Boron Removal from Aqueous Solutions using an Amorphous Zirconium Dioxide

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ABSTRACT: A novel adsorbent, an amorphous zirconium dioxide (ZrO_2), was prepared and characterized for the removal of boric acid from water. The adsorption behavior of this adsorbent for boron was investigated in a batch system and found to obey Langmuir, Freundlich and Dubinin-Radushkevich isotherm models. Due to Langmuir model, boron adsorption on ZrO_2 was monolayer, favorable and irreversible in nature. The adsorption energy value calculated from Dubinin-Radushkevich model corresponds to chemisorption of boron onto ZrO_2. Boron removal occurred both by adsorption on external surface and by formation of sparingly soluble compounds and variable compositions, e.g. $Na[ZrO(OH)_x(B_4O_7)_n]$ following the chemical reaction. The influence of pH, temperature, contact time, initial boron concentration and adsorbent dose on the removal of boron were studied. The results showed that the adsorption was strongly dependent on the pH of solution and was optimum in pH range 8-9. Furthermore, at pH of 8.5 and at contact time of 24 hrs the removal of boron increased while the adsorbent dose increased and the temperature decreased. At optimum conditions, the maximum boron percentage removal from the solution containing 20 mg B/L was 97.5% and the final boron concentration reached under the recommended limit for drinking water (< 1.0 mg/L). The thermodynamic studies indicated the spontaneous and exothermic nature of the adsorption process while the kinetic researches confirmed the chemisorption as a dominating mechanism of boron removal using amorphous ZrO_2. The pseudo-second-order model adequately described the boron adsorption on the adsorbent.

Key words: Boron removal, Amorphous zirconium dioxide, Chemisorption

INTRODUCTION

Boron occurs naturally throughout 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 in freshwaters to approx. 4 mg/L in seawaters (Alloway and Ayres, 1998). During the production of boron compounds and its applications, many of these are introduced into the environment in the form of waste.

Boron is an essential element for normal growth of plants and animals, however, excessive amounts of boron are harmful. Furthermore there is little difference between boron deficiency and its toxicity levels (Parks and Edwards, 2005). 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 effects of boron poisoning, which are yellowish spots on the leaves and fruits,

accelerated decay and ultimately plant death (Kabata-Pendias and Pendias, 1999). Referring to others (Nable *et al*., 1997) safe concentrations of boron in irrigation water are 0.3 mg/L for sensitive plants, 1–2 mg/L for semi tolerant plants, and 2–4 mg/L for tolerant plants. Boron is not classified as an element indispensable to human life, but the one which favorably affects the functioning of human organism. Excessive amounts of boron in drinking water and food might poison the organism, damage the central nervous system, skin, digestive system, mucous membranes, liver and kidney. The natural boron amount taken in by an adult human being is 0.3-20 mg per day (1-3 on average) (Kabata-Pendias and Pendias, 1999), while the toxic intake is estimated to be 4 g per day (Bobrowska-Grzesik *et al*., 2013). For this reason, the boron level in drinking water is limited to 2.4 mg/L (Drinking-Water Quality Committee regulations) and to 1 mg/L (EU Drinking Water Directive) and to 1 mg/L in the case of water discharged to the environment (Polish government regulation). Consequently, removal of boron from

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water and wastewater assumes importance. For boron removal, the main processes that have been studied are: coagulation and co-precipitation (Xu and Jiang, 2008; Remy *et al.*, 2005; Turek *et al.*, 2007), ion exchange using boron-selective resins (Özdemir and Кýрçak, 2003; Popat *et al.*, 1988; Badruk *et al.*, 1999a), solvent extraction (Matsumoto *et al.*, 1997; Bisak *et al.*, 2003), membrane technologies (Rendolo, 2003; Dydo *et al.*, 2005; Turek *et al.*, 2005) and adsorption on activated carbon (Choi and Chen, 1979; Rajakovic and Ristic, 1996; Kluczka *et al.*, 2007; Köse *et al.*, 2011). Among them, the use of boron-selective resins is the most efficient one, but no economic because of high regeneration costs and expensive resins (Badruk *et al.*, 1999b; Simonnot *et al.*, 1999). The adsorption is the competitive method and the using novel and low-cost sorbents, seems to have the point. In recent literature many adsorbents such as fly ashes (Ahmaruzzaman and Gupta, 2011; Yüksel and Yürüm, 2010), clays (Goldberg *et al.*, 1996; Karahan *et al.*, 2006) and some inorganic materials (Öztürk and Kavak, 2004; Ferreire *et al.*, 2006; Kavak, 2009; Bouguerra *et al.*, 2008), such as oxides and hydroxides including LDHs (layered double hydroxides) (Kentjono *et al.*, 2010; Jiang *et al.*, 2007; Koilraj and Srinivasan, 2011) were used for boron removal from aqueous solution. For high concentration of boron dissolved in water, hydrated oxides of some metals like Mg, Fe, Ce and Al can effectively remove boron (Bouguerra *et al.*, 2008; Demetriou and Pashalidis, 2012; Öztürk and Kavak, 2008; Seki *et al.*, 2006).

Long ago some works relating to boron-containing wastewater treatment using granulated zirconium hydroxide prepared by freezing technique (Ryabinin *et al.*, 1972) and by the sol-gel method have been cited in literature (Pospelov *et al.*, 1980; Galkin *et al.*, 1986). They showed the high affinity of zirconium dioxide hydrate to boron dissolved in aqueous solution. The reduction of boron concentration in brine was also observed by zirconium dioxide (ZrO_2) on the matrix of the anion exchanger (Ryabinin *et al.*, 1975; Atamanyuk *et al.*, 2002) and on the other carriers (Xu and Jiang, 2008; Pangeni *et al.*, 2012). Our preliminary experiments showed that amorphous zirconium dioxide had the ability to adsorb boron in contrast to the crystalline form of ZrO_2 (commercial reagent), which showed slight affinity with boric acid dissolved in water (Kluczka *et al.*, 2007). Therefore in the present study, amorphous ZrO_2 prepared in our laboratory was used for the first time to remove boron from water. The influence of the boron concentration pH, time, temperature, and dosage of the new adsorbent on boron adsorption in the batch system has been examined.

MATERIALS & METHODS

A basic standard solution of boron in the form of borax - 1 g B/L; ammonium oxalate, zirconyl chloride, sodium hydroxide solution - 0.1 mol/L, hydrochloric acid solution – 1 mol/L, ammonia aq. 38% (w/w). All reagents were analytically pure and supplied by POCh situated in Gliwice (Poland). Amorphous zirconium dioxide – adsorbent used in the present study - was produced in our own laboratory.

In the first step, zirconyl oxalate was precipitated following ammonium oxalate and zirconyl chloride mixing in the molar ratio of 1.1 to 1. In the second step, the mixture was dried at room temperature and roasted at 390°C for 1 hour in muffle furnace(Ćeśla – Drożdż *et al.*, 2008). Following, adsorbent was powdered in agate mortal and passed through a sieve with a mesh of 100 μm. In this way an amorphous zirconium dioxide was prepared. SEM image and BET analysis of adsorbent were performed. 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), 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), pH-meter Basic 20+ (CRISON); laboratory glassware and small equipment: conical flasks with ground glass joint, measuring flasks, beakers, chemical funnels.

A series of batch mode sorption studies are conducted to evaluate the effects of the initial boron concentration, pH, temperature and time on boron adsorption. Experiments were carried out with 0.1-2 g of adsorbent and 50 mL of boron solution of concentration 5-100 mg B/L at pH 2-10 at 25°C and 35°C and 45°C temperature for 0.5-96 hours in 250-mL conical flask with ground glass joint. Boron solution and adsorbent were shaked 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 in order to have average values was at least repeated 3 times.

The boron sorption (q) per unit mass of sorbent [mg/g] 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 initial concentration of boron in the solution [mg/L], c final concentration of boron in the solution [mg/L], V_0 volume of the solution [L], m mass of the sorbent [g].

The Langmuir, Freundlich and Dubinin—Radushkevich isotherms were checked for the sorption of boron on the amorphous zirconium dioxide used in the present study as a sorbent. The Langmuir model assumes that the adsorption occurs in surface sites where the energy is equal in each size. Langmuir equation is given by Eq. 2:

$$q = q_m \frac{B \cdot c}{1 + B \cdot c} \qquad (2)$$

where q_m and B are the Langmuir parameters, q_m is the adsorption capacity [mg/g] expressed as maximum amount of boron that can be adsorbed by adsorbent as monolayer and B is an equilibrium constant that correspond to the adsorption energy [L/mg].

The Freundlich model allows for several kinds of adsorption sites on the solid, each kind having a different energy of adsorption. Freundlich model is usually applied to adsorption process onto heterogenous surfaces. Freundlich isotherm is represented by Eq. 3:

$$q = Kc^{1/n} \qquad (3)$$

where the parameters K [mg/g] and n correspond to the relative adsorption capacity and the adsorption intensity of the adsorbent, respectively.

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

$$\frac{1}{q} = \frac{1}{q_m \cdot B \cdot c} + \frac{1}{q_m} \qquad (4)$$

$$log\ q = log\ K + 1/n\ log\ c \qquad (5)$$

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

$$R_L = \frac{1}{1 + Bc_0} \qquad (6)$$

According to Hall *et al*. (Hall *et al*., 1966), 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

fitness 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 (Treybal, 1980).

In order to explain the adsorption type, equilibrium data was applied to the Dubinin-Radushkevich (D-R) isotherm. D-R isotherm is given by the general Eq. 7:

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

where ε is Polanyi potential, equals to $RT\ ln\ (1+1/c)$, x_m the adsorption capacity [mol/g], k a constant related to the adsorption energy [mol²/kJ²], T the temperature [K], and R the gas constant [kJ/mol.K]. This expression can be linearized as Eq. 8:

$$ln\ q = ln\ x_m - k^2 \qquad (8)$$

X_m and k values were obtained by plotting $ln\ q$ versus ε^2 at various temperatures. 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 equation:

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

If E is less than 20 kJ/mol, the adsorption is physical nature due to weak van der Waals forces. Energy for chemisorption lies in the range 40-800 kJ/mol (Bansal and Goyal, 2005).

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

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

where q_t and q_e are the amounts of boron adsorbed [mg/g] at any time t and at equilibrium time, respectively, and k_1 is the pseudo-first-order rate constant for the boron adsorption process [1/hr].

The pseudo-second-order kinetics is expressed by the equation:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \qquad (11)$$

where k_2 is the pseudo-second-order rate constant [g/mg.hr].

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.

$$q_t = k_p t^{1/2} \qquad (12)$$

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

The plots of *log* $(q_e$-$q_t)$ versus *t*, t/q_t versus t and q_t versus $t^{1/2}$ obtained from above models checked statistically and graphically should be a straight line with inclination -k_f/2.303 and intersection log q_e, an inclination $1/q_e$ and an intersection $1/k_2q_e^2$ respectively, and k_p as a slope of the plot of q_t versus $t^{1/2}$ 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:

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

where *r* is the initial sorption rate [mg/g.hr].

In order to understand the effect of temperature on the adsorption process thermodynamic values ($\Delta G°$, $\Delta H°$ and $\Delta S°$) were calculated. The molar free energy change of the adsorption process is related to the equilibrium constant (K_c) and calculated from the Eq. 14:

$$\Delta G° = -RT \ln K_c \qquad (14)$$

where *R* is the gas constant (8.314 J/mol.K), T the temperature [K]. K_c values were estimated as:

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

Each *Kc* value was the average of all experimental values (c_0 and *c*) obtained at constant temperature that the adsorption experiments were done.

Standard enthalpy change, $\Delta H°$, and the standard entropy change, $\Delta S°$, of adsorption can be estimated using the following equation:

$$\ln K_c = - \Delta H°/RT + \Delta S°/R \qquad (16)$$

Plotting ln *Kc* versus *1*/T renders a straight line with inclination - $\Delta H°/R$ and an intersection $\Delta S°/R$.

RESULTS & DISCUSSION

A novel adsorbent was characterized by Scanning Electron Microscopy (SEM) and specific surface area measurements by Brunauer–Emmett–Teller analysis (BET). From the SEM Image (Fig. 1) it can be seen that ZrO_2 has amorphous structure and the particles are fine with specific surface area. The BET surface area, pore volume and average pore size found to have values of 184.32 m^2/g, 0.159 cm^3/g and 2.235 nm, respectively (Table 1). Results show that adsorbent is characterised by a microporous and an average developed surface.

The pH value of the solution was an important controlling parameter in the adsorption process. The adsorption of boron as a function of pH onto ZrO_2 at 25°C, with an adsorbent concentration of 20 g/L and an initial boron concentration of 10 mg/L and adsorption time of 4 hrs. is presented in Fig. 2. The results show that the adsorption process was strongly dependent on the pH of the solution. The maximum adsorption of boron takes place in a pH range of 8-9 of aqueous solution. Decreased adsorption values were observed at lower and higher pH values. When the pH was 8.5, boron removal by ZrO_2 increased to 90%. However a relationship between the initial and equilibrium pH for boron adsorption suggested that new adsorbent has high pH buffering capacities and keeps acid reaction at the pH c.a. 2.5 – see Fig. 3 (the plot of pH versus time while initial pH was 8.5). Therefore, ammonia buffer solution was used to all adsorption experiments which were conducted at optimum pH=8.5.

The effect of time on the boron adsorption was studied using 1 g of ZrO_2 per 50 mL of solution and an initial boron concentration of 10 mg/L at the optimum pH=8.5, temperature of 25ºC and shaking time from 0.5 to 96 hrs. The variation of the boron adsorption as a function of time is shown in Fig. 4.

The equilibrium adsorption with 98% removal of boron was reached after 24 hrs. There was almost no change in the adsorption during 24-96 hrs. The time of the 24 hrs. was accepted as the optimum contact time. The pseudo-first-, pseudo-second-order and intraparticle diffusion models were employed to evaluate the adsorption kinetic data for amorphous ZrO_2. The resultant parameters of these models calculated and the correlation coefficients R^2 are listed

Table 1. BET analysis of amorphous zirconium dioxide

Measurement Properties	Values
BET Surface Area [m^2/g]	184.32
Pore Volume [cm^3/g]	0.159
Average Pore Size [nm]	2.235

S-3400N x3.00k SE   10.0um
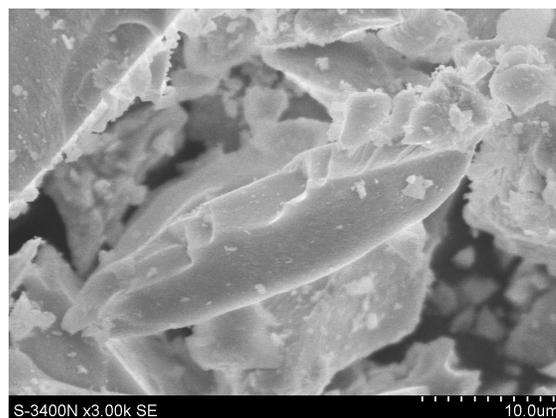
Fig. 1. SEM image of amorphous ZrO_2

Table 2. Kinetic parameters for boron adsorption on amorphous ZrO_2 at 25°C, initial boron concentration 10 mg/L, adsorbent dose 1 g/50 mL, optimum pH=8.5

Model of adsorption kinetics	Parameters of kinetic models			
Pseudo-first-order	q_1 [mg/g]	k_1 [1/hr]	R_1^2	
	0.01824	0.0513	0.6268	
Pseudo-second-order	q_2 [mg/g]	k_2 [g/mg·hr]	R_2^2	r [mg/g·hr]
q_e(expt.)=0.49058 mg/g	0.49092	16.97083	1	4.0899
Diffusion	C [mg/g]	k_p [mg/g·(hr)$^{1/2}$]	R_p^2	
	0.4552	0.0045	0.7427	
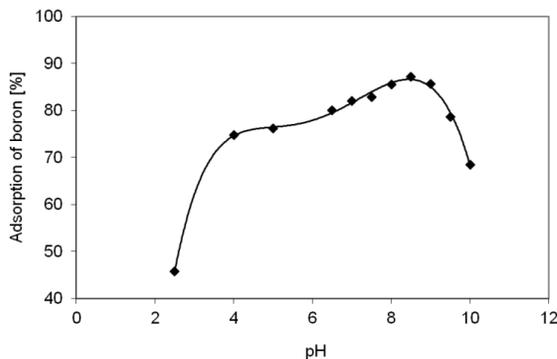
Fig. 2. Adsorption of boron as a function of pH, temperature: 25°C, adsorbent dose: 1 g/50 mL, initial boron concentration: 10 mg/L, adsorption time: 4 hrs
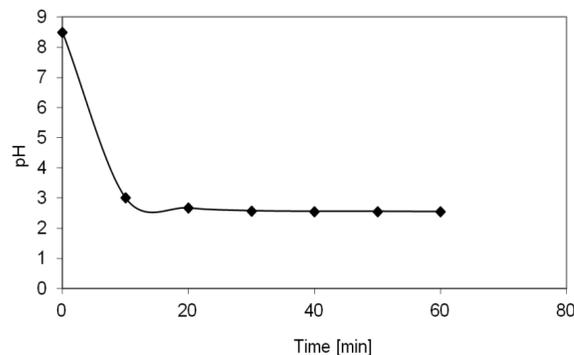
Fig. 3. Changes of pHs during adsorption of boron onto amorphous ZrO2 at temperature of 25°C, initial pH=8.5, adsorbent dose: 1 g/50 mL, initial boron concentration: 10 mg/L

in Table 2, where the experimental values of q_e are also presented. The results showed that 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 well correlation of the experimental data. The high value of the $R_2^2 = 1$ 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 ZrO_2. Because the overall kinetics of the adsorption from solutions may be governed by the diffusional process as well as by the kinetics of the surface chemical reaction, the results showed that intraparticle diffusion model was not applicable for the present process due to the low correlation coefficient (R_p^2=0.7427) and the chemisorption is suspected the dominating process.

Standard entropy and enthalpy changes of the adsorption of boron on amorphous ZrO_2 were calculated as, $\Delta S°$=-0.11 kJ/mol.K and $\Delta H°$=-34.75 kJ/mol, respectively. The negative value of $\Delta S°$ indicated a decreased randomness at the solid-solution interface

during the adsorption boron on the adsorbent. The negative value of $\Delta H°$ showed the exothermic nature of the process. As can be seen from Table 3, boron adsorption and K_c (equilibrium constant) values decreased with an increase of temperature. In contrast, the $\Delta G°$ values increased when the temperature increased. The negative values of $\Delta G°$ at 25 and 35°C implied that the adsorption of boron on ZrO_2 was spontaneous. The negative $\Delta S°$ value corresponds to a decrease in the degree of freedom of the adsorbed species. In addition to this, since the values of $\Delta G°$ increased with an increase of temperature, the spontaneous nature of adsorption is inversely proportional to the temperature.

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 the adsorbent) - q_e [mg/g] and the residual boron concentration in the solution - c_e [mg/L] are graphically depicted in Fig. 5. The uptake of boron was studied at temperature of 25°C and 35°C with stabilization of solution reaction by ammonia buffer (pH=8.5), and at temperature of 25°C without buffer stabilization (initial pH=8.5, final pH=2.5) and in the

Table 3. Thermodynamic parameters of boron adsorption on amorphous ZrO$_2$ at different temperatures

Temp. [°C]	Boron adsorption [%]	K_c	$\Delta G°$ [kJ/mol]	$\Delta H°$ [kJ/mol]	$\Delta S°$ [kJ/mol·K]
45	94.50	0.86	0.40		
35	96.50	1.38	-0.82	-34.75	-0.11
25	97.65	2.08	-1.81		
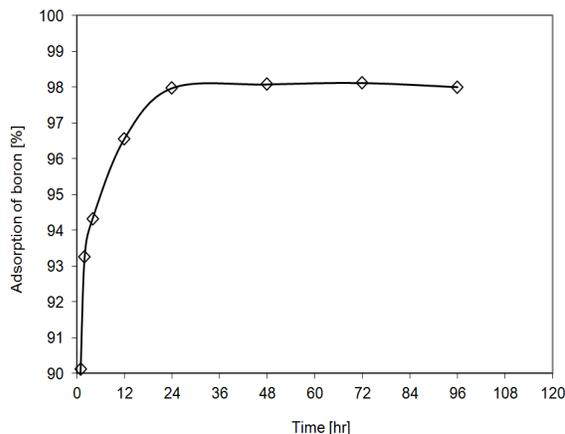
Fig. 4. Kinetics of boron adsorption onto amorphous ZrO2 at temperature of 25°C, pH=8.5, adsorbent dose: 1 g/50 mL, initial boron concentration: 10 mg/L

Fig. 5. and 35°C with stabilization of solution reaction by ammonia buffer (pH=8.5), and at temperature of 25°C without buffer stabilization (initial pH=8.5, final pH=2.5); adsorbent dose: 1 g/50 mL, initial boron concentration: 5-100 mg/L, adsorption time: 24 hrs

boron concentration range of 5-100 mg/L while the dose of adsorbent (amorphous ZrO$_2$) was held constant at 20 g/L and adsorption time of 24 hrs. The adsorption isotherms, as shown in Fig. 5 are regular, positive and concave to the concentration axis for ZrO$_2$.

The data obtained from the adsorption experiments was fitted into the linearly transformed Langmuir, Freundlich and Dubinin-Radushkevich isotherms. The parameters obtained from the linear fits and correlation coefficients obtained at 25°C and 35°C with stabilization of solution reaction by ammonia buffer (pH=8.5), and at temperature of 25°C without buffer stabilization (initial pH=8.5, final pH=2.5) while adsorbent dose was 1 g/50 mL, initial boron concentration 5-100 mg/L and adsorption time was equal 24 hrs. are presented in Table 4. It was found that the experimental data satisfy the Langmuir, Freundlich and Dubinin-Radushkevich models. The Langmuir isotherm provided excellent correlation of the experimental equilibrium data, yielding correlation coefficient values of R^2=0.9888 and 0.9900 at 35°C and 25°C, respectively. The calculated Langmuir parameters for the maximum capacity (q_m) and B were 2.7 mg/g and 0.7 L/mg at 35°C and 2.8 mg/g and 1.2 L/mg at 25°C. The equilibrium constant B corresponds to the adsorption energy and was higher at 25°C than at 35°C.

Very good applicability of the Langmuir isotherm at 25°C suggests the monolayer coverage of the boron adsorption onto ZrO$_2$ and probably the L type of isotherm (according to the Giles *et al.*'s classification, 1974). The calculated equilibrium parameters R_L (for c_0=10 mg/L is listed in the Table 4) in the range 0-1 indicate favorable adsorption for boron onto amorphous ZrO$_2$ in the whole studied range of initial boron concentration (5-100 mg/L), however, values of R_L near the 0.1 and below, can suggest the irreversible adsorption.

The Freundlich model is less suitable than the Langmuir model for the representation of the adsorption data, as reflected by lower correlation coefficients (R^2), obtained from the linear fits of the data in all cases. The values of the Freundlich constants, K and n, were 0.921 mg/g and 1.664, 1.234 mg/g and 1.742 at 35°C and 25°C, respectively. The value of K corresponds to the maximum capacity of the adsorbent sites and indicates that efficiency of adsorption decreases with the increase of temperature. According to Treybal (Treybal, 1980) n value between 1 and 10 represents beneficial adsorption. Moreover, n values are related to the Giles *et al.*'s classification (Giles *et al.*, 1974) S, L and C type of isotherm. The value of n>1 corresponds to S shape, n=1 to C type and n<1 to L type. The n values calculated

Table 4. Langmuir, Freundlich and Dubinin-Radushkevich isotherms parameters for amorphous ZrO$_2$

Temperature [°C], pH=8.5 (Ammonia buffer)	Langmuir parameters				Freundlich parameters			Dubinin-Radushkevich parameters	
	R^2	q_m [mg/g]	B [L/mg]	R_L for C_0=10 mg/L	R^2	K [mg/g]	n	R^2	X_m [mg/g]	k [mol^2/J^2]
35°C	0.9888	2.7226	0.7222	0.122	0.9716	0.921	1.664	0.9678	17.20569	5E-10
25°C	0.9900	2.7593	1.2404	0.075	0.9673	1.234	1.742	0.9631	17.8578	5E-10

Table 5. Comparison of boron adsorption capacity of amorphous ZrO$_2$ with some reported adsorbents type metal oxides

Adsorbent	Boron concentration range (mg/L)	pH	Adsorbent dose	Adsorbent characteristics (Producer/Surface Area (m^2/g))	Models used to calculate q_e	q_e / K_f	References
Iron oxide FeO(OH)	0.1-7	~8	100 g/L	Aldrich Co./ 3.265	Langmuir	0.03 mol/kg	Demetriou and Pashalidis (2012)
Cerium oxide	5-600	6.18	20 g/L	200-275 mesh	Freundlich	0.048 mg/g	Öztürk and Kavak (2008)
Al$_2$O$_3$ (Siral 30 Pural)	-	-	-	Condea AG/Germany	Freundlich	0.057 mmol/g 0.031 mmol/g	Seki *et al.* (2006).
Activated aluminia	5-50	6.0	20 g/L	Powder (90 neutral) Merck	Langmuir	1.965 mg/g	Kluczka *et al.* (2007a)
Crystalline zirconium dioxide	5-50	6.0	20 g/L	Reachem, Russia	Langmuir	0.428 mg/g	Kluczka *et al.* (2007a)
Amorphous zirconium dioxide	5-100	8.5	20 g/L	184.32 m^2/g	Langmuir Freundlich D-R	2.759 mg/g 1.234 mg/g 17.857 mg/g	Present work
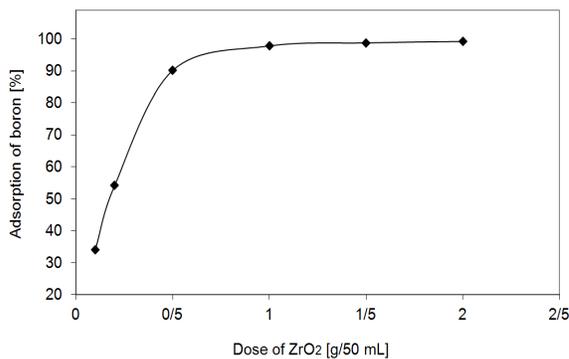
Fig. 6. Adsorption of boron as a function of adsorbent dose, temperature: 25°C, pH=8.5, initial boron concentration: 10 mg/L, adsorption time: 24 hrs

of the Freundlich model (see Table 4) conform to the S-shape for boron isotherms onto ZrO$_2$ at both room and elevated temperature. However, as can be seen in Fig. 5, the amount adsorbed component increases steadily with concentration until a plateau is reached where the surface of the adsorbent practically is saturated and no further adsorption occurs at this stage. This behavior indicates that all isotherms onto ZrO$_2$ can be classified as L type. Furthermore, the adsorption of

boron on the ZrO$_2$ was not rapid and increased even at high concentrations that supports the L type of isotherm (or I type according to YUPAC classification) which characterizes the microporous adsorbents.

The equilibrium adsorption data was fitted to the linear model of the Dubinin-Radushkevich equation. At temperature of 25°C and 35°C, the correlation coefficients (R^2) for the linear regression fits were found to be >0.96. The values of the parameter x_m - maximum amount of boron that can be adsorbed by the amorphous ZrO$_2$ – were estimated to be about 17 mg/g. The adsorption energy value calculated as 31.6 kJ/mol indicates that the adsorption of boron onto ZrO$_2$ is chemical in nature. The chemisorption can be explained by the possibility of the reaction of hydrous ZrO$_2$ with boric acid. At low boron concentration (d" 216 mg/L) B(OH)$_3$ is one of two dominant forms of dissolved boron which are present in aqueous solution at pH=8.5 (Power and Woods, 1997).

$$B(OH)_3 + H_2O \longleftrightarrow B(OH)_4^{3-} + H^+ \qquad (17)$$
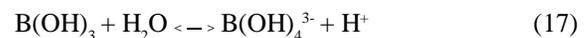
As a result of the reaction between amorphous zirconium dioxide and boric acid, a sparingly soluble and stable compounds, e.g. Na[ZrO(OH)$_x$(B$_4$O$_7$)$_n$], can be formed (Galkin *et al.*, 1986). Other authors (Ryabinin

et al., 1972) suggested that the boron removal could occur by adsorption and chemical reaction according to scheme:

$$ZrO_2 \cdot xH_2O + 4\,B(OH)_3 = ZrOB_4O_7 + (x+6)\,H_2O \qquad (18)$$

that indicated a reversible process of chemisorption. However, in present study, the adsorption and desorption results confirmed the irreversibility of adsorption process.

It was observed from the Table 4 that maximum adsorption capacity of amorphous zirconium dioxide on boron adsorption is 2.759 mg/g. The maximum adsorption capacity was comparable to the adsorption capacities of other boron removal adsorbents type oxides of metals (Table 5). From Table 5, it was cleared that there was a huge difference between the adsorption capacities and the surface area of the two adsorbents (based on Al_2O_3), although both the two adsorbents were almost same in nature. The adsorption capacity of an adsorbent mainly depends on the adsorbent surface area and the initial adsorbate concentration. The differences were observed with adsorbent based on ZrO_2. It was found that very important is the crystal structure because boron capacity on crystalline ZrO_2 is far lower than on amorphous zirconium(IV) oxide. This was due to large surface area of amorphous ZrO_2 and availability of active centers. To investigate the effect of adsorbent dosage on boron removal, the concentrations of ZrO_2 were changed to between 2–40 g/L at 25ºC while the solution concentration of boron 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. 6. The adsorption increased with an increase in the adsorbent dose. The boron removal efficiencies varied from 34 to 99%. An increase in adsorption with the adsorbent dose can be attributed to availability of more adsorption sites. The optimum removal of boron was obtained for the adsorbent dose of 1 g per 50 mL of solution (20 g/L). There was no significant change in the boron removal for higher doses of adsorbent.

CONCLUSIONS

The amorphous ZrO_2 was prepared, characterized and used as a novel adsorbent for removal of boron from aqueous solutions. The results showed that pH, temperature and mass of adsorbent affected the boron adsorption on amorphous ZrO_2. The boron removal reached maximum at pH=8.5 and increased with an increase in adsorbent dose, but decreased with an increase in temperature. The optimum conditions were found as pH=8.5, temperature of 25°C, contact time of 24 hrs, and adsorbent dose of 1 g per 50 mL of solution. At these conditions, the boron adsorption percentage on amorphous ZrO_2 was approximately 98% and final

boron concentration in solution was 0.2 mg/L (initial concentration 10 mg B/L).

Boron adsorption on zirconium dioxide can be described by the linear Langmuir, Freundlich and Dubinin – Radushkevich isotherm models. The Langmuir model fits the best for the experimental results and hints that the boron adsorption on ZrO_2 is monolayer, favorable and irreversible nature. The modeling of the adsorption kinetics was applied with a view to finding out the adsorption mechanism of boron onto the amorphous zirconium dioxide. The pseudo-second-order mechanism was the rate determining step for this adsorbent. The adsorption energy value was calculated as 31.6 kJ/mol, which corresponds to chemisorption of boron onto ZrO_2. The calculated negative value of "S°" indicates a decreased randomness at the solid-solution interface during the boron adsorption. The negative value of "H°" shows the exothermic nature of the process while the negative values of "G°" implies that the adsorption of boron on amorphous ZrO_2 at 25°C and 35°C was spontaneous. Detailed mechanism of boron adsorption on ZrO_2 can be explained by the formation of sparingly soluble compound and variable composition: $Na[ZrO(OH)_x(B_4O_7)_n]$ due to the high affinity of zirconium dioxide hydrate to boric acid in aqueous solution[39].

In general, it was found that the pH of the suspension and dose of the adsorbent are two critical factors in determining the removal efficiency. The pH of the aqueous solution affects the adsorption behavior considerably. The efficient adsorption takes place in the range of pH=8-9. It indicates that boron can be removed by chemisorption either as $B(OH)_3$ or as $B(OH)_4^-$. After treatment of a solution containing 20 mg B/L with amorphous zirconium dioxide the final boron concentration reached the recommended limit by WHO and several European countries for drinking water (2.4 and 1.0 mg/L, respectively).

It was found that this novel adsorbent is characterized by high adsorption of boron. Boron removal from fresh water using amorphous ZrO_2 can be satisfactory.

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