Equilibrium and Kinetic Mechanisms of Fluoride Ions Adsorption onto Activated Alumina

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In this work, the fluoride adsorption by activated alumina (AAD) was evaluated in batch system. The point of zero charge of adsorbent was obtained. The effects of pH (2 to 12), temperature (30, 40 and 50 °C) and agitation (70, 100, 130 and 160 rpm) in the process were investigated. The adsorption kinetics and equilibrium were evaluated. The results show that the pH_{PZC} of AAD is 7.04 and the highest adsorption capacities were obtained at pH 2 and 130 rpm. The temperature did not influence on the process. The equilibrium was achieved in 4 hours and the model that best described the kinetic data it was the pseudo-first order. The best fit to the experimental equilibrium data was obtained by Langmuir isotherm and the maximum adsorption capacity was 1.57 mg g-1, demonstrating the high efficiency of AAD on fluoride adsorption in batch system.

1. Introduction

Fluoride contamination in groundwater has been recognized as a serious problem worldwide (Who, 2011). In Brazil, the maximum concentration allowed for the presence of fluoride in drinking water is 1.5 mg L^{-1} (Brazil, 2011). However, even at concentrations considered safe for human consumption, the toxic effects of fluoride can cause significant damage to teeth and put consumers at risk of bone damage, including bone fracture and joint pain (CDC, 2006).

Adsorption is one of the most widely used techniques for water defluoridation due to the high efficiency, low cost and easy application (King et al., 2007). Considering the high affinity between fluoride and aluminum, an interesting material for study of fluoride removal from water is activated alumina. This material is produced from hydrated alumina by thermal dehydration and recrystallization at elevated temperatures (Ruthven, 1984). In this context, the aim of the present work is the evaluation of fluoride removal by activated alumina (AAD) in batch system to obtain drinking water.

2. Materials and Methods

The fluoride solutions were prepared by dissolving of sodium fluoride (NaF) in ultrapure water (Milli-Q, Millipore®) at different concentrations varying with the test to be performed. This procedure followed the specific standard methods (2.21 g of NaF diluted in 1000 mL of ultrapure water for the preparation of a solution with fluoride concentration of 1000 mg L^{-1}), described in Apha/Awwa/Wef (2012).

The adsorbent evaluated was the activated alumina (AAD) provided by Celta Brasil Company of city of Cotia / SP. Some physical and chemical properties of this material are presented in Table 1. Prior to experiments, the adsorbent was dried in oven (Cienlab) at 50 ºC for 6 hours, until obtaining a constant mass.

Table 1: Physical and chemical properties of Activated Alumina (AAD)

Physical form	Porous spheres
Surface area	250 a 350
Pore volume	0.40
PH range	2 a 12
Density	0.75

2.1 Fluoride Quantification

Fluoride ions were quantified by high performance liquid chromatography (HPLC) using an ICS 2500 from Dionex equipped with an IonPac® AS18 (4 x 250 mm) column and electrochemical detector. The equipment was operated isocratically. The mobile phase was a solution of KOH 22 mM, with a flow rate of 1 mL min^{-1} and electric current of 55 µA. The data processing was carried out by Chromaleon software from Dionex.

2.2 Adsorption Tests

Determination of pH$_{PZC}$ followed the methodology proposed by Noh and Schwarz (1989). The adsorbent (50 mg) were placed in contact with 0.01 mol L^{-1} aqueous NaCl solution (50 mL) under 11 different pH conditions (2 to 12), adjusted with solutions of 1 mol L^{-1} HCl and 1 mol L^{-1} NaOH. After, the mixture was left under orbital shaking (180 rpm) at 30 °C for a period of 24 h. Thus, the pH of solutions was again analyzed.

To evaluate the effects of pH (2 - 12), temperature (30, 40 and 50 °C) and agitation (70, 100, 130 and 160 rpm), 50 mL of fluoride solution with initial concentration of 6 mg L-1 were placed in contact with 0.2 g of adsorbent. The samples were left under constant stirring and temperature controlled for a period of 12 hours. All tests were performed in duplicate and the amount of fluoride adsorbed by AAD was determined by Eq(1).

$$q_{eq} = \frac{V(C_{A,i} - C_{eq})}{m} \tag{1}$$

where q_{eq} is the fluoride concentration in the adsorbent at equilibrium (mg g^{-1}), V is the solution volume (L), $C_{A,i}$ and C_{eq} are, respectively, the initial and final (equilibrium) concentrations of the fluoride in solution (mg L^{-1}), and m is the mass of adsorbent (g).

For studies of kinetics and adsorption equilibrium, 50 mL of fluoride solution with initial concentration of 6 mg L^{-1} were placed in contact with a certain adsorbent mass (kinetic test: m = 0.2 g, equilibrium test: 0.05 g < m <1 g). At the pH of solution (close to 5.5), the samples were left under orbital shaking (130 rpm) at 30 °C. For kinetic test, the samples were removed from the shaker at predetermined time intervals up to 12 h contact time. For equilibrium test, all samples were removed from the shaker only after 12 hours of operation. Both tests were performed in duplicate and the amount of fluoride adsorbed was determined by Eq(1).

The experimental data of adsorption kinetics were adjusted to the models of pseudo first order (Lagergren, 1898) and pseudo second order (Ho and McKay, 1998), represented by Eq(2) and Eq.(3), respectively.

$$\frac{dq_t}{dt} = k_1 q_{eq,1} - q_t \tag{2}$$

$$\frac{dq_t}{dt} = k_2 q_{eq,2} - q_t^2 \tag{3}$$

where q_t is the fluoride concentration in the adsorbent at time t (mg g^{-1}); $q_{eq,1}$ and $q_{eq,1}$ are the equilibrium concentrations of fluoride in the solid phase (mg g^{-1}) estimated by the kinetic models of pseudo first order and pseudo second order, respectively; k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the adsorption kinetic constants of pseudo first order and pseudo second order kinetic models, respectively.

The Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) isotherms was adjusted to the equilibrium experimental data, according to Eq.(4) and Eq.(5).

$$q_{eq} = \frac{q_{max} b_L C_{eq}}{1 + b_L C_{eq}} \tag{4}$$

$$q_{eq} = K_F C_{eq}^n \tag{5}$$

where q_{max} is the maximum adsorption capacity of adsorbent (mg g^{-1}); b_L is the Langmuir affinity constant (L mg^{-1}), K_F is the Freundlich equilibrium constant (L mg^{-1}) and n is the Freundlich constant that represents the intensity of adsorption (dimensionless).

3. Results and Discussion

3.1 Point of Zero Charge (PZC)

The pH_{PZC} of AAD was obtained from a graph of the difference between the initial and final pH (ΔpH) as a function of the initial pH (Figure 1) and corresponds to the graph region where ΔpH is zero.
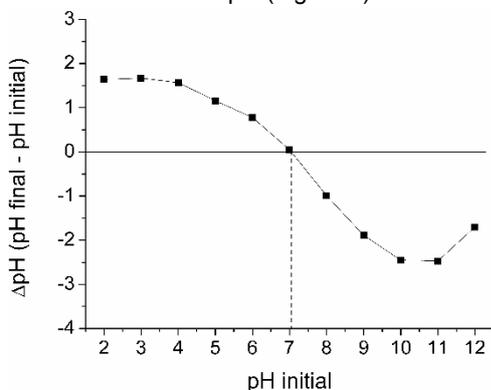
Figure 1: Experimental determination of pH_{PZC}.

According to the methodology proposed by Noh and Schwarz (1989), the pH_{PZC} corresponds to the point where there is no variation between the final and initial pHs. Thus, from Figure 1, the pH_{PZC} of AAD was estimated as 7.04.

3.2 Effect of pH

The results of pH evaluation on fluoride removal by AAD (Figure 2) show that the highest adsorption capacities were reached for the solutions with the lowest pHs, and the maximum amount of fluoride removed by AAD was reached at pH 2 and is equal to 2.68 mg g^{-1}.
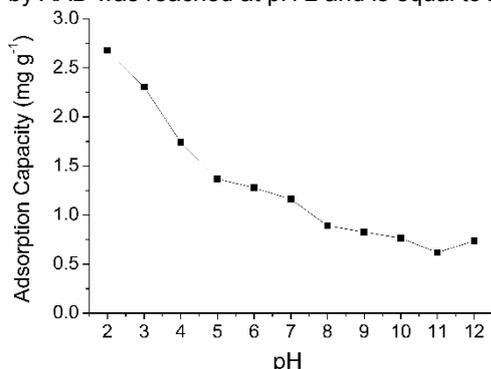
Figure 2: Effect of pH in the fluoride adsorption by AAD.

Between pHs 5 and 7, there was no major difference in adsorption efficiency. However, at high pHs, the adsorption capacity reduced drastically, being minimal at pH 11 with q_{eq} = 0.62 mg g -1. These results confirm the data obtained in the pH_{PZC} analysis, which shows that the surface of the adsorbent is positively charged at pHs lower than 7.04.

However, although most removal efficiency was obtained at pH 2, one of the aims of this work is to evaluate the applicability of the process to obtain drinking water and therefore, pH control is not feasible. Thus, by analyzing the results without adjusting this parameter, which results in solutions with pH ranging from 5 to 7, the adsorption capacity varied between 1.16 mg g^{-1} and 1.37 mg g^{-1}.

3.3 Effect of agitation

The results obtained for adsorption capacity of fluoride by AAD as a function of agitation (Figure 3) show that the increase in this parameter from 70 to 100 and from 100 to 130 rpm caused an increase in the adsorption capacity. However, when the agitation was increased from 130 to 160 rpm, the differences between the adsorption capacities were not significant within the error range.
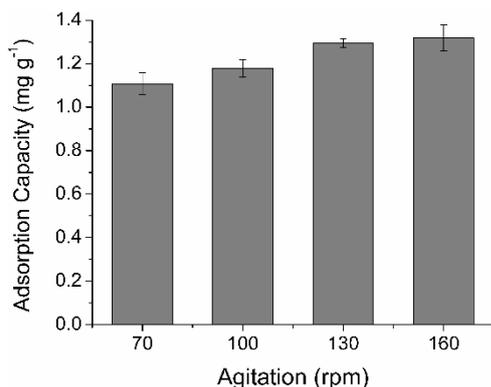
Figure 3: Effect of agitation in the fluoride adsorption by AAD.

The increase of removal capacity with the addition of agitation suggests that the diffusion in the external film of particle can be the controlling step of the process, since the higher the stirring speed, smaller is the liquid film stagnant around the adsorbent and, consequently, the adsorption will be favored.

3.4 Effect of temperature

The results obtained for the adsorption capacity of fluorine by the AAD as a function of the operating temperature are shown in Table 2.

Table 2: Physical and chemical properties of Activated Alumina (AAD)

Temperature (°C)	30	40	50
q_{eq} (mg g^{-1})	1.28 ± 0.06	1.17 ± 0.07	1.04 ± 0.08

The maximum amount of fluoride removed by AAD occurred at 30 °C, being equal to 1.28 ± 0.06 mg g^{-1}. In the range of temperature and conditions studied, an increase in this parameter caused a negative effect on the adsorption capacity. This result suggests that fluorine adsorption by AAD may be an exothermic process. However, it can be said that the temperature had no influence on the process, since, within the margin of error, there was no variation in adsorption capacity.

3.5 Kinetic test

Figure 4 shows the adsorption kinetics of fluoride by the AAD and the adjustment of pseudo first order and pseudo second order kinetic models to the experimental data.
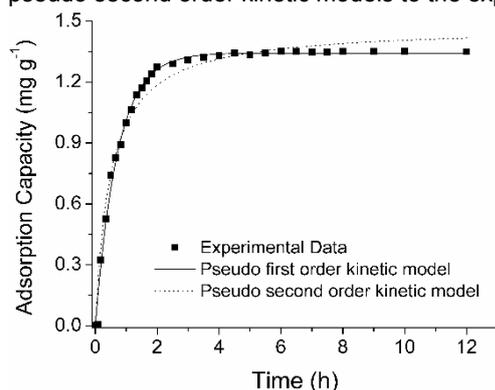
Figure 4: Adjustment of pseudo first order and pseudo second order kinetic models to the experimental data.

The adsorption kinetics of fluoride show that the removal occurs more rapidly in the early stages of the process, while it is slower near equilibrium, achieved in approximately 4 hours of operation. At equilibrium, the concentration of fluoride in the solid phase was 1.34 mg g^{-1}.
The parameters estimated by each kinetic model are shown in Table 3.

Table 3: Parameters adjusted by the pseudo-first order and pseudo-second order kinetic models.

Pseudo first order	Pseudo second order
$q_{eq,1}$ = 1.34 mg g^{-1}	$q_{eq,2}$ = 1.47 mg g^{-1}
k_1 = 1.40 min^{-1}	k_2 = 1.39 mg g^{-1} min^{-1}
r^2 = 0.9932	r^2 = 0.9772

The kinetic model that best fit the experimental data was the pseudo-first order with a coefficient of determination (r²) equal to 0.9932. Both models estimated that at equilibrium the fluoride concentration in the solid phase was greater than 1.34 mg g^{-1}. However, the value estimated by the kinetic model of pseudo-first order ($q_{eq,1}$) was closer to that obtained experimentally (q_{eq}), thus validating its applicability in the description of the fluorine adsorption kinetics data by AAD.

3.6 Equilibrium Tests

The adsorption equilibrium data were obtained at 30 °C. The Langmuir and Freundlich isotherm adjustments to these data are shown in Figure 5 and the parameters estimated by both models are shown in Table 4.
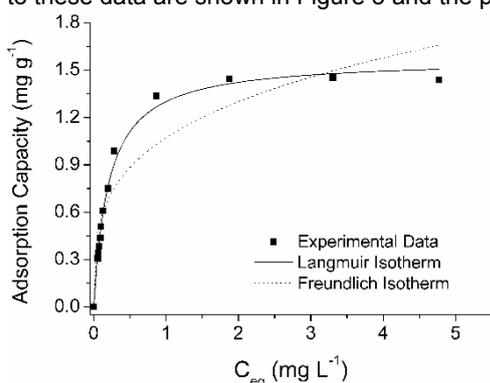
Figure 5: Adjustment of pseudo first order and pseudo second order kinetic models to the experimental data.

Table 4: Parameters adjusted by the Langmuir and Freundlich isotherm models.

Langmuir	Freundlich
q_{max} = 1.57 mg g^{-1}	K_F = 1.07 L g^{-1}
b_L = 0.314 min^{-1}	n = 0.278
r^2 = 0.9913	r^2 = 0.8858

Evaluating the obtained results, it can be concluded that the Langmuir isotherm model better represented the experimental equilibrium data. This fact is confirmed by the coefficient of determination (r²), equal to 0.9913. The results suggest that the hypotheses on which the Langmuir isotherm model is based can be applied to fluorine adsorption by AAD, such as: adsorption in monolayer; interaction forces between the adsorbed molecules are negligible; all molecules are adsorbed on a fixed number of identical sites (Langmuir, 1918). This model also considers an adsorption limit for the solid phase (q_{max}), which indicates the maximum capacity of a material to remove a certain component. The value of q_{max} obtained by the Langmuir isotherm model was 1.57 mg g^{-1}. This value proves the high efficiency of this material when compared to other adsorbents already used for the same purpose and under similar experimental conditions (Table 5).

Table 5: Parameters adjusted by the Langmuir and Freundlich isotherm models.

Material	q_{max} (mg g^{-1})	Referência
AAD	1.57	In this work
Magnesium-incorporated hydroxyapatite	1.40	Mondal et al., 2016
Limestone treatment in H_3PO_4	1.10	Gogoi et al., 2015
Regenerated spent bleaching earth	0.60	Malakootian et al., 2011
Aluminum Titanate	0.85	Karthikeyan and Elango, 2009
Chitin-based biocomposite	0.29	Davila-Rodriguez et al., 2009

In addition to the good ability to remove fluoride, the interest in the alumina as adsorbent is also motivated by the low cost. This material is usually obtained during the process of industrialization of bauxite ore, being one of the tailings of the aluminum production (Sutar et al., 2014), which contributes to its economic viability.

4. Conclusions

In this work, activated alumina was evaluated as adsorbent in the fluoride removal in batch process. The analysis of pH_{PZC} indicated that fluoride removal is favored when working with solutions of low pH. The best sorption results were obtained at pH 2 and stirring values of 130 rpm. The temperature had no influence on the process. The equilibrium time was achieved in 5 h of operation and the kinetic model that best represented the experimental data was the pseudo-first order. The best description of the equilibrium data was attributed to the Langmuir isotherm model and the maximum adsorption capacity of fluoride by AAD was 1.57 mg g^{-1}.

Based on the results obtained in this work, it is concluded that the activated alumina presented good results when compared to other types of adsorbent materials already researched and can therefore be successfully used in the process of fluoride removal from water.

Acknowledgments

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