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RESEARCH ARTICLE

Effectiveness of fly ash in boron removal from Tuzla (Çanakkale) geothermal fluid

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ABSTRACT

The heat accumulated in the inner parts of the earth's crust is transmitted to the fluid in the geothermal aquifer by means of transportation. The geothermal fluid is transported to the surface either by wells or naturally. In this study, the geothermal fluid in Tuzla geothermal field in Çanakkale city was examined due to its high boron content (10.3 mg L^{-1}). It was aimed to remove boron from geothermal fluid by adsorption in order to prevent possible negative effects on the environment. Fly ash was obtained from Çan thermal power plant. The specific surface area of the fly ash was 14.6 m^2 g^{-1} and the particle size was between 1.45 and 186 µm. According to ASTM C618 standard, fly ash was classified as Class C. Fly ash was composed of anhydrite, lime, hematite, cristobalite, quartz, calcite and feldspar. Various parameters such as initial pH, adsorbent dosage, contact time, and temperature were studied experimentally for the removal of boron from the geothermal fluid. The suitability of pseudo-first-order, pseudo-second-order, and intraparticle kinetic models to experimental data was examined. The data obtained from the isotherm studies were applied to the Langmuir, Freundlich and Dubinin-Radushkevich models.

Keywords: Adsorption, boron, fly ash, geothermal fluid

1. INTRODUCTION

Water contaminated with boron is handled as an environmental problem because the small amounts of boron in irrigation water cause plant growth to stop and can be toxic to organisms [1]. According to the boron sensitivity of the plants, irrigation water safe boron content is in the range of 0.3-4 mg L^{-1} [2]. For this reason, the excess boron in the water must be removed by a suitable method.

Different methods are used to remove boron from wastewater, including ion exchange, adsorption, chemical precipitation, reverse osmosis, solvent extraction, and membrane filtration [1-5]. Among these methods, adsorption is the most widely used [6]. Fly ash is a good adsorbent and, also cheap and plentiful [7, 8]. Worldwide, waste materials from thermal power plants are estimated to be around 700 million tonnes, of which at least 70% is fly ash [9]. During the electricity generation in thermal power plants in Turkey annually approximately 14.26 million tons of fly ash are emerging and it's only a small amount is used [10, 11].

Within Turkey, 227 geothermal fields with a temperature range of 20-287 °C have been discovered and almost 2000 hot and mineral springs have been determined [12]. Geothermal fluid is used for electricity generation, residential, spa and greenhouse heating, CO_2 extraction, balneological uses and tourism in Turkey. Geothermal fluids of Turkey are highly mineralized with elevated levels of As, B, Cd, and Pb [13]. The high element content of geothermal fluid has certain detrimental environmental consequences, such as pollution of surface water, groundwater, and soil [14]. Tuzla geothermal field located in northwestern Turkey, approximately 70 km southwest of the Çanakkale city. Tuzla is one of the major high-enthalpy geothermal field of Turkey and the boron concentration in geothermal fluid is high [15].

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In this study, boron removal from Tuzla geothermal fluid by batch adsorption experiments was investigated using fly ash. Optimum conditions were determined by examining the effects of various parameters for the removal of boron from geothermal fluid.

2. MATERIALS AND METHODS

2.1. The study area

Fly ash was provided as a waste material from fluidized bed combustion Çan thermal power plant, Çanakkale, northwestern Turkey. Thermal power plant works 2*160 MW electric power and produces approximately 450.000 tons of ash waste per year. The characterization of fly ash was determined by BET, SEM-EDX, XRD and XRF analysis.

Physicochemical parameters (pH, temperature, electrical conductivity and salinity) of the Tuzla geothermal fluid were measured by using a WTW 340i multiparameter (Table 1). Geothermal fluid was sampled in 500-mL*20 polyethylene bottles and stored at 4 °C until further analysis.

Table 1. Physicochemical parameters of the geothermal fluid

Electrical conductivity (mS/cm)	Salinity (‰)	pH	Temperature (°C)
76.1	56	8.07	92.2

A series of batch adsorption experiments were performed to evaluate the effects of certain parameters, such as initial pH, adsorbent dosage, contact time, and temperature. A certain amount of fly ash and 50 mL of geothermal fluid was contacted with a shaking water bath at 140 rpm for a certain period of time. After all samples were filtered, the boron in the filtrate was analyzed according to the Carmine Method and measured using spectrophotometer (Hach DR 5000). The boron concentration of Tuzla geothermal fluid was determined as 10.3 mg L^{-1}.

The amount of boron adsorbed from the geothermal fluid to the fly ash surface was calculated by the following equation:

$$q = \frac{(C_o - C_e)V}{m} \quad (1)$$

where q is the amount of boron adsorbed (mg g^{-1}); C_0 and C_e (mg L^{-1}) are the boron concentration at initial and equilibrium, respectively; V is the geothermal fluid volume (L) and m is the amount of fly ash (g).

3. RESULTS AND DISCUSSION

3.1. Characterization of fly ash

The particle size of fly ash was between 1.45 and 186 µm, with surface area of 14.6 m^2 g^{-1}. The main components of the fly ash were SiO_2 (32.16%), CaO (29.05%), Al_2O_3 (19.22%) and Fe_2O_3 (7.03%), and the loss on ignition value was 4.7%. According to ASTM C618 standard [16], fly ash was classified as Class C. The total sulfur and carbon contents of fly ash were 5.88% and 1.43%, respectively. The metal concentrations contained in the fly ash was identified as Al> Fe> Mn> Zn> Cr> Cu> Pb> Co> Ni. The Al and Mn concentrations of the fly ash were identified to be above the average for continental crust determined by Krauskopf and Bird [17]. The mineralogical composition of the fly ash comprises anhydrite, lime, hematite, cristobalite, quartz, calcite and feldspar. The shape of the fly ash particles showed an irregular morphology in the SEM images (Fig 1). The EDX analysis of fly ash indicated that the ash was mainly composed of O, C, Si, Al, Fe, Ca, S, Na and Ti. The pH and EC of fly ash leachate was measured as 12.19 and 4.83 mS cm^{-1}, respectively.

3.2. Effect of initial pH on boron removal

The pH effect on boron adsorption was investigated at different pH values. The range of pH was 2–12. The pH of the geothermal fluid were adjusted with NaOH and HCl solutions. Then, 0.5 g of fly ash was added to 50 ml of the samples and it was kept in a shaking water bath at 25 °C for 24 h. The results were given in Fig 2. Fig 2 showed that boron removal was affected by the change in pH. It was observed that the maximum boron removal efficiency was obtained at pH 4. The main components of fly ash were Si, Ca and Al oxides. The reaction Si, Ca and Al-rich fly ash with geothermal fluid causes co-precipitation of metal hydroxides. The interaction of borate anions with positively charged hydroxylated oxide surfaces is more favorable. Also, under low pH condition this metal compounds were leached to the solution. We suggested that boron was co-precipitated and accumulated with Si, Ca and Al hydroxides. Similar result was found by Öztürk and Kavak [6].

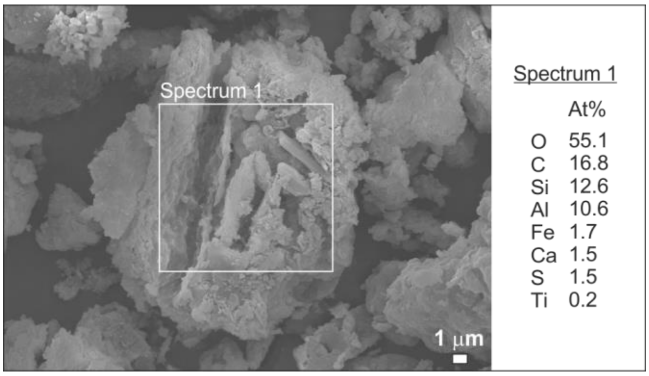

Fig 1. SEM image and EDX result of fly ash

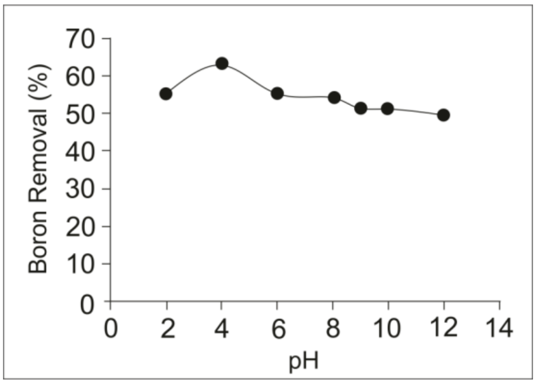

Fig 2. Effect of initial pH on boron removal

3.3. *Effect of adsorbent dosage on boron removal*

The effect of the amount of adsorbent was investigated by adding different amounts of fly ash (0.25-2.5 g 50 mL^{-1}) to the geothermal fluid at pH 4 and contacting it in a shaking water bath at 25 °C for 24 hours. The effect of fly ash content on boron removal was given in Fig 3. The boron removal efficiency of the fly ash was varied approximately from 64 to 88% at adsorbent amount of 0.25 and 2.5 g 50 mL^{-1}, respectively. Boron removal percentage increased as the surface area increased with the increase in the amount of fly ash.

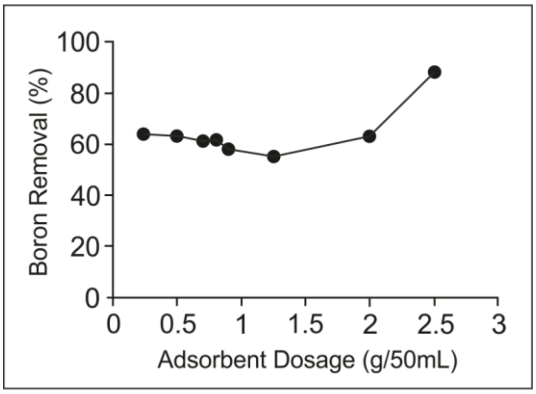

Fig 3. Effect of adsorbent dosage on boron removal

3.4. *Adsorption isotherms*

The Langmuir, Freundlich and Dubinin-Radushkevich (DR) isotherm equations were discussed. The Langmuir equation is given below [18]:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (2)$$

where C_e (mg L^{-1}) and q_e (mg g^{-1}) are the solution concentration in the equilibrium and the amount of boron adsorbed by fly ash in the equilibrium, respectively. Q_o and b indicate the monolayer capacity and absorption energy constant, respectively.

Freundlich equation is given by the following equation [18];

$$\log q_e = \log K + \frac{1}{n} \log C_e \quad (3)$$

Here, Freundlich capacity constant is K((mg g^{-1})(L mg^{-1})$^{1/n}$), and Freundlich intensity constant is n.

Dubinin-Radushkevich (D-R) isotherm equation is given by Equation (4) [19]

$$\ln q_e = \ln q_s + B\varepsilon^2 \quad (4)$$

where q_s is the D-R constant and ε can be correlated as

$$\varepsilon = RT\ln\left[1 + \frac{1}{C_e}\right] \quad (5)$$

where R represents the ideal gas constant (8.314 J mol^{-1} K^{-1}) and T represents the absolute temperature. The constant B gives the mean free energy. The constants of all isotherm equations were given in Table 2. The results showed that the experimental data fitted well with the Langmuir isotherm (R^2=0.95) (Fig 4). It can be said that monolayer adsorption occurs on surface.

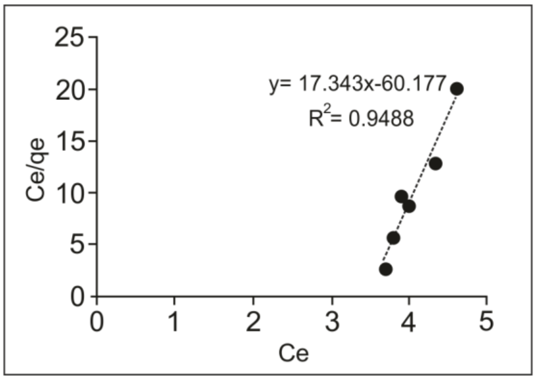

Fig 4. Langmuir isotherm plots for boron removal

3.5. *Effect of contact time on boron removal*

Inadequate contact time of the fluid and adsorbent may not provide good removal. Therefore, optimal contact time was determined. For this purpose, geothermal fluid at pH of 4 was shaken with 2.5 g fly ash at 25 °C for different periods. The results were shown in Fig 5. The boron removal was not determined until the 400th mins. Boron removal increased gradually after this period and 88% boron removal was obtained in 24 h.

Table 2. Constants of different isotherm models

	O_o (mg g^{-1})	b(L mg^{-1})	R^2
Langmuir Isotherm	0.058	-0.286	0.95
	K (mg g^{-1}) (L mg^{-1})$^{1/n}$)	n	R^2
Freundlich Isotherm	4365	-0.15	0.78
	qs (mg g^{-1})	B (mol^2 $k^{-1}$$J^{-2}$)	R^2
D-R Isotherm	1.7x10^{-8}	-2x10^{-6}	0.80

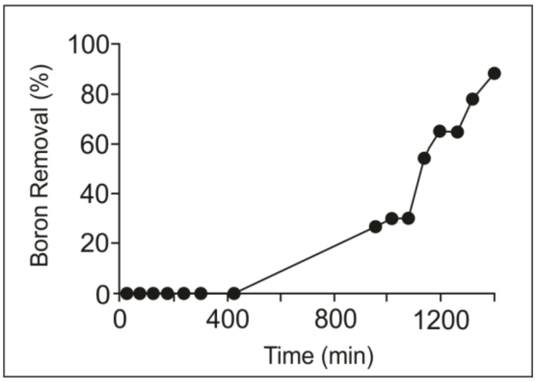

Fig 5. Effect of contact time on boron removal

3.6. Kinetic models

In order to explain the mechanism of adsorption process, pseudo-first-order, pseudo-second-order and intraparticle kinetic models were examined. The Lagergren equation was used to find the rate constant of the pseudo-first-order adsorption [20, 21]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

q_t is the amount of boron adsorbed (mg g^{-1}) at time t (min). k_1 (min^{-1}) is the rate constant.

The equation for the pseudo-second-order kinetic model is used as follows [22, 23]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

Here, k_2 (g mg^{-1} min^{-1}) is the rate constant.

The adsorption process takes place in a few steps that involves the transport of solute molecules from the solution to the solid particle surface, followed by diffusion of these molecules into the pores of the particle. The intraparticle diffusion equation can be given as [18],

$$q = kt^{1/2} \quad (8)$$

where k_i is the intraparticle diffusion rate constant (mg g^{-1} min$^{-1/2}$). The k_i is the slope of straight line portions of the plot of q_t vs. $t^{1/2}$ (Fig 6).

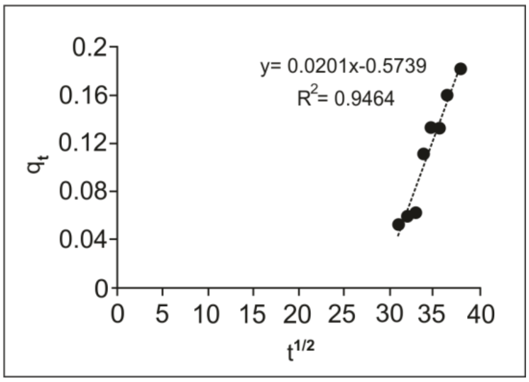

Fig 6. Intraparticle model for boron adsorption onto fly ash

The kinetic constants were shown in Table 3. According to the results, it could be said that the kinetic data were more compatible with the pseudo-first order and intra-particle kinetic models. These results showed that the adsorption of boron was physical and was controlled by diffusion mechanism. Halim et al. [24] obtained similar results.

3.7. Effect of temperature on boron removal

The data obtained showed that the boron removal decreased as the temperature increased (Table 4). The standard free energy change ($\Delta G°$), enthalpy change ($\Delta H°$) and entropy change ($\Delta S°$) of adsorption can be expressed with the following equations:

$$\Delta G^o = -RT\ln K \quad (9)$$

where K is the equilibrium constant and T is the temperature. Equilibrium constant (K) is calculated according to the equation below;

$$K = \frac{C_s}{C_e} \quad (10)$$

C_s indicates the concentration of adsorbent (mg L^{-1}), while C_e indicates the equilibrium concentration of solution (mg L^{-1}).

Van't Hoff equation is represented by Eq. (11);

$$\ln K = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (11)$$

Fig 7 showed the plot of ln K versus 1/T. The enthalpy change values from the slope of this graph and $\Delta S°$ (J mol^{-1} K^{-1}) from the intercept point were found (Table 4). The negative free energy change at various temperatures showed that the adsorption process occurred spontaneously. A negative enthalpy change value indicated that adsorption was exothermic. The negative entropy change suggested the system exhibits random behavior.

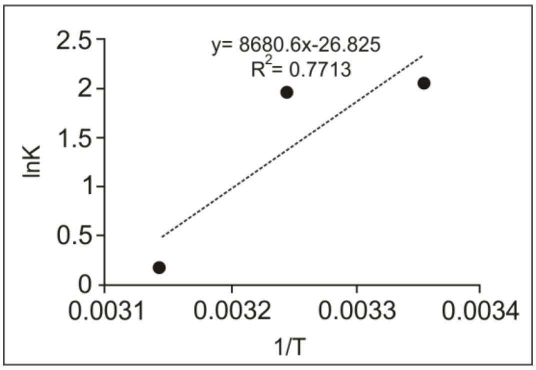

Fig 7. Van't Hoff plot

Table 3. Different kinetic parameters for boron removal

Pseudo-first-order			Pseudo-second-order			Intraparticle model	
k_1 (min^{-1})	q_e (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2	k_i (mg g^{-1} min$^{-1/2}$)	R^2
0.0048	3.24	0.90	0.8902	9.9701	0.78	0.02	0.95

Table 4. Thermodynamic parameters

T(°C)	Ce (mg L^{-1})	K	ΔG° (kJ mol^{-1})	ΔH°(kJ mol^{-1})	ΔS°(J mol^{-1} K^{-1})
25	1.2	7.58	-5.019	-72.17	-223.02
35	1.3	6.92	-4.954		
45	4.7	1.19	-0.463		

4. CONCLUSIONS

In this study, fly ash as a waste material from fluidized bed combustion Çan thermal power plant was used as an adsorbent for boron removal from Tuzla geothermal fluid. This process seems economical as fly ash is available in large quantities and inexpensively. The maximum amount of boron adsorption from the geothermal fluid onto fly ash was obtained at the initial pH of 4. The boron removal efficiency was determined 88% at 25 °C, initial pH 4 and 2.5 g of fly ash per 50 mL solution. According to the experimental results, the Langmuir isotherm model was the most suitable for this process. Among these kinetic models considered for the removal of boron with fly ash, the intra-particle model best fitted the experimental data. Parameters from thermodynamic studies ($ΔG^o$ and $ΔH^o$) indicated that the boron adsorption onto fly ash was spontaneous and exothermic process.

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