

Adsorption of fluoride from aqueous solution by acid treated spent bleaching earth[☆]

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Abstract

Acid treated spent bleaching earth was studied to assess its capacity for the adsorption of fluoride from aqueous solutions. Adsorption isotherms have been modeled by Langmuir and Freundlich equations and isotherm constants for both isotherms were calculated. The effect of the adsorbent concentration on the adsorption was studied. The dependence of the adsorption of fluoride on the pH of the solution has been studied to achieve the optimum pH-value and a better understanding of the adsorption mechanism. It has been found that maximum adsorption of fluoride from aqueous solutions takes place at pH-value of 3.5. Second-order equation was used to describe the adsorption rate of fluoride and adsorption rate constant was calculated. Intraparticle and mass transfer coefficients were calculated. The influence of addition of the anions on the adsorption of fluoride was also studied to simulate industrial waste waters and the addition of anions decreased the adsorption of fluoride on the acid treated spent bleaching earth (SBE). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Fluoride; Adsorption; Spent bleaching earth; Fluoride removal; Waste water treatment; Mass transfer; Intraparticle diffusion; Adsorption kinetics

1. Introduction

Fluorine usually in combined fluoride forms is naturally present in varying amounts in the atmosphere, water and soils. A large amount of fluorides have been generated from glass industry, chemical industry, metal industry and high tech industry such as manufacturing semiconductors and integrated circuits.

Fluoride is recognized as an essential constituent in the human diet. Skeletal and dental problems can be prevented by maintaining fluoride concentration of about 1 ppm in the dietary intake [1]. Drinking water is considered to be safe for human consumption, if fluoride concentration does not exceed 1.0 mg dm^{-3} .

Although, it is necessary to take trace amounts of fluoride for the formation and conservation of teeth in children, large fluoride doses result in mottling as well as fluoride deposition in bone leads to structural damages in ligaments.

Several methods have been tried to remove fluorides from water, namely adsorption, precipitation, electro dialysis, ion exchange and reverse osmosis.

Among these methods, adsorption is still one of the most extensively used methods for defluoridation of water and activated carbon prepared from various materials exhibits good capacity for removal of fluorides and other pollutants from waters.

In recent years, attention of scientists have been devoted to the study of different types of low cost materials such as spent bleaching earth [2,3], wollastonite and chine clay [4], bentonite and activated bentonite [5–8], kaolinitic clay [9], agricultural by products [10], fly ash [11], carbon slurry [12], biogas residual slurry [13], zeolite [14], bone char [15] and flax shive [16] since activated carbon is expensive.

Spent bleaching earth (SBE) that is a solid waste from edible oil processing industry was chosen as raw material [2,17,18]. SBE has two components: residual oil not removed by filter pressing and montmorillonite clay. This material is disposed of directly to landfill either dry or as a wet slurry. But the landfill option causes problems, the most dangerous being the pyrogenic nature of the unsaturated oil which rapidly oxidizes on the clay surface to the point of spontaneous ignition. The constant changes in environmental legislation has led to restrictions in solid waste management. Therefore, it is necessary to study on the minimization of pollutant such as SBE from oil industry and a good solution from an environmental and economic standpoint is the application in the waste water industries as low cost adsorbent after suitable regeneration process. Therefore, in

[☆] A new adsorbent was produced and used in the removal of fluoride. Activated bentonite → SBE → a new adsorbent for the removal of fluoride.

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this study SBE was chosen as a raw material to produce a new adsorbent.

In this context, the aim of this study is (1) to develop a new adsorbent for the removal of fluoride, (2) to show applicability in fluoride treatment systems.

2. Results and discussion

2.1. Contact time

Fig. 1 shows the variation of concentration of fluoride with contact time for different initial concentrations. It is seen that in all the concentrations studied the concentration of fluoride decreased with time up to 15 min and then the curves become flattened. It is also seen that the equilibrium time is independent of solution concentration. Based on these findings, the shaking time of 30 min was used in all further experiments.

2.2. Adsorption dynamic

Kinetic studies of fluoride by adsorption on acid treated SBE were concerned with obtaining essential information for the application of adsorbent used in treatment systems.

Fluoride removal by acid treated SBE tends to follow the second-order rate equation given by

$$\frac{1}{C} = \frac{1}{C_0} + k_a t$$

where C is the equilibrium concentration, C_0 the initial concentration, t the time and k_a is the rate constant [19].

As can be seen from Fig. 2, the linearity of the plots indicates the applicability of the second-order kinetics equation for the system under experimental conditions.

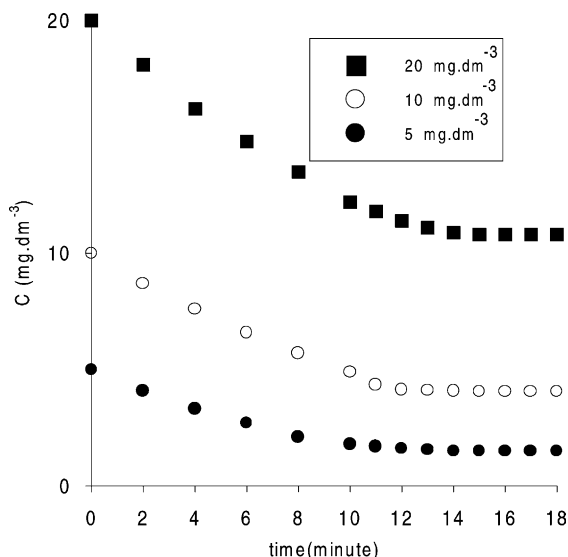


Fig. 1. Variations in the fluoride concentrations with time.

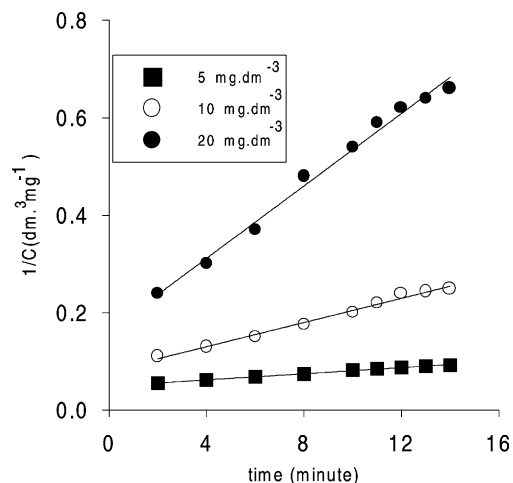


Fig. 2. Second-order kinetic plot for the adsorption of fluoride on acid treated SBE.

The values of rate constant k_a were calculated from the slope of the linear plot of $1/C$ versus t and were found to be as 0.036, 0.0121, and 0.00318 $\text{dm}^3 \text{mol}^{-1} \text{min}^{-1}$ for the concentrations of 5, 10, and 20 mg dm^{-3} , respectively.

2.3. Intraparticle diffusion

In adsorption studies, it is necessary to determine the rate-limiting step. Therefore, the results obtained from the experiments were used to study the rate-limiting step in the adsorption process.

In order to show the existence of intraparticle diffusion in the adsorption process, the amount of fluoride sorbed at time t , q was plotted versus the square root of time, $t^{0.5}$ (Fig. 3). The k -values were obtained from the slope of the linear portions of the curves and were found to be as 0.145, 0.414,

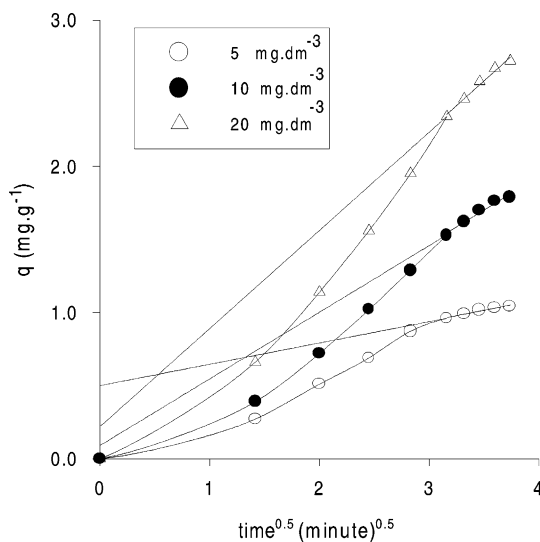


Fig. 3. Plots of amount of fluoride adsorbed vs. $t^{1/2}$ for intraparticle diffusion of fluoride.

and $0.615 \text{ mg g}^{-1} \text{ min}^{0.5}$ for the initial concentrations of 5, 10, and 20 mg dm^{-3} , respectively. It is seen from Fig. 3, that all the plots have the same general features (the initial curved portion and a linear portion). The initial curved portion is attributed to the boundary layer diffusion, while the linear portion is responsible for the intraparticle diffusion. The linear portion of the curves do not pass the origin in Fig. 3. This indicates that mechanism of fluoride removal on acid treated SBE is complex and both, the surface adsorption as well as intraparticle diffusion contribute to the rate determining step [20,21].

2.4. Adsorption isotherms

The distribution between the solid and the solution interface at equilibrium has been described by the Freundlich and the Langmuir equations. These two models are widely used, the former being purely empirical and the latter assuming that maximum adsorption occurs when the surface is covered by adsorbate.

The Freundlich equation is commonly presented as

$$q = kC^n$$

where k and n are temperature-dependent constants, C the equilibrium concentration (mg dm^{-3}) and q is the amount adsorbed at equilibrium (mg g^{-1}). The Freundlich equation can be linearized by logarithmic transfer of both sides.

$$\ln q = \ln k + n \ln C$$

Experimental results were plotted as $\ln q$ against $\ln C$ (Fig. 4). The best slope n and intercept, $\ln k$, were obtained by the least squares method. The Freundlich isotherm constants, k and n were found to be as 0.943 and 0.461.

To quantify the adsorption capacity of the adsorbent for the removal of fluoride from aqueous solutions, Langmuir

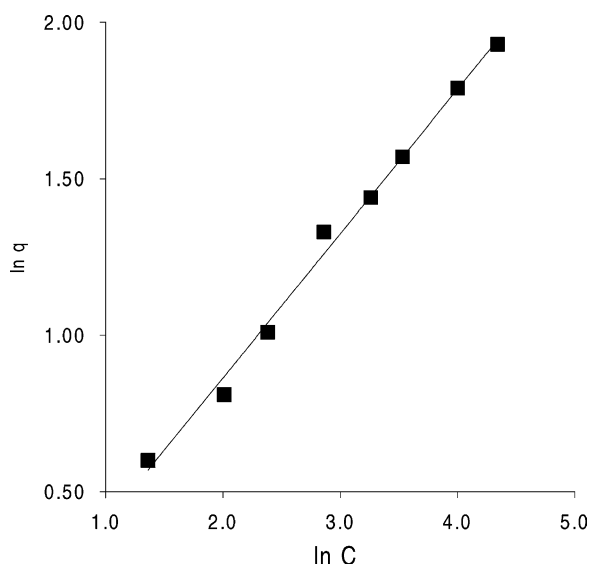


Fig. 4. Freundlich plots for the adsorption of fluoride.

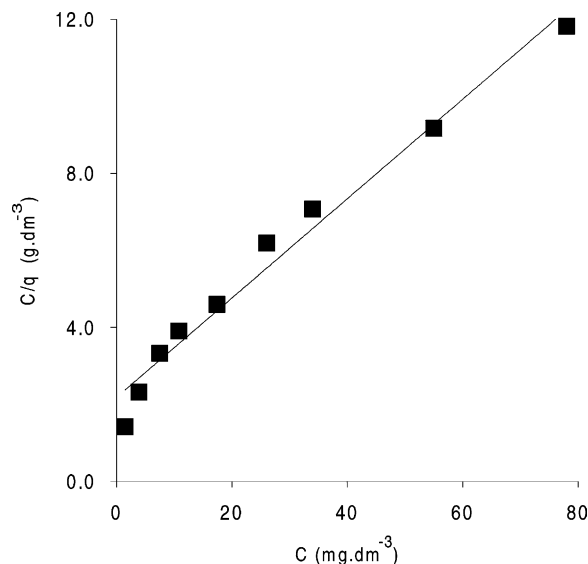


Fig. 5. Langmuir plots for the adsorption of fluoride.

equation is applied. Langmuir adsorption isotherm can be written as follows:

$$q = \frac{QbC}{1 + bC}$$

where C is the equilibrium concentration (mg dm^{-3}), q the amount adsorbed at equilibrium (mg g^{-1}), and Q and b are the Langmuir constants related to the capacity and energy of adsorption, respectively.

The Langmuir equation can be rearranged as follows:

$$\frac{C}{q} = \frac{1}{Qb} + \frac{C}{Q}$$

The linear plot of C/q versus C (Fig. 5) indicates the applicability of Langmuir adsorption isotherm. The values of Q and b were calculated from the slope and the intercept of the linear plots C/q versus C and were found to be as 7.752 mg g^{-1} and $0.059 \text{ dm}^3 \text{ g}^{-1}$.

In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter was determined by using the following equation [20,22]:

$$r = \frac{1}{1 + bC_0}$$

where C_0 is the initial concentration and b is the Langmuir isotherm constant.

Values of $r < 1$ represent favorable adsorption and values greater than 1.0 represent unfavorable adsorption. The r -value for the initial concentration of 20 mg dm^{-3} was found to be 0.459. The value obtained shows that our system is favorable.

The removal of fluoride by different adsorbents has been studied in recent years and some of these publications provide Q -values [8,23–25]. Although, these values were obtained at different pH range they can be useful criterion of the adsorbent capacity. The Q -value obtained in this study is

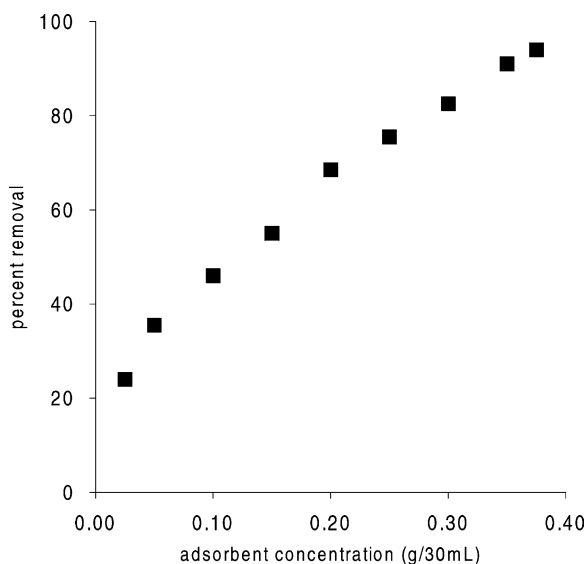


Fig. 6. Effect of adsorbent concentration on the adsorption of fluoride.

greater than the values reported for alum sludge ($Q = 5.394 \text{ mg g}^{-1}$), lignite (7.09 mg g^{-1}), bituminous coal (7.44 mg g^{-1}), but is lower than fly ash (20 mg g^{-1}). This result is very interesting since fly ash has a very small surface area. It is known that fly ash contains SiO_2 and Al_2O_3 as the major constituent and it is expected that either any of these major oxides present in the adsorbent or their combined influence are likely to be responsible for the adsorption hence, the Q -value obtained is greater than other adsorbents although it has a smaller surface area.

2.5. Effect of adsorbent dose on the adsorption process

The effect of the adsorbent concentration on the adsorption of fluoride for the initial concentration of 20 mg dm^{-3} was studied and shown in Fig. 6. It is seen that the adsorption increased with the increase in the dose of adsorbent. The maximum removal percentage was exhibited at a dosage of $0.375 \text{ g adsorbent per } 30 \text{ ml}$ (96%). This is due to enhanced active sites with an increase in amount of adsorbent.

2.6. Effect of pH on the adsorption of fluoride

The pH of the aqueous solution is an important variable which controls the adsorption at the water–adsorbent interfaces. Therefore, the adsorption of fluoride on the acid treated SBE was examined at different pH-values ranging from 3.5 to 8 and were presented in Fig. 7. It can be seen from the Fig. 7 that fluoride removal decreases with increasing pH, and the removal of fluoride is maximum (49%) at pH = 3.5 and is minimum (12%) at pH = 8. Therefore, all the experiments were conducted at pH = 3.5. This can be explained by the change of surface charge of the adsorbent. It is known that in highly acidic medium, the surface of adsorbent is highly protonated while it is neutralized and tended to have negative charge in alkaline

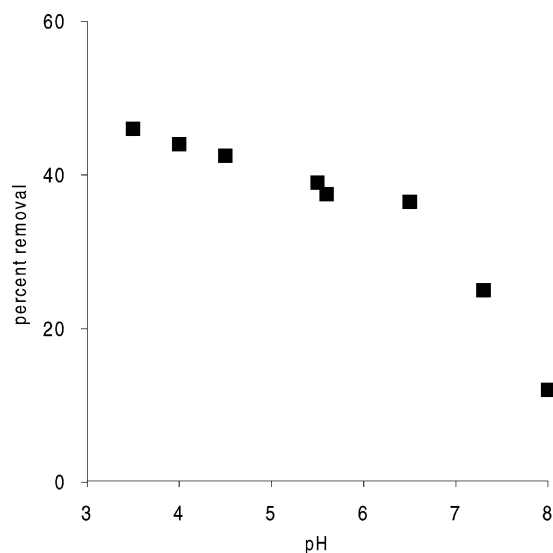


Fig. 7. Effect of pH on the adsorption of fluoride by acid treated SBE.

medium. Therefore, high efficiency in acidic medium can be attributed to the gradual increase in attractive forces and low efficiency in alkaline medium can be explained by the repulsion between the negatively charged surface and fluoride.

2.7. Mass transfer coefficient

Mass transfer analysis for the removal of fluoride was carried out using the following equation [26]:

$$\ln\left(\frac{c_t}{c_0} - \frac{1}{1+mK}\right) = \ln\left(\frac{mK}{1+mK}\right) - \left(\frac{1+mK}{mK}\right)\beta S_s t$$

where c_0 is the initial solute concentration (mg dm^{-3}), c_t the solute concentration after time t (mg dm^{-3}), K is the constant obtained by multiplying Q_0 and b ($\text{dm}^3 \text{ g}^{-1}$), m is the mass of the adsorbent per unit volume of particle free adsorbate solution (g dm^{-3}).

S_s is the outer surface of adsorbent per unit volume of particle free slurry (cm^{-1}), β the mass transfer coefficient (cm min^{-1}). $\ln((c_t/c_0) - 1/(1+mK))$ versus t for the initial concentration of 20 mg dm^{-3} gives the straight line of slope $[(1+mK)/mK]\beta S_s$ and the value of mass transfer coefficient β was calculated from the slope of the plots and was found to be as 0.0195 cm s^{-1} (Fig. 8.) A number of mass transfer coefficients have been reported in the literature for the adsorption of various pollutants onto adsorbents [27]. The β obtained in this study is greater than the values reported for benzaldehyde-carbon ($9 \times 10^{-3} \text{ cm s}^{-1}$), phenol-carbon ($3.9 \times 10^{-3} \text{ cm s}^{-1}$), *p*-bromophenol-carbon ($3.9 \times 10^{-3} \text{ cm s}^{-1}$). The mass transfer coefficient obtained in this study is higher than the values obtained for organic pollutants. This can be explained by the fact that large organic molecules will restrict their mobilities in the solution while fluoride anions move easily since it is smaller than large organic molecules.

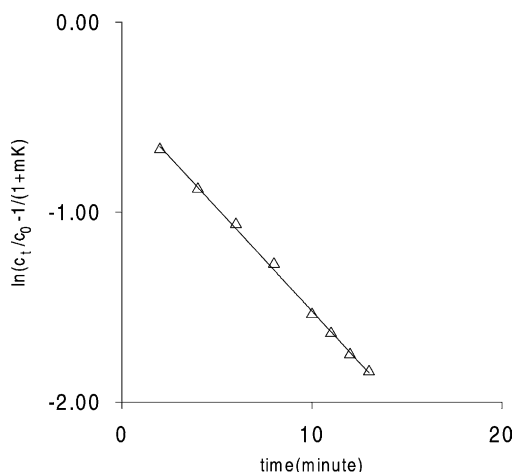


Fig. 8. Mass transfer plot for the adsorption of fluoride on the acid treated SBE.

2.8. Effect of different anions

The drinking water and waste waters contain many anions. Therefore, the effect of different anions namely sulphate, nitrate and phosphate on the adsorption of fluoride on the adsorbent produced from SBE was also examined. The initial concentration of fluoride was fixed at 20 mg dm^{-3} while the initial concentrations of other anions varied from 5 to 25 mg dm^{-3} . The results of these studies are given in Fig. 9. It is seen from Fig. 9 that the presence of these anions reduced the adsorption of fluoride on acid treated SBE, since these anions were coadsorbed along with fluoride anions. The anions reduced the fluoride adsorption in order phosphate > sulphate > nitrate. These results are at

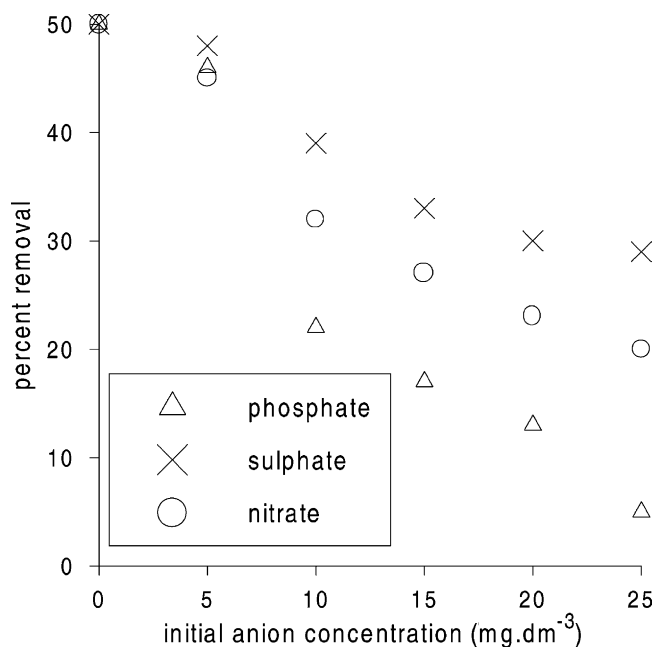


Fig. 9. Effect of different anions on the adsorption of fluoride by the acid treated SBE.

agreement with those of Sujana et al. for the removal of fluoride with alum sludge [23]. The decreased adsorption of fluoride in the presence of anions may be because of the lower affinity for adsorption. The adsorption of these anions will be subject of other studies.

2.9. D.R. isotherm

It is known that the Langmuir and Freundlich isotherm constants do not give any idea about the adsorption mechanism. In order to understand the adsorption type, equilibrium data was tested with D.R. isotherm [28,29].

D.R. equation can be written as

$$X = X_m - e^{-K\varepsilon^2}$$

where ε (polanyi potential) = $RT \ln(1+(1/C))$, X is the amount of fluoride adsorbed per unit weight of adsorbent (g g^{-1}), X_m the adsorption capacity (g g^{-1}), C the equilibrium concentration of fluoride in aqueous solution (g l^{-1}), K the constant related to the adsorption energy, R the gas constant and T is the temperature (K).

D.R. isotherm can be linearized by logarithmic transfer of both sides.

$$\ln X = \ln X_m - K\varepsilon^2$$

Fig. 10 shows the plot of $\ln X$ against ε^2 . D.R. isotherm constants, X_m and K can be calculated from the slope and intercept of the plot and were found to be as $0.0091 \text{ mol}^2 \text{ kJ}^{-2}$ and 0.0093 g g^{-1} .

The mean free energy of adsorption (E), defined as the free energy change when 1 mol of ion is transferred to the surface of the solid from infinity in solution can be calculated from the K -value using the equation [28]:

$$E = (-2K)^{-0.5}$$

The calculated value of E is 7.41 kJ mol^{-1} . It is known that magnitude of E is useful for estimating the type of adsorption and if this value is between 8 and 16 kJ mol^{-1} , the

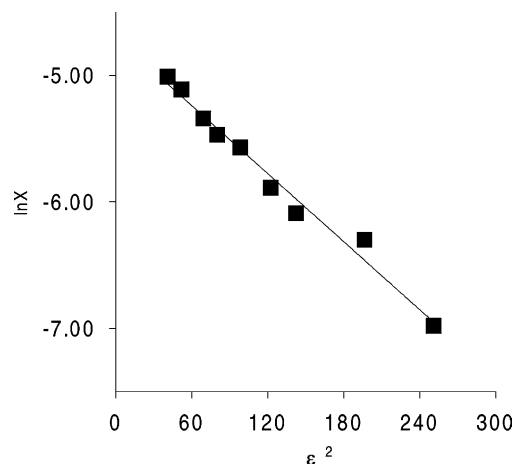


Fig. 10. D.R. plot for the adsorption of fluoride.

adsorption type can be explained by ion exchange. But the value of E found in this study is within the energy range of physical adsorption ($E < 8$).

3. Conclusions

The following conclusions can be drawn from our investigations.

The removal of fluoride from aqueous solutions depends on the contact time, pH of the solution and adsorbent concentration. Mechanism studies show that mechanism of fluoride removal on acid treated SBE is complex and both the surface adsorption as well as intraparticle diffusion contribute to the rate determining step. The presence of other anions affect the uptake of fluoride.

Comparative studies of the adsorption capacities show that the acid treated SBE can be used effectively for the treatment of waste waters enriched with fluoride as low cost adsorbent.

The cost of acid treated SBE may be slightly higher than some cheap adsorbents. But it is not a crucial problem if the adsorbent produced can provide enough adsorption in waste water systems. It is very difficult and expensive to store SBE whereas it is easier and less costly to use as raw material for producing adsorbent. The results obtained in this study are expected to provide useful guidelines for engineers and chemists who work in waste water systems which are much more complex.

4. Experimental

All the chemicals used in the study were of analytical grade. All the solutions used in the study were prepared using bidistilled water. SBE was obtained from an oil plant in Marmara region.

4.1. Preparation of the adsorbent

Impregnation with H_2SO_4 was performed by mixing 24 ml acid solution (8 ml water + 16 ml H_2SO_4 , 96%) with 25 g SBE into a paste which was then carbonized in a static air muffle furnace in covered crucibles at 350 °C for 5 h. Post-treatment was carried out with 0.1 M HCl solutions, hot and cold water, then acetone and finally impregnated samples were dried for 16 h at 105 °C. The surface areas of the fresh activated bentonite and the adsorbent produced were measured by N_2 gas adsorption method and found to be 207 and 198 $m^2 g^{-1}$, respectively. The carbon and hydrogen contents were measured to be 21.52 and 3.17% for SBE and 7.49 and 0.56% for the adsorbent produced from SBE. Similar results were reported by Pollard et al. [17]. The results of the pore structure measurements for both the fresh activated bentonite and the adsorbent produced from SBE are presented in Table 1. It is seen from the comparison of the activated bentonite and adsorbent produced from SBE

Table 1

Pore distribution for fresh bentonite and adsorbent produced from SBE

Pore diameter (nm)	Volume of pores ($cm^3 g^{-1}$)	
	Fresh bentonite	Adsorbent produced from SBE
0–5	0.010	0.010
0–14	0.271	0.258
0–25	0.303	0.281
0–80	0.343	0.329

that there is not significantly change in the volume of pores. It is also seen from the results for 0–5 nm pore diameter that there is no change in the values of volume of pore for both materials. This can be explained by the fact that large molecules in the oil can not access these narrow pores. Therefore, some of the pores are not covered with organic layer. The adsorbent produced was different from activated bentonite ($Na_{0.34}[Al_{1.50}Mg_{0.28}](Si_4O_{10}) \cdot (OH)_2$) used in bleaching process. A black layer is formed on the surface of bentonite due to carbonization.

Treatment process removed the much of the substances existing in the pores of SBE. This was supported by elemental analysis results for SBE and adsorbent produced from SBE. Activated bentonite used in bleaching process was also acid treated to develop adsorption capacity in bleaching process. Acid treatment of SBE does not regenerate SBE back to fresh activated bentonite used in bleaching process. A different adsorbent that shows a patchwise topography was obtained with treatment process in the study. An organic layer forms on the surface of the bentonite. Carbon deposits on the surface like other carbon mineral adsorbents. The new adsorbent consists of uncovered original acid treated bentonite surface and carbon deposits on the bentonite surface. This was supported by pore distribution results.

4.2. Adsorption studies

Batch technique was selected to obtain equilibrium and kinetic data. A number of polyethylene bottles containing 30 ml solution of fluoride of known concentrations (5–45 $mg dm^{-3}$) and 0.1 g of the adsorbent were shaken in a shaking bath. At predecided intervals of time, the solutions were separated from the adsorbent by centrifugation and supernatant was analyzed. Measurement of fluoride concentrations in the solutions were based on fluoride ion selective electrode operated in conjunction with a Jenway 3040 model ion-meter, calibrated against standard NaF solutions. An appropriate pH of the aqueous solutions were maintained by HCl and NaOH.

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