adsorption energy (mol^2 kJ^{-2}), T is the temperature (K), and R is the gas constant (kJ mol^{-1} K^{-1}). This expression can be linearized as Eq. (8):

$$\ln q = \ln x_m - k\varepsilon^2 \tag{8}$$

The x_m and k values were obtained by plotting ln q vs. ε^2 at various temperatures. The adsorption energy (the energy required to transfer 1 mol of adsorbate species to the surface of the adsorbent from infinity in the bulk of the solution) was obtained from the following Eq. (9):

$$E = -(2k)^{-0.5} \tag{9}$$

If E is less than 20 kJ mol^{-1}, the adsorption is physical in nature due to weak van der Waals forces. The energy for the chemisorption lies in the range 40–800 kJ mol^{-1} [48].

2.6. Adsorption kinetics

In order to explain the mechanism involved in the adsorption process, several different kinetic models e.g. the Lagergren pseudo-first and pseudo-second-order, the Elovich equation, and the parabolic diffusion model were used [50]. The pseudo-first-order model is given by the Eq. (10):

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \tag{10}$$

where q_t and q_e are the amounts of boron adsorbed (mg g^{-1}) at any time t and at the equilibrium time, respectively, and k_1 is the pseudo-first-order rate constant for the boron adsorption process (h^{-1}).

The pseudo-second-order kinetics is expressed by the Eq. (11):

$$t/q_t = 1/k_2 q_e^2 + t/q_e \tag{11}$$

where k_2 is the pseudo-second-order rate constant (g mg^{-1} h^{-1}).

The overall kinetics of the adsorption from solutions may be governed by the diffusional processes as well as by the kinetics of the surface chemical reaction. In diffusion studies, the rate is often expressed in terms of the square root time (Eq. (12)):

$$q_t = k_p t^{1/2} \tag{12}$$

where k_p is the intraparticle diffusion rate constant (mg g^{-1} h$^{-1/2}$).

The plots of log $(q_e - q_t)$ vs. t, t/q_t vs. t, and q_t vs. $t^{1/2}$ obtained from above models checked statistically and graphically should be a straight line with an inclination $-k_1/2.303$ and intersection log q_e, an inclination $1/q_e$ and intersection $1/k_2 q_e^2$, respectively, and k_p as a slope of the plot of q_t vs. $t^{1/2}$ if the adsorption process fits to the related equation. Moreover, constant k_2 is used to calculate the initial sorption rate at $t = 0$, r, which is defined by Eq. (13):

$$r = k_2 q_e^2 \quad (13)$$

where r is the initial sorption rate (mg g^{-1} h^{-1}).

2.7. Thermodynamics of adsorption

In order to understand the effect of temperature on the adsorption process thermodynamic values (ΔG°, ΔH° and ΔS°) were calculated [40]. The molar free energy change of the adsorption process is related to the equilibrium constant (K_c) and calculated from the Eq. (14):

$$\Delta G^\circ = -RT \ln K_c \quad (14)$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature (K). The K_c values were estimated as (Eq. (15)):

$$K_c = (c_0 - c)/c \quad (15)$$

Each K_c value was the average of all experimental values (c_0 and c) obtained at constant temperature that the adsorption experiments were carried on.

Standard enthalpy change, ΔH°, and the standard entropy change, ΔS°, of adsorption can be estimated using the following equation (Eq. (16)):

$$\ln K_c = -\Delta H^\circ/RT + \Delta S^\circ/R \quad (16)$$

Plotting ln K_c vs. $1/T$ produces a straight line with an inclination $-\Delta H^\circ/R$ and intersection $\Delta S^\circ/R$.

3. Results and discussion

3.1. Characterization of the adsorbent

A novel adsorbent was characterized by SEM, powder XRD, and specific surface area measurements by BET analysis using scanning electron microscope Hitachi S-3400 N, X-ray diffractometer Seifert XRD-3003 TT, and ASAP 2020 automatic adsorption/chemisorption analyzer, respectively. From the SEM Image (Fig. 1) it can be seen that the tested material has a zeolitic structure and the particles are fine with a specific surface area. The specific surface area calculated by the BET method increases significantly (up to 165.90 m^2 g^{-1}) after zeolitization process because of the microporous texture of the zeolite structure. The identification of mineral phases based on the PDF-2 database formalized by the International Centre for Diffraction Data indicates that the sodalite ($Na_4Cl(Al_3Si_3O_{12})$), quartz, and calcite are the main components of the adsorbent. The above-mentioned results point at the zeolitic features of tested adsorbent.

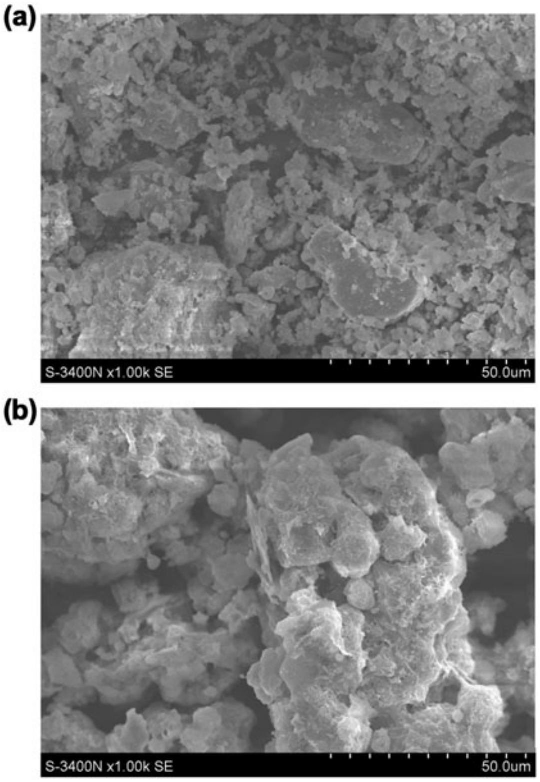

Fig. 1. SEM images of FA (a) and (b) FAZ.

3.2. Effect of pH on adsorption of boron

The pH value of the solution was an important controlling parameter in the adsorption process. The adsorption of boron was studied over the pH range 4–12 for an initial boron concentration of 50 mg L^{-1}, a shaking time of 0.5 h, and an adsorbent dose of 1 g per 50 mL of solution at a temperature of 25˚C.

However, the adsorption of boron on FAZ proceeds at alkaline pH irrespective of initial pH (see Fig. 2), the maximum adsorption of boron takes place at around pH 7 of aqueous solution (Fig. 3). Decreased adsorption values were observed at lower and higher initial pH values. The results shown on Fig. 2 (the plot of pH vs. time while initial pH was 8, 9, and 10) suggest that FAZ has high pH buffering capacity and

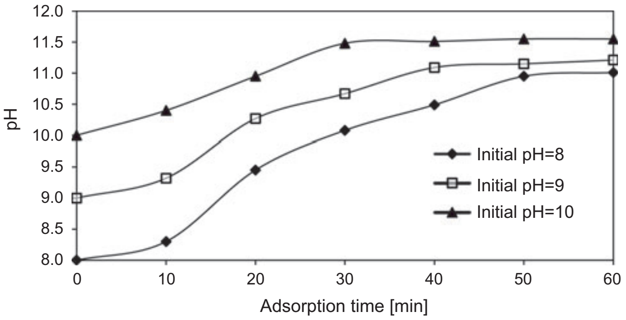

Fig. 2. Changes of pH during adsorption of boron on FAZ at temperature of 25°C, initial pH = 8, 9, and 10, adsorbent dose: 1 g per 50 mL, and initial boron concentration: 50 mg L^{-1}.

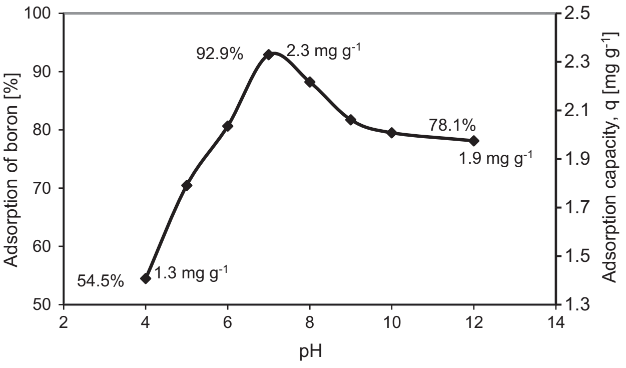

Fig. 3. Adsorption of boron on FAZ as a function of pH, temperature: 25°C, adsorbent dose: 1 g per 50 mL, initial boron concentration: 50 mg L^{-1}, and adsorption time: 0.5 h.

keeps acid reaction at the pH c.a. 11.5 at equilibrium. Therefore, adsorption experiments were conducted at equilibrium value of pH 11.5.

3.3. Effect of adsorption time

The effect of time on the boron adsorption was studied using 1 g of FAZ per 50-mL of solution and an initial boron concentration of 50 mg L^{-1} at the pH 11.5, temperature of 25°C, and shaking time from 2 to 240 min. The variation of the boron adsorption as a function of time is shown in Fig. 4.

The maximum adsorption with 77% removal of boron was reached after 30 min, however, the equilibrium adsorption (a little less than maximum value) was reached after 120 min. Thus, the time of 2 h was accepted as the optimum contact time for the experiment. The pseudo-first-order, pseudo-second-order, and intraparticle diffusion models were employed to evaluate the adsorption kinetic data for FAZ. The resultant parameters of these models calculated and the correlation coefficients R^2 are listed in Table 2, where the experimental values of q_e are also presented. The results showed that the pseudo-first-order rate kinetic model and intraparticle diffusion model were not applicable for the present process due to the lower correlation coefficients. Furthermore, for the pseudo-first-order rate kinetic model, the experimental q_e value did not agree with the calculated one. The pseudo-second-order model expression provided the appropriate correlation of the experimental data. The high value of the $R_2^2 = 0.9996$ and the good agreement between the calculated and the experimental values of q_e in this model; demonstrate that the pseudo-second-order model adequately describes the boron adsorption on FAZ and suggest physisorption as the dominating process.

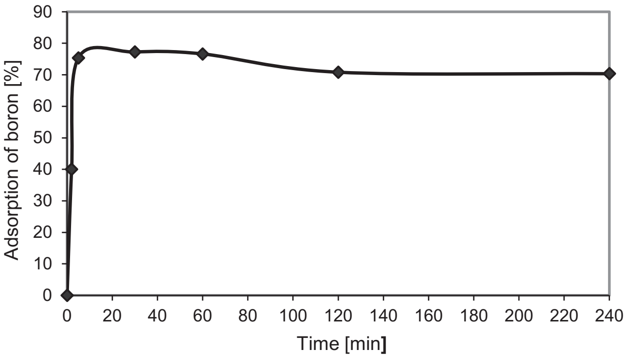

Fig. 4. Kinetics of boron adsorption on FAZ at temperature of 25°C, pH 11.5, adsorbent dose: 1 g per 50 mL, and initial boron concentration: 50 mg L^{-1}.

3.4. Effect of temperature on adsorption of boron

The effect of temperature on the adsorption of boron on FAZ was carried out at pH 11.5 and a temperature of 25, 50, and 75°C for an initial boron concentration of 50 mg L^{-1}, a shaking time of 2 h (equilibrium adsorption), and an adsorbent dose of 1 g per 50 mL (Table 3). Standard entropy and enthalpy changes of the adsorption of boron on FAZ were calculated as, $\Delta S^\circ = -0.03$ kJ mol^{-1} K^{-1} and $\Delta H^\circ = -11.69$ kJ mol^{-1}, respectively. The negative value of ΔS° indicated a decreased randomness at the solid-solution interface during the adsorption boron on the adsorbent. The negative value of ΔH° showed the exothermic nature of the process. As can be seen from Table 3, boron adsorption and K_c (equilibrium

Table 2
Kinetic parameters for boron adsorption on FAZ at 25℃, initial boron concentration 50 mg L^{-1}, FAZ dose 1 g per 50 mL, and pH 11.5

Model of adsorption kinetics	Parameters of kinetic models		
Pseudo-first-order	q_1 (mg g^{-1})	k_1 (h^{-1})	R_1^2
	0.08847	0.011054	0.91179
Pseudo-second-order	q_2 (mg g^{-1})	k_2 (g mg^{-1} h^{-1})	R_2^2
q_e (expt.) = 0.825 mg g^{-1}	0.812744	−0.4813	0.9996
Diffusion	C (mg g^{-1})	k_p (mg g^{-1} $h^{-1/2}$)	R_p^2
	0.9144	−0.006	0.6499

constant) values decreased with an increase of temperature. In contrast, the ΔG° values increased when the temperature increased. The negative values of ΔG° at 25, 50, and 75℃ implied that the adsorption of boron on FAZ was spontaneous. The negative ΔS° value corresponds to a decrease in the degree of freedom of the adsorbed species. In addition to this, as the values of ΔG° increased with an increase of temperature, the spontaneous nature of adsorption is inversely proportional to the temperature.

3.5. Adsorption isotherms

The study of adsorption isotherm is helpful in determining the maximum adsorption capacity of adsorbate for a given adsorbent and in explaining the mechanism of adsorption. Correlations between the equilibrium adsorption of boron (the amount of boron adsorbed per unit mass of adsorbent)—q_e (mg g^{-1}) and the residual boron concentration in the solution—c (mg L^{-1}) are graphically depicted in Fig. 5. The uptake of boron was studied at a temperature of 25℃, pH 11.5 for FAZ and pH 12.5 for FA, and in the boron concentration range of 5–100 mg L^{-1} while the dose of FAZ was held constant at 20 and 40 g L^{-1} and the dose of FA was 20 g L^{-1}, and adsorption time of 2 h. The adsorption isotherms, as shown in Fig. 5 are regular, positive, and concave to the concentration axis for FAZ.

The data obtained from the adsorption experiments were fitted into the linearly transformed Langmuir, Freundlich, and D–R isotherms. The parameters obtained from the linear fits appropriately and the correlation coefficients are presented in Table 4. It was found that the experimental data satisfies the Langmuir, Freundlich and D–R models. The Langmuir isotherm provided a good correlation of the experimental equilibrium data, yielding a correlation coefficient value of $R^2 = 0.9552$. The calculated Langmuir parameters for the maximum capacity (q_m) and B were 1.5 mg g^{-1} and 0.33 L mg^{-1} at 25℃. Rather good applicability of the Langmuir isotherm can suggest the *L* type of isotherm according to the Giles et al.'s classification [49]. The calculated equilibrium parameters R_L (listed in the Table 4) in the range of 0–1, indicate favorable adsorption for boron on FAZ in the whole studied range of initial boron concentration (5–200 mg L^{-1}), however, values of R_L near the 0.1 and below (for $c_0 >$ 20 mg B L^{-1}), can suggest the irreversible adsorption.

The Freundlich model is more suitable than the Langmuir model for the representation of the adsorption data, as reflected by higher correlation coefficients (R^2), obtained from the linear fits of the data in all cases. The value of the Freundlich constant, K (corresponds to the maximum capacity of the adsorbent sites), was calculated as 0.322 mg g^{-1}. According to Treybal's [47] interpretation the calculated value of $n = 1.693$ indicates beneficial adsorption. As can be seen in Fig. 5, the amount of component adsorbed increases steadily with concentration until a plateau is reached, where the surface of the adsorbent is practically saturated and no further adsorption occurs at this stage. This behavior indicates that all isotherms on FAZ can be classified as L type. Furthermore, the adsorption of boron on the FAZ was rapid (in opposite to adsorption on FA—see Fig. 5) and

Table 3
Thermodynamic parameters of boron adsorption on FAZ at different temperatures

Temp. (℃)	Boron adsorption (%)	K_c	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})
75	24.08	1.30	−0.76	−11.69	−0.03
50	40.75	1.65	−1.35		
25	62.07	2.55	−2.32		

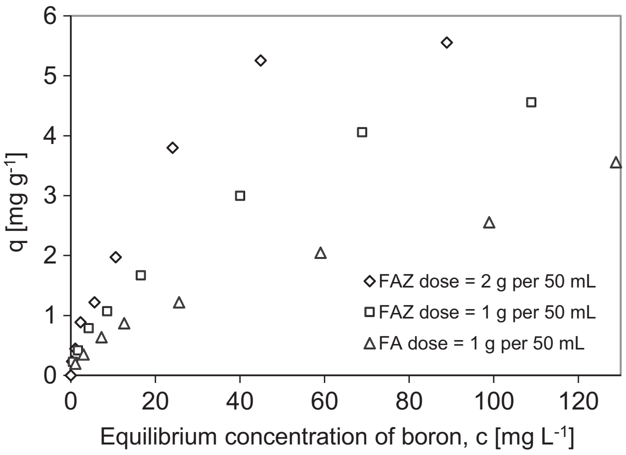

Fig. 5. Isotherms of boron adsorption on FAZ and FA at 25°C, pH 11.5 (1 and 2 g FAZ per 50 mL) and pH 12.5 (1 g FA per 50 mL), initial boron concentration: 5–200 mg L^{-1}, and adsorption time: 2 h.

increased even at high concentrations which supports the L type of isotherm (or I type according to YUPAC classification) and characterizes the microporous adsorbents. The adsorption on FA is less favorable and efficient than on FAZ.

The equilibrium adsorption data were fitted to the linear model of the D–R equation. At a temperature of 25°C the correlation coefficient (R^2) for the linear regression fits was found to be 0.977. The value of the parameter x_m—maximum amount of boron that can be adsorbed by the FAZ—was estimated to be 8.116 mg g^{-1}. The adsorption energy value calculated as 9.13 kJ mol^{-1} indicated that the adsorption of boron on FAZ was physical and probably reversible in nature. As the FA samples used in this study were waste materials, desorption studies were not performed on saturated FAZ in this research.

Furthermore, it was found that the adsorption capacity of FAZ after regeneration could be limited and the cost of regeneration would be substantial [39].

3.6. Effect of adsorbent dosage

To investigate the effect of adsorbent dosage on boron removal, the concentration of FAZ was varied from 2 to 100 g L^{-1} at 25°C while the initial concentration of boron was held constant at 50 mg L^{-1} and pH of 7.0 adjusted by addition of 1 M HCl solution.

The effect of adsorbent dosage on boron removal during 0.5 and 2 h are shown in Fig. 6. The adsorption increased with an increase in the FAZ dose. The result is in agreement with the results of boron removal using FA described by other authors [42]. The boron removal efficiencies varied from 15 to 82% and 31 to

Table 4
Parameters of Langmuir, Freundlich and D–R isotherms for FAZ at 25°C, pH 11.5

Langmuir parameters									Freundlich parameters			Dubinin–Radushkevich parameters			
			R_L for c_0 (mg L^{-1})												
R^2	q_m (mg g^{-1})	B (L mg^{-1})	5	10	20	30	50	100	R^2	K (mg g^{-1})	n	R^2	X_m (mg g^{-1})	k (mol^2 J^{-2})	E (kJ mol^{-1})
0.9552	1.5140	0.3303	0.377	0.232	0.131	0.092	0.057	0.029	0.9969	0.322	1.693	0.977	8.1161	6E-09	9.13

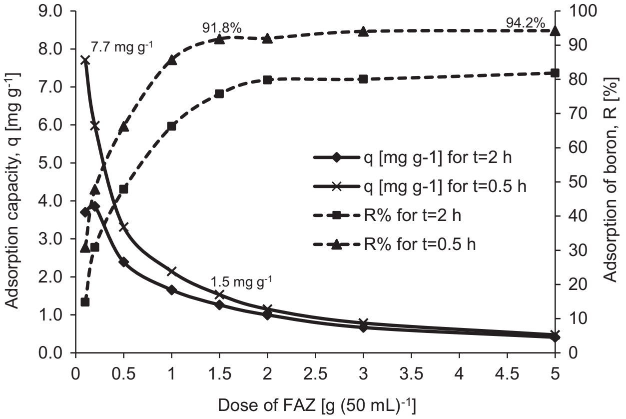

Fig. 6. Removal of boron as a function of FAZ dose, temperature: 25℃, pH 7.0, initial boron concentration: 50 mg L^{-1}, adsorption time: 0.5 and 2 h.

94% for 2 h and for 30 min, respectively (Fig. 6). An increase in adsorption with the FAZ dose can be attributed to the availability of more adsorption sites and contributed to the physical nature of the process. For equilibrium adsorption time (2 h), the removal of boron at about 76% was obtained for the FAZ dose of 1.5 g per 50 mL of solution (30 g L^{-1}) while for time 0.5 h and FAZ dose of 1.5 g per 50 mL of solution (30 g L^{-1}) removal of boron can be obtained at almost 92%. There was no significant change in the boron removal for higher doses of FAZ.

Boron adsorption capacities varied from 0.4 to 3.7 mg g^{-1} and 0.5 to 7.7 mg g^{-1} for 2 h and for 30 min, respectively (Fig. 6).

4. Conclusions

In the present study a zeolite synthesized from FA (a product of brown coal combustion) was used for removal of boron from aqueous solutions. The results showed that pH and temperature of boron solution, dose of adsorbent, and time of adsorption affected the boron removal by FAZ. It was found as follows:

- The adsorption of boron on FAZ was maximum around pH 7 in the investigated pH range (4–12). However, natural pH imposed by FAZ was about 11.5.
- The thermodynamic experiments showed that boron removal decreased with an increase in temperature of the solution. The calculated negative value of ΔS° indicates a decreased randomness at the solid-solution interface during the boron adsorption. The negative value of ΔH° shows the exothermic nature of the process while the negative values of ΔG° implies that the adsorption of boron on FAZ was spontaneous in the investigated range of temperature 25–75℃.
- The kinetic study revealed that the pseudo-second-order mechanism was the rate determining step in the adsorption of boron on FAZ. Optimum time of adsorption was determined as 0.5 h however, equilibrium of adsorption was stabilized after 2 h.
- Boron removal increased with an increase in FAZ dose, which is due to the increase in adsorbent surface area. However, a meaningful increase took place up to 1.5 g of FAZ per 50 mL of solution (30 g L^{-1}).
- The experimental data were fitted better by using the Freundlich isotherm than the D–R and Langmuir models. It indicates the heterogenous nature of boron adsorption on FAZ. The adsorption energy value was calculated as 9.13 kJ mol^{-1}, and corresponds to physisorption.
- The maximum adsorption capacity was found as 7.7 mg g^{-1}, while the maximum removal achieved was 94%. Final boron concentration in solution was determined as 1 and 3 mg L^{-1} while the initial boron concentration equaled 10 and 50 mg L^{-1}, respectively.
- The higher adsorption capacity of zeolite compared to ash was attributed to the developed area and porous structure as a result of the zeolitization of FA.
- FA can be a low-cost and available material to synthesize zeolite-type adsorbent (FAZ) for removal of boron dissolved in aqueous solution.

As the FA used in this study is a waste material, desorption of FAZ was not considered. Furthermore, the cost of regeneration is high and adsorption capacity is limited. Another lab-scale study will check whether synthesized FAZ is an applicable material for boron removal from real media (seawater, geothermal water, wastewater, etc.).

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