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ADSORPTION OF FLUORIDE FROM AQUEOUS SOLUTION BY EUCALYPTUS BARK ACTIVATED CARBON: THERMODYNAMIC ANALYSIS

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ABSTRACT: In this experimental study, batch adsorption experiments were implemented to survey the potential of eucalyptus bark activated carbon (EBAC) in the adsorption of fluoride (F^-). The studied adsorbent was synthesized using the chemical activation method in the presence of phosphoric acid. The effect of several parameters, e.g., the contact time, the initial F^- concentration, and the temperature on the F^- adsorption onto the EBAC was investigated under constant values for the pH (6.5) and the adsorbent dosage (2 g/L). The calculation of the standard free energy changes (ΔG^0), the standard enthalpy change (ΔH^0), and the standard entropy change (ΔS^0) were carried out at different temperatures and initial F^- concentrations. The ΔG^0 values were negative and the ΔH^0 values and the ΔS^0 values were positive at all temperatures and concentrations which suggests that the F^- adsorption onto the EBAC was a spontaneous and endothermic process.

Keywords: Activated carbon; Batch adsorption; Eucalyptus bark; Fluoride; Thermodynamic parameters.

INTRODUCTION

Fluoride (F^-), the ion of the element fluorine, is one of the water-soluble ions that originate from natural and artificial sources, e.g., the industrial effluents discharged from plants producing aluminum and steel, semiconductors, and glass, etc.[1,2] Although topical F is widely used for the prevention and treatment of dental caries, fluorine is neither an essential trace element for humans nor necessary for the development of healthy teeth and bones and an excessive intake may cause chronic fluoride poisoning, such as dental fluorosis, skeletal fluorosis, and non-skeletal fluorosis including cancer and neurological disorders.[3-8] Due to these problems, the World Health Organization (WHO) has recommended an upper limit for fluoride in drinking water of 1.5 mg/L.[9] However, in northern Ghana, which has a hot climate and an average water intake approximately two times higher than that in more temperate climates, it is recommended that in order to protect the population against dental fluorosis the maximum concentration of F in drinking water for children under 6–8 years should be 0.6 mg/L and that there is a lower level for the first two years of life.[10] The recommended upper limit for older children and adults is 1.0 mg/L.[10] Thus, reducing and eliminating excessive concentrations of fluoride from the drinking water is important.[11,12]

Today, among the various methods identified for the removal of fluoride, adsorption is recognized as being a superior method due to accessibility, economic benefits, ease of operation, and a great efficiency in removing fluoride from water.[13-15] However, due to the issues associated with the commercial adsorbents, e.g., their high regeneration cost, various studies have been conducted to produce activated

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carbon from low-cost and easily-available material.[16,17] The results of fluoride removal using prepared activated carbon indicates that this method gives acceptable results.[18,19]

Thus, in the present study, the potential of eucalyptus bark activated carbon (EBAC) for the removal of fluoride has been studied. The effect of different parameters including contact time, initial F^- concentration, and temperature on fluoride removal efficiency was also assessed and thermodynamic studies of the adsorption of fluoride onto the studied adsorbent were performed.

MATERIALS AND METHODS

Materials: The eucalyptus bark used to synthesize the adsorbent used in this study was collected from the northern part of Iran. The analytical grade chemicals used in present study, such as NaF, HCL, and NaOH, were purchased from Merck Co., Germany.

Preparation of adsorbent: In order to prepare the activated carbon, the collected eucalyptus bark was washed several times with distilled water and then dried in an oven at 110ºC for 24 hr. Afterwards, the bark was cut into 5 mm pieces and impregnated with phosphoric acid solution (35%, v/v) as an activating agent. Then, the pieces were placed in a kiln at 800ºC for approximately 1–2 hr. Thereupon, the resultants were washed with distilled water four to five times until the filtrate reached neutral pH and were then immediately dried in an oven at 100ºC for 3–4 hr. The eucalyptus bark activated carbon was screened using 18 and 30 mesh sieves and then stored until its use in the present study, as an adsorbent, to remove F^-.

Adsorption experiments: To prepare the stock solution (1000 mg/L) of F, 0.221 g NaF was dissolved into 1000 mL of distilled water and the required concentrations of F solution were provided by the diluting the stock solution. Batch experiments were conducted at 20–60ºC in a temperature-controlled shaker at 150 rpm. The EBAC (0.2 g) was added to 100 mL of synthetic fluoride solutions (concentrations of 5 to 25 mg/L). After equilibrium, the samples were filtered by Whatman filter paper (pore size 0.45 µm) and the filtrate was then analyzed to determine the residual concentration of F^-. 1 mL of $ZrOCl_2.8H_2O$ and 1 mL Spadns was added into prepared samples. The measurement of the residual F^- concentration in the samples was accomplished using the spectrophotometer at λ_{max}=570 nm. All experiments were carried out at the constant pH value of 6.5.

Thermodynamics tests: The study of the dependency levels of the adsorption reactions on temperature provides valuable knowledge about the enthalpy and entropy changes which occur during adsorption. Thermodynamic parameters related to the F^- adsorption onto the EBAC are determined by the following equations (Equations 1–3): [20-22]

$$K = \frac{q_e}{C_e} \qquad (1)$$

$$\Delta G^0 = -RT \ Ln \ K \qquad (2)$$

$$Ln\ (K) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (3)$$

Where, in Equations 1–3, Ce is the equilibrium concentration (mg/L) of the F^- solution, q_e is the equilibrium adsorption capacity (mg/g), R (8.314 J/K.mol) is universal gas constant, K is the equilibrium constant, and T (K) is the temperature of the system. Also, ΔG^o is the Gibbs free energy change in sorption (kJ/mol), ΔS^o is the entropy change in sorption (kJ/mol. K), and ΔH^o is the change in enthalpy in sorption (kJ/mol).

Data analysis: Equations 4 and 5 were applied to calculate the F^- adsorption capacity and F^- adsorption efficiency, respectively.[23,24]

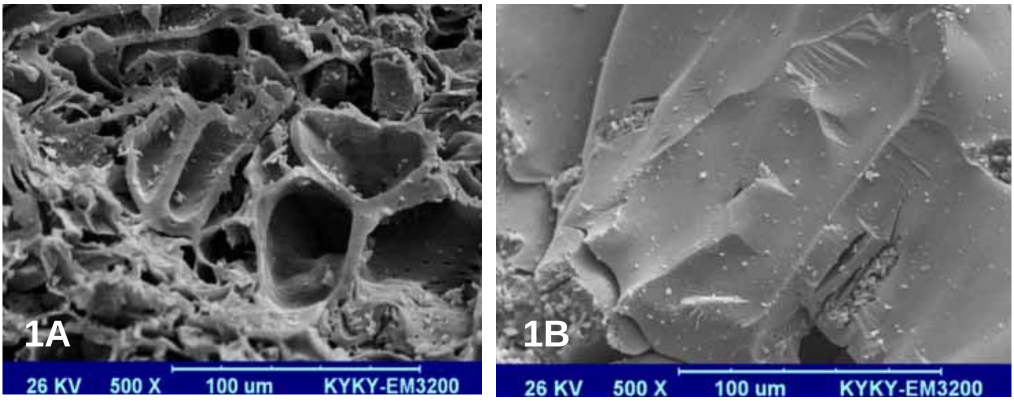
$$\text{Adsorption capacity}\quad q_e = \frac{(C_0 - C_e)V}{M} \qquad (4)$$

$$\text{Adsorption efficiency,\%} = \frac{(C_0 - Ce)}{C_0} .100 \qquad (5)$$

Where, in Equations 4 and 5, q_e, (mg/g), C_0, and C_e are representative of the adsorption capacity, and the initial and the equilibrium concentrations (mg/L) of F^-, respectively. Moreover, V (L) and M (g) indicate the volume of the F^- solution and the weight of the EBAC, respectively.

RESULTS AND DISCUSSION

The scanning electron microscope (SEM) images of the adsorbent before and after adsorption are shown in Figures 1A and 1B.



Figures 1A and 1B. Scanning electron microscope (SEM) images of the of eucalyptus bark activated carbon (EBAC) before (1A) and after (1B) the adsorption process.

The plot obtained from the amount of F^- adsorbed (mg/g) vs. contact time at different temperatures (293, 303, 313, and 323 K) is represented in Figure. 2. It was observed that the amount of F^- uptake, q_t (mg/g), increases by increasing the contact time at all temperatures. Further, the amount of F^- adsorbed increased with an increase in temperature. It was also observed that the F^- uptake occurred rapidly during the first 30 min and that after this the uptake process was slower until equilibrium was finally attained.[25-27] This indicated that the equilibrium time was not affected by the temperature.

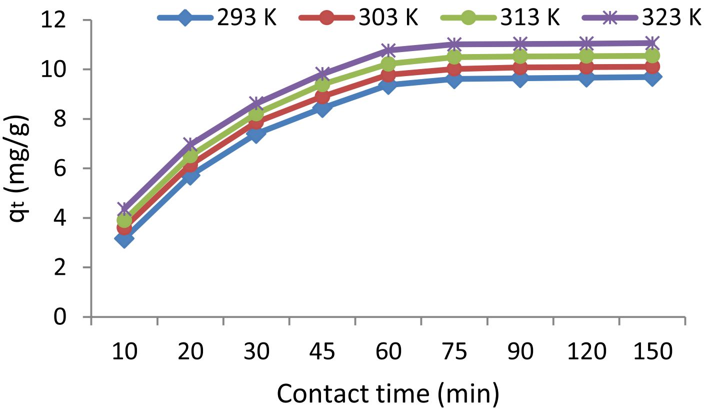


Figure 2. The effect of the contact time and the temperature on the removal efficiency of F^- (C_0 = 25 mg/L, adsorbent dosage = 2 g/L, and pH = 6.5).

Figure 3 shows the effect of the different parameters (contact time and initial F^- concentration) on the removal of F^- with EBAC. It was observed that an increase in the F^- concentration from 5 to 25 mg/L led to an increase in the adsorption capacity. Thus, a greater interaction between the F^- molecules and the surface of the EBAC sorbents is achieved by increasing the initial concentration of F^-.[28,29]

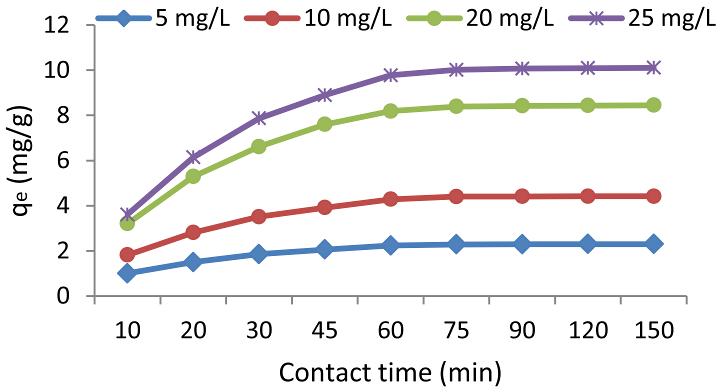


Figure 3. Fig 3. The effect of the contact time and the initial F^- concentration on the removal efficiency (T = 30ºC, adsorbent dosage = 2 g/L, and pH = 6.5).

The studies to evaluate the effect of different temperatures on the F^- adsorption using the EBAC were carried at the pH value of 6.5. Figure 4 depicts the linear plot obtained from Ln K versus 1/T at different initial F^- concentrations and the slope and intercept of this plot is used to determine the ΔH^o and ΔS^o values, respectively.

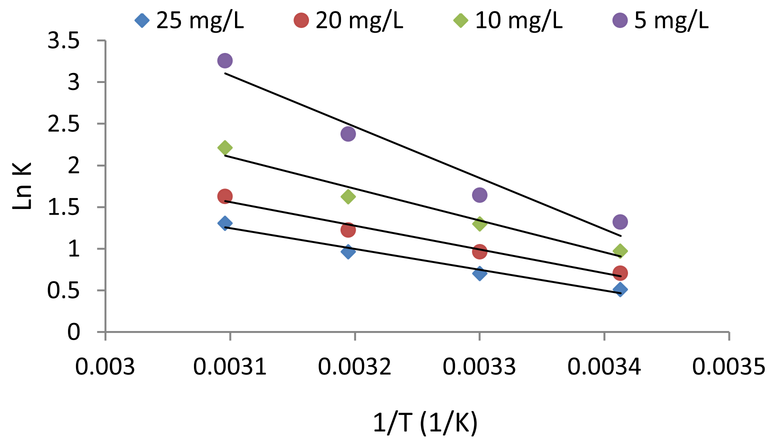


Figure 4. Effect of temperature on the adsorption of F^- ion onto EBAC

The ΔH°, ΔS°, ΔG°, and K parameters were calculated and are summarized in the Table.

Table. Thermodynamic parameters for the adsorption of F^- on EBAC

C_0 (mg/L)	T (K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
5	293	–3.21	25.79	0.074
	303	–4.13		
	313	–6.18		
	323	–8.74		
10	293	–2.36	29.67	0.086
	303	–3.26		
	313	–4.22		
	323	–5.94		
20	293	–1.72	37.71	0.115
	303	–2.42		
	313	–3.18		
	323	–4.36		
25	293	–1.23	51.17	0.184
	303	–1.76		
	313	–2.51		
	323	–3.50		

The values were observed to be between –1.23 and –8.74 kJ/mol for different initial F^- concentrations. The negative values of ΔG° confirms the occurrence of the spontaneous physisorption.[30,31] The enhancement of the ΔG° negative values by increasing the temperature at all initial F^- concentrations (5, 10, 20, and 25 mg/L) indicates that this process is carried out more rapidly and more spontaneously at higher temperature.[32] The positive value of ΔH° can justify the endothermic nature of F^- adsorption at all concentration.[33] ΔH° values between 8 and 25 kJ/mol demonstrate that an adsorption process is generally physisorption while when the values are in range of 83–830 kJ/mol it is considered to be chemi-adsorption.[34,35] Moreover, ΔH° values between 25 and 83 kJ/mol indicate that there is a contribution from both chemi-adsorption and physisorption in the adsorption process. Accordingly, it can be concluded that F^- sorption onto the EBAC (ΔH°= 25.79, 29.67, 37.71, and 51.17 kJ/mol for concentrations of 5, 10, 20, and 25 mg/L respectively) involves both chemi-adsorption and physisorption.[36,37] The positive value of ΔS° (Table) indicates an enhancement in the degree of freedom of the irregularities at the solid/liquid interface during the adsorption of F^- onto the EBAC.[38,39] Thus, the adsorption onto the EBAC is favorable.

CONCLUSION

In the present work, the activated carbon adsorbent was prepared with eucalyptus bark and used for the removal of F^- ion from aqueous solution. At the maximum equilibrium capacity, 99.2 % of the F^- ions were removed and it was reached by using the EBAC after 75 min at pH 6.5, an adsorbent dosage of 2 g/L, and an initial F^- concentration of 5 mg/L. The positive value of ΔS° shows a increase in randomness at the solid/liquid interface during the adsorption, which indicates that the adsorption was favorable at higher temperatures. The standard Gibbs free energy changes (ΔG°) for all the initial F^- ion concentrations (5, 10, 20, and 25 mg/L) were negative, which indicates that this adsorption process is spontaneous.

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