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KINETIC AND EQUILIBRIUM STUDIES OF FLUORIDE ADSORPTION BY A CARBONACEOUS MATERIAL FROM PYROLYSIS OF WASTE SLUDGE

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The efficiency of the adsorption for fluoride by sludge from the treatment of starch industry wastewater was investigated. Batch experiments were conducted in order to determine the parameters that affect the adsorption process. The activation for waste sludge and specific surface area and porosity effects in enhancing the pyrolysis conditions were determined. The adsorption parameters of initial fluoride concentration, pH and adsorbent dosage were investigated with carbonaceous material. As a result of pyrolysis of samples treated with $ZnCl_2$ 1196 m^2/g, the specific surface area was reached. Correlation coefficient of 0.99 and 12.75 mg/g adsorption capacity and adsorption isotherm model were revealed as convenient. Experimental results show that the adsorption of fluoride waste sludge will be effective in many ways in which the adsorbent is applied.

Keywords: adsorption, adsorption isotherm, waste sludge, fluoride.

Introduction

As a result of water solubility of the minerals in the soil, Ca, Mg, Na, K, Li and NH_4 as cation and SO_4, PO_4, NO_3, F and Cl as anion are available in natural waters. Living things need these minerals to carry out their vital activities. However, the high concentration of anions and cations present in the aquatic environment has negative effects. Fluoride is found in the form of fluorite and fluorapatite in the earth's crust. Fluoride concentrations range from 0.01 to 0.3 ppm in fresh water and 1.2 to 1.5 ppm in oceans. However, there are low concentrations in drinking water and foods. In particular, fluoride emissions are spread into the environment during industrial activities used inorganic and organic fluorine compounds [1]. Major sources of fluoride in the environment are the food, pharmaceutical, cosmetics, glass and ceramics industry, electroplating coating applications, steel and aluminium, rubber, pesticides, fertilizers and semi-con-

ductive material industries [2]. The concentration of fluoride in drinking water is important for human health. In recent years, high concentrations of fluoride removal from waters have become an important research issue. The consumption of drinking water containing more than 1.5 mg /L of fluoride ions over long periods causes fluorosis disease in the teeth and skeleton. When exposed to more than 4 mg/L, neurologic damage and serious toxic effects are seen [3]. However, the concentration of fluoride ions in drinking water must be between 1 to 1.5 mg/L for healthy tooth development in children [4].

Methods for the removal of fluoride from water include chemical precipitation [5], membrane process [6], ion-exchange [7], electrolytic defluoridation, electrodialysis and adsorption. The adsorption process is an important application in these methods. A variety of adsorbents are used for the removal of fluoride from aqueous solutions [8].

These are activated and impregnated alumina [9 – 11], rare earth oxides [12], activated clay [13], infused silica [14], carbon materials [15, 16], red mud, catalysts and industrial waste such as fly ash [17 – 19], zeolites and ion exchangers [20], biosorbents [21], alum [22], alum sludge [23], modified chitosan [24] and other low-cost adsorbents [25].

Adsorption is an important method for the treatment of industrial wastewaters. However, due to the cost of activated carbon, the production of activated carbon from alternative waste materials is being investigated [26].

High amounts of sludge exist as a result of industrial wastewater treatment. It has large amounts of water and organic content. Several methods are applied for the disposal of sewage such as thickening, stabilization, conditioning and dewatering. In addition, sewage sludge can be reused as cement raw material, compost, padding material and low cost adsorbent [27 – 29]. Various organic wastes can be used as activated carbon and the resulting final properties of the product (not the properties of the raw materials used) as well as the activating agent depend on the process conditions and the activation. Pyrolysis under controlled conditions and/or some chemical treatments are acceptable for converting sewage sludge into activated carbon. The adsorption efficiency of contaminants should be determined for pyrolysis products.

In this study, we applied pyrolysis for the carbonization of wastewater treatment of sludge from a facility that produces starch. It was intended to improve surface properties to be used for the removal of fluoride that can create water pollution. The adsorption of fluoride in natural waters can be found in high concentrations, which is an important consideration when using the adsorbent obtained from waste sludge.

Experimental

Adsorbent. Industrial waste sludge samples were obtained from a starch industry wastewater treatment facility in Pendik, Istanbul. Industrial sludge was dewatered through decantation, and then dried and ground for 24 at 103–105°C. The carbon, hydrogen and nitrogen constituents were analyzed with an elemental analyzer (Carlo Erbo 1106 and Leco CHNS, 932 systems). Raw sludge samples [IS] were prepared using $ZnCl_2$/raw sludge [IS1] mixture and H_2SO_4/raw sludge [IS2] mixture in proportions of 1:2 (0.5), 1:1 (1.0), 3:2 (1.5), 2:1 (2.0), 5:2 (2.5); the activation process was conducted at 50 – 60°C for 24. The samples were then dried and pyrolysis was realized at 15°C /min heating speed at 700°C (two hours holding time), in a vertical furnace with a controlled heating (PID) circuit (Lenton Thermal Designs). Carbonized material was cooled and treated with HCl to remove $ZnCl_2$ residuals, and re-washed with deionized water. Carbonized material was filtered with a 0.5–1 mm size sieve and characterized in order to be used in adsorption studies [30].

Activated carbon samples were dried in a vacuum furnace at 105°C for 16, and then in the degasification part of the device at 300°C for five hours under N_2 gas. Then, BET specific surface area and pore size analysis was measured using Quantachrome Nova 4000E device from nitrogen adsorption/desorption isotherms.

Reagents. All chemicals used in the present work were analytically pure. The stock solution of fluoride was prepared from sodium fluoride-NaF by dissolving it in distilled water. All the working solutions of varying concentrations were obtained by diluting the stock solution with distilled water. Zinc chloride-$ZnCl_2$ and sulphuric Acid-H_2SO_4 used in activation of sludge samples were analytically pure ("Merck Chemicals"). Hydrochloric Acid-HCl solution was used in cleaning carbonized materials. All analytically pure chemicals were obtained from "Merck Chemicals".

Batch adsorption studies. Adsorption experiments were conducted in order to determine the adsorption capacity of activation carbon obtained through pyrolysis process in different conditions for fluoride. For adsorption experiments, 100 mg adsorbent was added to 100 cm^3 solution, and the study was conducted at different concentrations and pHs, at 160 rpm agitation speed and in a thermostat orbital shaker (Gallenkamp) at 25°C. Samples were centrifuged at the end of determined studying periods ("Boeco", Germany), and fluoride contents of the samples were analyzed via ion chromatography method 4110 (APHA, 2010). Adsorbents (0.1 – 0.01 g) were added to fluoride solutions at 5; 10 – 25 and 50 mg/L concentrations, respectively, in order to determine

the effect of adsorbent amount on adsorption, and the study was conducted at equilibrium. Solutions at 25 mg/L concentration were used in adsorption studies. pH values of solutions were adjusted to 3; 4; 5; 6 and 9 using 0.1 M HCl and 0.1 M NaOH, and calibrated via a pH meter ("Hanna", HI 9124). The adsorption of fluoride at equilibrium, q_e (mg/g), was computed as follows:

$$q_e = ((C_0 - C_e)V)/W, \qquad (1)$$

where C_0 and C_e are the initial and equilibrium solution concentrations of fluoride (mg/L), respectively, V is the volume of the solution (l), and W is the weight of activated carbon used (g).

Desorption and regeneration studies. Desorption of the adsorbed fluoride from adsorbent was also studied 0.05 g adsorbent was kept in 0.1 M HNO_3 solution for 24 for regeneration, washed with 100 ml distilled water, then dried and used in the second adsorption. It was used in a third adsorption after the same regeneration process.

Results and discussion

Characterization of the adsorbent. Elemental analysis of starch from industrial sewage sludge samples (C, H, N) and ash were conducted and 31.7% of carbon, 5.7% hydrogen, 3.6% nitrogen and 25% ash were determined. There were appropriate amounts of carbon and ash content in the samples to obtain an activated carbon [31]. In previous studies, sludge samples with the addition of H_2SO_4 and $ZnCl_2$ were pyrolyzed and properties of the samples of surface area and porosity were determined [32]. A raw sludge sample had a 16 m²/g surface area, 0.006 cc/g micropore volume and pore radius of 8.5 Å. Surface area of $ZnCl_2$/raw sludge [IS1] and H_2SO_4/raw sludge [IS2] mixture samples varied in the range 1051 – 1196 m²/g and 92 – 898 m²/g respectively. As the rates of raw sludge with used chemicals increased, so did the specific surface area of product obtained from waste sludge. Even by the addition of excess amounts of chemical the surface area did not change much but decreased slightly.

The products had 1196 m²/g of specific surface area that was obtained by pyrolysis with a mixture of zinc chloride/raw sludge (3/2) delayed for 24 h at 50 – 60°C and 700°C, 15°C/min heating rate.

pH and initial concentration of fluoride adsorption is quite effective and varying adsorption capacity (q_e, mg/g) of fluoride removal from aqueous solutions with different pH values is given in Fig. 1. Despite the high adsorption capacity at low pH values, at pH > 5, it seriously decreased.
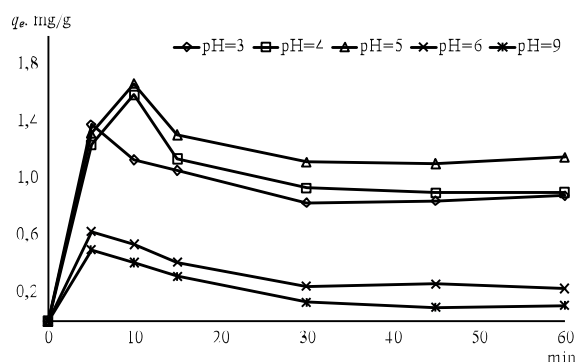
Fig. 1. Dependence of adsorption capacity of pyrolysis coke at different pH levels on sorption duration ($C_0 = 25$ mg/L, adsorbent 0.05 g).

The amount of adsorbed material with pyrolysis coke increases with the increase of the initial fluoride concentration. Different initial concentrations in the removal of fluoride from aqueous solution are given in Fig. 2.
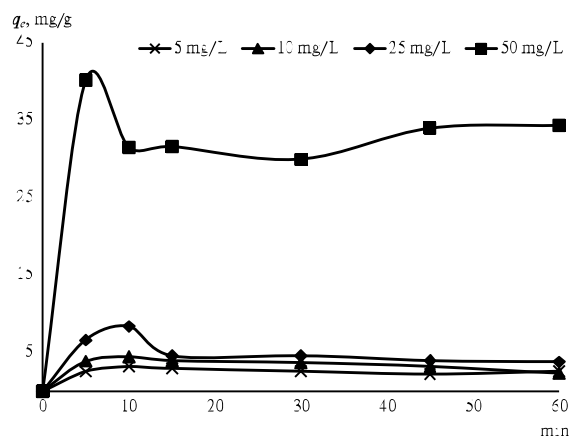

Fig. 2. Dependence of adsorption capacity of pyrolysis coke on fluoride concentration and on sorption duration (0.01 g adsorbent, pH 5).

As for fluoride adsorption at low and high pH values, the adsorption capacity increases depending on the pH. In particular, q_e were achieved 8.27 and 4.59 mg/g in the studies carried out at pH 4 and pH 11, respectively. Adsorption capacity decreases at a neutral pH [33]. The solubility of the fluoride compounds in water is extremely high and the presence of high amounts of dissolved fluoride ions promotes the adsorption capacity. The highest adsorption capacities (40 mg/g) were determined with the initial fluoride concentration of 50 mg/L.

Adsorption kinetics. *First-order kinetic model.* The Lagergren first-order equation was defined as a pseudo-first-order equation in order to separate the kinetic equation depending on the adsorption capacity of the solid and the concentration of the solution. It is an equation suggested by Lagergren depending on the adsorption capacity of solid in liquid-solid adsorption systems:

$$dq_t/dt = k_1 (q_e - q), \tag{2}$$

where the formula is integrated for $t = 0$, $t = t$, $q = 0$ and $q = q$ limit values:

$$\ln (q_e - q) = \ln q_e - k_1 t/2.303, \tag{3}$$

where t — time (min), k_1 — pseudo first-order kinetic constant (min^{-1}), q_t — adsorbed material amount (mg/g) in t time.

The graph is drawn by taking t values against $\ln (q_e - q_t)$, and k_1 and q_e values are obtained. Values of q_e calculated from the first-order model do not agree with the experimental q_e values. However, the experimental data deviated significantly from the theoretical data (Table 1). The correlation coefficients for the first-order kinetic model obtained from different conditions were low. This indicates that this adsorption system is not a first-order reaction.

Table 1. Comparison of first-order and second-order adsorption rate constants

Parameter		First-order kinetic model		Second-order kinetic model	
		k_1	R^2	k_2	R^2
Initial fluoride, mg/L	100	-0,0329	0,468	-0,0143	0,9999
	50	0,0090	0,6123	0,0210	0,9933
	25	-0,0140	0,6313	-0,0120	0,9939
	10	-0,0274	0,9155	-0,0221	0,954
Adsorbent, g	0,01	-0,0274	0,9155	-0,0221	0,954
	0,1	-0,0204	0,9215	-0,0592	0,997
pH	3	-0,0414	0,8535	-0,1147	0,9852
	4	-0,0110	0,4867	-0,0538	0,9962
	5	-0,0140	0,6313	-0,0602	0,9939

Second-order kinetic model. The second-order kinetic model is represented as:

$$dq_t/d_t = k_2 (q_e - q_t)^2. \qquad (4)$$

When the formula is integrated for $t = 0$, $t = t$, $q_t = 0$ and $q_t = q$ limit values:

$$1/(q_e - q) = 1/q_e + k_2 t, \qquad (5)$$

where k_2 — pseudo-second-order kinetic constant (g/mg · min). If the formula is re-organized to obtain a linear definition:

$$t/q = 1/k_2 q_{e_2} + t/q_e. \qquad (6)$$

Values of k_2 and q_e were calculated from the slope and intercept of the plots t/q vs. t. The appropriateness of first-order and second-order kinetic models was examined in order to determine the ratio of fluoride adsorption. Consequently, kinetic coefficients depending on initial concentration, pH and adsorbent dose were obtained. Similar to the results of the initial experiment, increasing the fluoride concentration increases the correlation between the adsorbent and the fluoride concentration (Fig. 3).
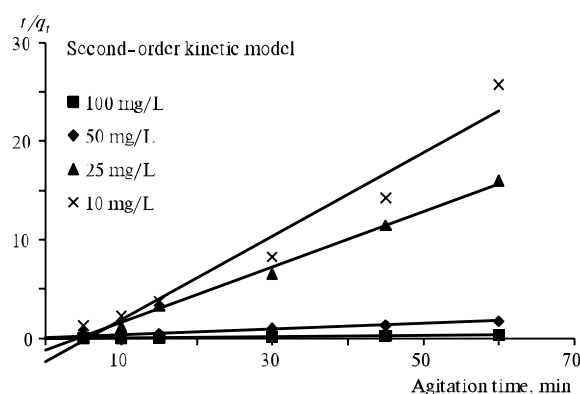

Fig. 3. Plots of the pseudo-second order model at different initial fluoride concent-rations (adsorbent dose — 0.01 g; pH 5 at room temperature).

The effect of the amount of adsorbent on adsorption is given in Fig. 4. High concentrations of dissolved fluoride are observed to have a high correlation with 0.1 g adsorbent. Similarly, a high correlation was determined in optimum of pH.
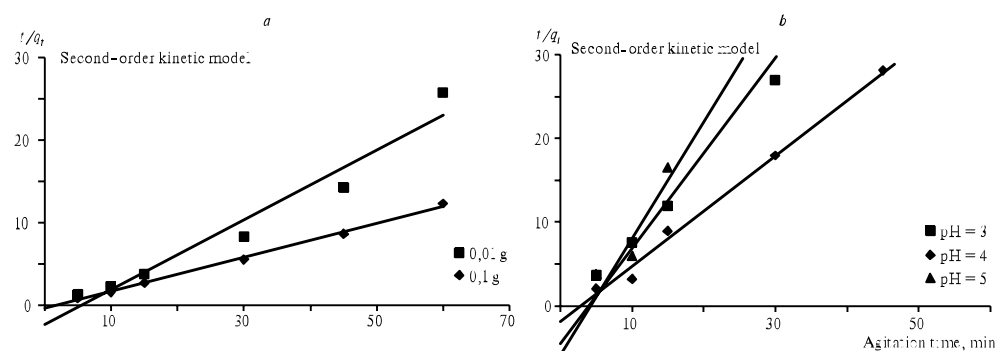
Fig. 4. Plots of the pseudo-second order model at different adsorbent doses (C_0= 10 mg/L, pH 5 at room temperature) (a) and different pH (adsorbent dose – 0.05 g, C_0=25 mg/L at room temperature) (b).

The results of fitting kinetic data to the first- and second-order models are presented in Table 1. The q_e values calculated from the second-order kinetic model are close to the experimental q_e values with good correlation coefficients. The correlation coefficients for the second-order kinetic models obtained were commonly greater than 0.99. These suggest that the adsorption system studied belongs to the second-order kinetic model.

Consistent with the results of similar studies, the adsorption system follows the second-order kinetic model. These results indicate that the nature of adsorption may be a chemical-controlling process.

Adsorption isotherms. The equilibrium of a solute separated between the liquid and solid phase is described by various models of adsorption isotherms, such as the Langmuir, Freundlich and Temkin models.

Freundlich determined the following equation in order to explain the adsorption of solutions:

$$q_e = K_F C_e 1/n. \qquad (7)$$

The linear form of the Freundlich isotherm equation is obtained by taking the logarithm of both sides of the equation

$$\log q_e = \log K_F + 1/n \log C_e, \qquad (8)$$

where K_F is related to adsorption capacity, and n is related to intensity of adsorption. The Freundlich constants K_F and n were calculated from the linear

plot of log q_e vs. log C_e, and are presented in Table 2; the theoretical Freundlich equation is shown in Fig. 5.
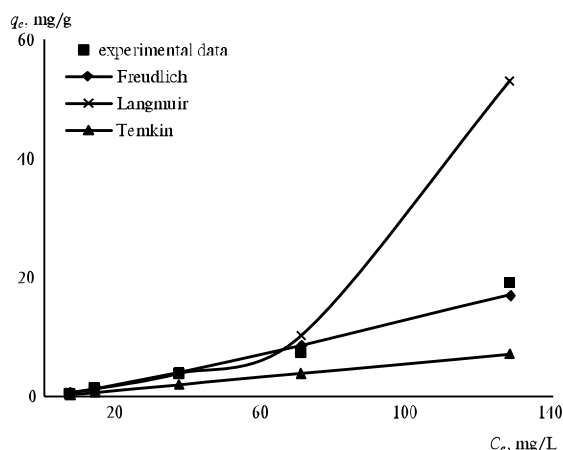

Fig. 5. Equilibrium isotherms of fluoride on carbonaceous material derived from waste sludge.

Table 2. Isotherm parameters for the removal of fluoride by carbonaceous material

Freundlich		Langmuir		Temkin	
$K_f = 0.6136$ $R^2 = 0.9932$	$n = 0.8613$	$Q_m = 12.75$ $R^2 = 0.9873$	$b = 0.0063$	$K_T = 56.601$ $R^2 = 0.7628$	$a_T = 10.1442$

The Langmuir isotherm is used to explain single-layer homogenous adsorption assuming that the surface of adsorbent is similar in terms of energy. The Langmuir isotherm is successfully applied in adsorption processes, and is explained by the following equation

$$q_e = Q_0 b C_e / (1 + b C_e). \qquad (9)$$

A linear form of this expression is:

$$C_e / q_e = 1/Q_0 b + C_e / Q_0 . \qquad (10)$$

The constant Q_0 gives the theoretical monolayer adsorption capacity (mg/g) and b is related to the energy of adsorption (L/g). The curve of the line and the intersection revealed by the plot of the change of C_e / q_e value depending on C_e value gives Q_0 and b constant values found to be 12.75 mg·g^{-1}

and 0.0063 L/g, respectively. The high surface area and micropore area of the ZnCl$_2$ activated sludge are responsible for the good adsorption capacity for fluoride. The values of the Langmuir constants Q$_0$ and b with the correlation coefficient are listed in Table 2, and the Langmuir isotherm is plotted in Fig. 5 together with the experimental data points. The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter RL:

$$RL = 1/(1+bC_0), \qquad (11)$$

where b is the Langmuir constant and C_0 is the initial concentration, RL values indicate the type of isotherm. RL values between 0 and 1 indicate favourable adsorption. The RL values were found to be between 0.53 and 0.95.

The Temkin adsorption isotherm considers the interaction between adsorbed materials, and was developed regarding the adsorbing temperatures of all molecules in solution. The Temkin isotherm is defined as follows:

$$q_e = (RT / b) \ln(A \, C_e). \qquad (12)$$

If the formula is made linear:

$$q_e = (RT / b) \ln A + (RT / b) C_e. \qquad (13)$$

The a_T and RT q_e constants can be found from the liner formula obtained from a graph drawn according to lnC_e. The values of the Temkin constants together with the correlation coefficient are presented in Table 2, and the theoretical Temkin equation is shown in Fig. 5.

When the correlation coefficients shown in Table 2 and theoretical isotherm curves shown in Fig. 5 are evaluated together, the Freundlich isotherm most closely fits the experimental data. In addition, Langmuir isotherm data had higher correlation coefficients than Temkin isotherms.

Accuracy of the results can be seen with an R^2 value of 0.90 on the Freundlich and Langmuir isotherms. In order to assess the potential improvements to fluoride removal offered by industrial sludge over other adsorbent systems, Q$_0$, the Langmuir parameter that has been used in most previous studies for defining fluoride adsorption capacity of different materials, can be applied to compare the difference of industrial sludge with those of other adsorbents reported in the literature (Table 3).

Table 3. Comparison of fluoride adsorption capacities of waste sludge with other low cost adsorbents

Material	Specific surface area, m²/g	Q_m, mg/g	Reference
Starch industry sludge	1196	12,75	This study
Calcite	0,057	0,39	[8]
Quartz	0,060	0,19	[8]
Fluorspar	0,048	1,79	[8]
Hydroxyapatite	0,052	4,54	[8]
Hydrous ferric oxide	25,8	8,9	[34]
Alumina	258,2	35,34	[35]
Bone char	104	6,66	[36]
Water treatment sludge	47,07	0,28	[37]
Kanuma mud	144,01	0,56	[38]
Bermuda grass	7,3	4,75	[39]
Kaolinite	–	175	[40]

Desorption and regeneration studies. The experiments on multiple adsorption of fluoride from aqueous solutions via pyrolysis coke samples gave 93.5% efficiency in the first stage. The second- and third-stage trials gave 27.4 and 23.8% efficiency, respectively. Initial adsorbent amounts decreased by 34 and 53% in the second- and third-stage trials, respectively, due to weight loss during regeneration.

Conclusions

In this study, pyrolysis coke derived from starch industry wastewater sludge was obtained and used for the removal of fluoride as adsorbent material. We measured 31.74% carbon content of the raw sludge used in this study. Ash content of 25% was the value of the medium level. In addition, the pyrolysis conditions are of very great importance. Therefore, to determine the optimum operating conditions of temperature, heating rate, and the rate of factors such as chemicals used must be determined.

Considering commercial activated carbon, the specific surface areas of 600 − 1100 m²/g, especially treatment sludge with low ash content, are expected to be suitable materials for adsorbent with chemical activation. As a result of the removal of fluoride found in high concentrations in nature, which is increasing with each passing day as a result of environmental pollutants, waste sludge from the starch industry with coke from the pyrolysis treatment sludge treatment system after a specific treatment should be considered as an alternative adsorbent.

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