

## **MODELLING OF KINETICS OF FLUORINE ADSORPTION ONTO MODIFIED DIATOMITE**

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**Abstract:** The paper presents kinetics modelling of adsorption of fluorine onto modified diatomite, its fundamental characteristics and mathematical derivations. Three models of defluoridation kinetics were used to fit the experimental results on adsorption fluorine onto diatomite: the pseudo-first order model Lagergren, the pseudo-second order model G. McKay and H.S. Ho and intraparticle diffusion model of W.J. Weber and J.C. Morris. Kinetics studies revealed that the adsorption of fluorine followed second-order rate model, complimented by intraparticle diffusion kinetics. The adsorption mechanism of fluorine involved three stages – external surface adsorption, intraparticle diffusion and the stage of equilibrium.

**Keywords:** *adsorption, diatomite, fluorine, kinetic models*

## INTRODUCTION

Equilibrium analysis is fundamental for the evaluation of the affinity or capacity of a sorbent. It is, therefore, important to determine how sorption rates depend on the concentrations of sorbate in a solution and how rates are affected by the sorption capacity or by the character of the sorbent in terms of kinetics.

Kinetics modelling allows the evaluation of effective capacity of sorbent, initial sorption rate and the rate constant of the models used.

Many attempts have been made to formulate a general expression describing the kinetics of sorption on solid surfaces. In recent years, sorption mechanisms have been reported and involved kinetics based on first order [1 – 3] and second order models [4]. Many works were devoted to the study of adsorption kinetics of fluorine and other components on a variety of sorbents. Thus, fluorine adsorption by using alum sludge [5], heavy metal ions on carbonaceous adsorbents [6], dye Rhodamine-B onto natural diatomite [7] and fluoride on low cost materials [8] are described by the equations of pseudo-first-order kinetics. Removal of fluoride ions with aluminum oxy-hydroxide [9] and alumina [10], by magnesia-amended activated alumina granules [11] and by alumina cement granules [12] were described by the model of pseudo-second order kinetics. The pseudo-second-order equation is based on the sorption capacity of the solid phase. It predicts the sorption system behavior over the whole range of data. Furthermore, it is in agreement with chemisorption, being the rate controlling step [13]. Pseudo-second order kinetic model has also been used in the works of Y.S. Ho and co-workers [14 – 17] for processing the experimental data on sorption of divalent metal ions and other substances from water solutions. The modified multiplex and the double exponential models have been evaluated in order to fit the experimental data of adsorption of fluorine by MgAl-CO<sub>3</sub> layered double hydroxides [18]. Application of the intraparticle diffusion model for description of kinetic sorption process is reflected in many works [19 – 27].

In the present work a kinetic analysis of experimental data of fluorine adsorption on modified diatomite DMA was carried out on the basis of kinetic models of pseudo-first, pseudo-second order and intraparticle diffusion model.

## MATERIALS AND METHODS

The initial raw diatomite D1 used in the present work was supplied from the deposits of Vyshkautsy village in the Orgeev region in Moldova. The diatomite was characterized by the following content: SiO<sub>2</sub> - 59.7 %; CaO - 12.8 %; Al<sub>2</sub>O<sub>3</sub> - 1.31 %; Fe<sub>2</sub>O<sub>3</sub> - 1.28 %. The content of contaminations of argillaceous minerals was no more than 10 %. The losses of ignition were 18.5 %. The specific surface area of natural untreated diatomite is usually not large (15 - 35 m<sup>2</sup>·g<sup>-1</sup>), and that limits its effectiveness as a sorbent for dissolved substances. Therefore, the essential modification of diatomite is needed for increasing its specific surface area and improving its adsorption characteristics. The aluminum compounds for filling the pores of diatomite in the present studies were chosen because they are the most active in the removal of fluorine from aqueous solutions. The diatomite, used as a sorbent, was processed according to [28]: a sample of diatomite (15 g) was added to 100 mL of a 3M NaOH solution and agitated for 40

min at 55 °C, then the mixture was centrifuged, and the precipitate was added to 100 mL of a 2M aluminum sulfate solution and left for 5 h to stir at room temperature. The filtrate after the centrifugation was rejected, and the precipitate was treated with a concentrated ammonia solution for 5 h at room temperature. Then, the mixture was centrifuged again and the precipitate was separated from the filtrate, washed with distilled water, and dried in the open air and then at 110 °C. It was kept in a desiccator at room temperature for its further use. Diatomite modified with aluminum compounds is denoted as DMA. The composition of the samples was determined by the method of atomic absorption spectrophotometry (AAS) using an AAS3 1N instrument. The composition of the obtained material characterized as follows: SiO<sub>2</sub> - 35.5 %; CaO - 9.0 %; Al<sub>2</sub>O<sub>3</sub> - 18.9 %; Fe<sub>2</sub>O<sub>3</sub> - 1.33 %. Adsorption-structural properties of DMA also undergone changes: the specific surface increased from 37.54 (D1) to 81.77 (DMA), sorption pore volume grew from 0.0442 to 0.106 cm<sup>3</sup>·g<sup>-1</sup>. The textural characteristics of the starting diatomite and DMA, i.e. specific surface area, size and volume of the pores and their size distribution, were determined by using BET method in compliance with the low temperature adsorption of nitrogen using an ASAP2000 micrometer device [28]. For fluorine adsorption experiments, the fraction of diatomite -0.25+0.044 mm has been used. Necessary sorbent fraction was obtained by sieving the ground material through sieves 60 and 350 mesh, and the fraction passed through the first sieve and detained with the second was taken. Fluorine solutions were prepared by dissolving an appropriate amount of reagent grade sodium fluoride NaF in distilled water. The concentration of fluoride ions in water was 1.0 - 20.0 mgF·L<sup>-1</sup>. To prevent the effect of pH change on the process indicators the experiments were conducted in acetate buffer. All the adsorption experiments were carried out at room temperature and atmospheric pressure. The concentration of fluorine in solution before and after the experiments was determined using the ionometer I-160M equipped with an ion-selective electrode. All the chemicals used in this study were of analytical reagent grade, purchased from Merck (Germany).

Adsorption equilibrium data are presented in [29], which show that modified diatomite has considerable potential for the removal of fluoride ions from aqueous solutions. The results of fluorine adsorption well described by the theoretical Freundlich and Henry isotherms. Values of equilibrium parameters of these models were obtained. The experimental data of adsorption equilibrium of fluorine onto modified diatomite are found to fit better to Freundlich isotherm model.

## Experimental

Batch adsorption experiments were conducted as follows: to 100 cm<sup>3</sup> of test solution of certain concentration of fluorine in acetate buffer, taken in a flask, the required quantity of sorbent D1 or DMA was added and, after establishing the needed pH, the ingredients were stirred with a magnetic stirrer at 350 rpm for different time intervals. All the kinetic experiments have been carried out under the same conditions: pH = 4.85, the adsorbent mass,  $m = 0.5$  g, solution volume,  $v = 100$  cm<sup>3</sup>, solution temperature,  $T = 20$  °C, initial fluorine concentration,  $C_o = 1.05$  mmol·L<sup>-1</sup>. To determine the equilibrium sorption time, samples were withdrawn after desired contact time from 0.25 to 180 minutes. The sorbent was separated from solution by centrifugation and the liquid part was analyzed for residual fluorine concentration.

The amount of fluorine adsorbed,  $a$  [mmol F<sup>-</sup>·g<sup>-1</sup>], was determined by the following expression:

$$a = \frac{(C_0 - C_e) \cdot v}{m}, \quad (1)$$

where:  $C_0$  and  $C_e$  are the initial and equilibrium fluorine concentration in the solution, [mmol·L<sup>-1</sup>],  $v$  - the solution volume, [cm<sup>3</sup>] and  $m$  - the sorbent mass, [g].

## RESULTS AND DISCUSSION

### Kinetics modelling

Kinetic study is important to an adsorption process because it depicts the uptake rate of adsorbate, controls the time of the whole process and evaluates adsorbent in removing the fluorine from solution. In order to investigate the mechanism of sorption and potential controlling steps, several kinetic models were tested including the pseudo first order kinetic model and the pseudo second order kinetic model for a batch contact time process, and an intraparticle diffusion model because of porous nature of the sorbent under study.

Theoretically, the adsorption of fluoride onto solid particles normally takes three essential steps:

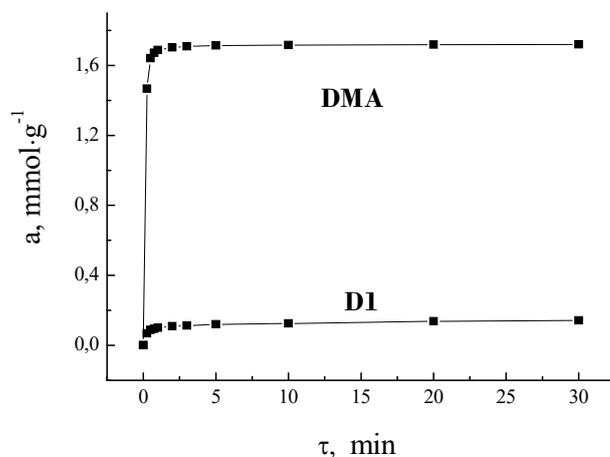
- (1) diffusion or transport of fluoride ions to the external surface of the adsorbent from bulk solution across the boundary layer surrounding the adsorbent particle (external mass transfer);
- (2) adsorption of fluoride ions onto particle surfaces;
- (3) the adsorbed fluoride ions are transferred to the inner surface of porous sorbent (intraparticle diffusion).

To understand the kinetics of the process, the data were fitted to different rate equations. A general rate expression is as follows:

$$\frac{da}{dt} = k_n \cdot (a_m - a_t)^n \quad (2)$$

where  $K_n$  is the constant rate of the process,  $n$  - the reaction order.

Kinetics of sorptive uptake of fluorine was investigated employing the natural diatomite D1 and modified with aluminosilicate sample DMA. Kinetic curves are shown in Figure 1.



**Figure 1.** The experimental kinetic curves of fluorine adsorption on initial (D1) and modified diatomite (DMA)

The adsorption capacity of modified sample DMA is almost an order of magnitude larger than of the original unprocessed D1. The kinetic curve of fluoride uptake by DMA shows 2 steps in adsorption rate. An initial step sorption phase wherein almost 95 % of removal of fluorine on modified diatomite is accomplished within 1 - 2 minutes of contact mainly due to strong interactive forces that are chemical (molecular) in nature. With prolonged contact time, sorption rate reduces gradually and eventually reaches a stationary level denoting completion of sorption reaction as either due to exhaustion of surface sites of sorbate molecules or inhibition of sorption interaction.

The initial rapid uptake reflects surface sorption, the slow second part corresponds to the long-range diffusion of fluoride ions into interior pores of the adsorbent [20, 21]. It is generally considered that, when the rate of sorption is rapid, the rate-limiting step is probably a transport process taking place in the liquid phase, such as diffusion in the bulk of the liquid, at the liquid film surrounding the solid particle, in liquid-filled pores, etc. When the rate of sorption is slow, it is probably that rate determining processes take place at the solid phase [21]. However, this slow phase, which denote the rate-limiting step (thereby govern the overall rate of sorption), may result from diffusion or other surface reactions.

Three possible models of defluoridation kinetics were used to fit the experimental results on adsorption fluorine onto diatomite:

- the pseudo-first order model of Lagergren:

$$a_t = a_m (1 - \exp(-k_1 \cdot t)) \quad (3)$$

- the pseudo-second order model G. McKay and H.S. Ho [16]:

$$a_t = \frac{k_2 \cdot a_m^2 \cdot t}{1 + k_2 \cdot a_m \cdot t} \quad (4)$$

- intraparticle diffusion model of W.J. Weber and J.C. Morris [19]:

$$a_t = k_{id} t^{0.5} + C \quad (5)$$

where  $k_{id}$  [ $\text{mmol}\cdot(\text{g}\cdot\text{min})^{-1}$ ] is the intraparticle diffusion rate constant and  $C$  is the thickness of the boundary layer (the larger is the value, the greater is the boundary effect).

### ***The pseudo-first order kinetics model***

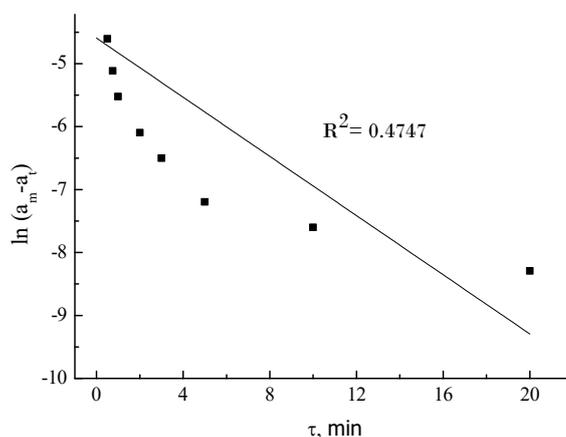
In the first model, the rate constant of defluoridation is determined from the following differential equation:

$$\frac{da_t}{dt} = k_1 \cdot (a_m - a_t) \quad (6)$$

After integration at the initial conditions  $t = 0$  to  $t = t$  and  $a_t = 0$  to  $a_t = a_m$  and then taking the natural logarithm the equation becomes:

$$\ln(a_m - a_t) = \ln a_m - k_1 \cdot t \quad (7)$$

The adsorption rate constant  $k_1$  can be determined from the slope of the linear plot of  $\ln(a_m - a_t)$  versus  $t$  (Figure 2).



**Figure 2.** Linear plot for pseudo-first order kinetics of fluorine adsorption on DMA

It is seen that this graph gives a straight line with a low correlation coefficient ( $R^2 = 0.4747$ ) indicating that the Lagergren equation is not quite applicable for description kinetics of adsorption of fluorine onto modified diatomite.

### ***The pseudo-second order kinetics model***

The rate law for this system is expressed as:

$$\frac{da_t}{dt} = k_2 \cdot (a_m - a_t)^2 \quad (8)$$

This model is based on the assumption that rate-limiting step involves chemisorption of the sorbate on the sorbent. After separation of variables in equation (8) we obtain:

$$\frac{d(a_m - a_t)}{(a_m - a_t)^2} = -k_2 \cdot dt \quad (9)$$

where  $k_2$  [ $\text{g}\cdot(\text{mmol}\cdot\text{min})^{-1}$ ] is the pseudo-second order rate constant of fluorine adsorption.

Integrating equation (9):

$$\frac{1}{a_m - a_t} = k_2 t + C \quad (10)$$

Here  $C$  is integration constant. At  $t = 0$   $a_t = 0$ , and  $C = 1/a_m$  and then equation (10) assumes the following form:

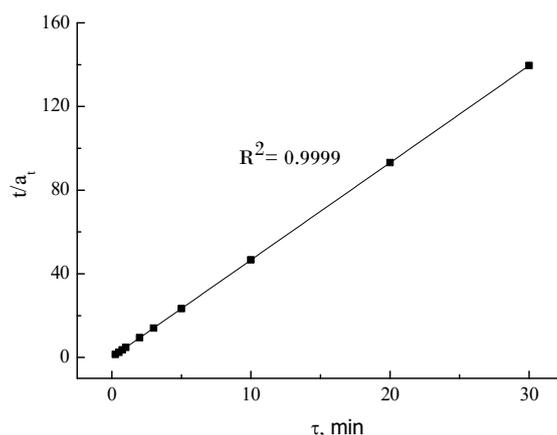
$$\frac{1}{a_m - a_t} = \frac{1}{a_m} + k_2 \cdot t \quad (11)$$

Rearranging the variables from equation (11) we obtain the linearized form of pseudo second order kinetic equation:

$$\frac{t}{a_t} = \frac{1}{k_2 \cdot a_m^2} + \frac{t}{a_m} \quad (12)$$

where  $k_2$  is the pseudo-second-order rate constant of adsorption [ $\text{g} \cdot (\text{mmol} \cdot \text{min})^{-1}$ ],  $k_2 \cdot a_m^2$  is the initial adsorption fluorine rate [ $\text{mg} \cdot (\text{g} \cdot \text{min})^{-1}$ ]. The larger is the  $k_2$  value, the slower is the adsorption rate.

Parameters  $a_m$  and  $k_2$  can be calculated from the slope and intercept of the plot  $t/a_t$  versus  $t$  (Figure 3):



**Figure 3.** Linear plot for pseudo-second order kinetics of fluorine adsorption on DMA

The values of  $k_2$  and  $R^2$  for the pseudo second-order rate model are found to be  $0.0338 \text{ g} \cdot (\text{mmol} \cdot \text{min})^{-1}$  and 0.9999. The low  $k_2$  and extremely high correlation coefficient value  $R^2$  suggest the fast adsorption rate and that the adsorption of fluorine on diatomite is governed by pseudo-second-order model.

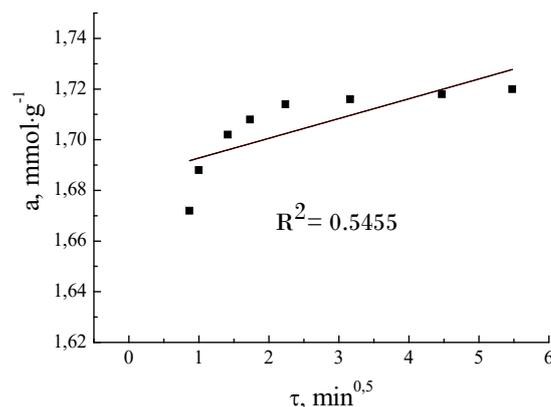
On the other hand, when the suspension of diatomite with solution of fluoride is intensively mixed it is reasonable to assume that mass transfer of fluorine ions from the bulk solution to the particle external surface does not limit the rate adsorption. In this case we can assume, that the rate determining step may be either film or intraparticle diffusion. The slower of them will be the rate-determining step. As shown in [23] the intraparticle diffusion is often the rate-limiting step in many sorption processes.

#### ***The intraparticle diffusion model***

During adsorption of fluorine on the surface of porous diatomite the molecules of adsorbate may also diffuse into the interior of the sorbent pores. The adsorption sites

present on the interior surface of a pore of adsorbent may not be as easily accessible because of the resistance to the pore diffusion.

In order to show the existence of intraparticle diffusion in the adsorption process, the amount of fluorine adsorbed per unit mass of adsorbent  $a_t$  at any time  $t$ , was plotted as a function of square root of time,  $t^{0.5}$ . The rate constant for intraparticle diffusion was obtained using equation (5).



**Figure 4.** Determination of intraparticle diffusion rate constant  $k_{id}$  of fluorine adsorption on DMA

It is believed that if the dependence of  $a_t$  on  $t^{0.5}$  gives straight line that passes through the origin, then it suggests that the intraparticle diffusion contributes predominantly in rate determining step for the adsorption [20].

In Figure 4 experimental (mark by dots) and calculated by the intraparticle diffusion model (mark by line) dependences of fluorine adsorption on  $\sqrt{t}$  are presented. As it is seen the straight line does not well match the experimental data ( $R^2 = 0.5455$ ), not to mention the fact that it does not pass through the origin. This is the evidence that this mechanism is not controlling the process.

In Table 1 there are shown the values of parameters of the above models determined from the linear plots of corresponding kinetic equations.

On the base of these parameters, the analytical expressions of equations describing the time dependence of fluorine adsorption on DMA were obtained.

**Table 1.** Parameters of models for kinetics of fluorine adsorption onto DMA

| Characteristics   | Kinetic models |          |                         |
|---|----------------|----------|-------------------------|
|   | Pseudo 1       | Pseudo 2 | Intraparticle diffusion |
| $k_1$ [ $\text{mmol}\cdot(\text{g}\cdot\text{min})^{-1}$ ]          | 0.0338         | -        | -                       |
| $a_m$ [ $\text{mmol}\cdot\text{g}^{-1}$ ]                           | 1.718          | 1.719    | 1.702                   |
| $a_e$ [ $\text{mmol}\cdot\text{g}^{-1}$ ]                           | 1.72           | 1.72     | 1.685                   |
| $k_2$ [ $\text{g}\cdot(\text{mmol}\cdot\text{min})^{-1}$ ]          | -              | 0.0338   | -                       |
| $k_{id}$ [ $\text{mmol}\cdot(\text{g}\cdot\text{min}^{0.5})^{-1}$ ] | -              | -        | 0.0078                  |
| $C$ [ $\text{mmol}\cdot(\text{g}\cdot\text{min}^{0.5})^{-1}$ ]      | -              | -        | 1.685                   |
| $R^2$   | 0.4747         | 0.9999   | 0.5455                  |

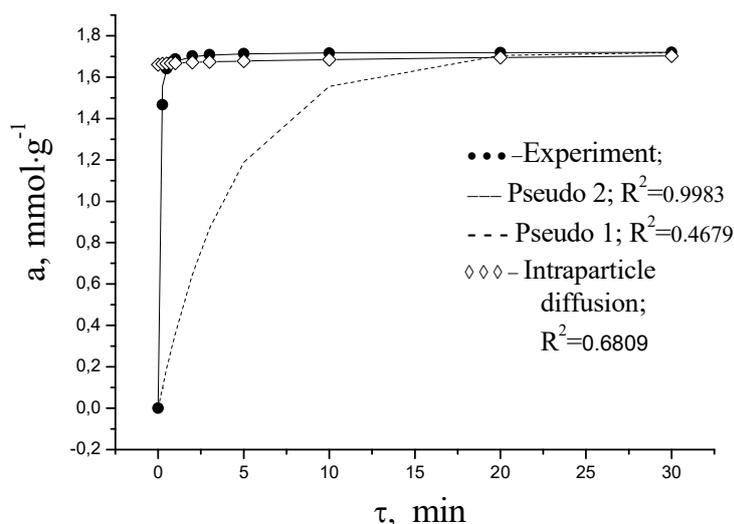
Analytical expressions of equations for description of adsorption kinetics of fluorine on DMA:

The pseudo-first order kinetics model  $a_{teor} = 1.718 \cdot (1 - e^{-0.235 \cdot t})$  (13)

The pseudo-second order kinetics mode  $a_{teor} = 0.0998 \cdot t / (1 + 0.0581 \cdot t)$  (14)

The intraparticle diffusion model  $a_{teor} = 0.0078 \cdot \sqrt{t} + 1.685$  (15)

Figure 5 shows the calculated kinetic curves of fluorine adsorption on DMA in comparison with the experimental results.



**Figure 5.** Experimental data and calculated by pseudo-first, pseudo-second order and intraparticle diffusion kinetic models of fluorine adsorption on DMA

As shown in Figure 5 the model of pseudo-second-order kinetics correlates perfectly with the experimental data on the adsorption of fluoride on DMA which is proved by high values of correlation coefficient. The pseudo first order kinetic model cannot be used to describe the adsorption of fluorine on DMA as supported by the very little correlation coefficient ( $R^2 = 0.4679$ ). The intraparticle diffusion model obviously is not quite applicable for the description of the process due to its rather low correlation coefficient ( $R^2 = 0.6809$ ), we can only talk about some degree of involving of intraparticle diffusion in the adsorption process.

Theoretically, there are two widely accepted mechanisms for the adsorption of a solute onto a solid surface. The first one, referred to as the outer-sphere surface complexation (nonspecific adsorption) involves electrostatic attraction between a charged surface and an oppositely charged ion in solution. Here, the adsorbed ion resides at a certain distance from the surface. The second one, referred to as the inner-sphere complexation (specific adsorption) involves the formation of a coordinative complex with the solid surface [28]. Since the inner-sphere complex bonds are difficult to break, it results in stronger adsorption of ions than outer-sphere complexes. The chemical evidence of inner-sphere complex formation derives from evaluating the effects of ionic strength and  $pH$  on adsorption. Experimental evidences suggest that anions that form inner-sphere complexes coordinate directly with the oxide surface without getting influenced by ionic strength [27]. It is known that fluorine adsorption on modified diatomite DMA

is sensitive to the pH value and there is not any significant desorption of fluorine from spent adsorbent [29]. In our previous research [30] the formation of chemical compounds of surface aluminum ions with fluoride ions from the solution is described in detail. The poor desorption characteristics of DMA together with the information on new chemical surface compounds formed during the fluorine adsorption process, suggesting strong adsorption of fluoride ions, support the formation of inner-sphere complexes.

Thus, the surface reactions will be the rate-limiting stage with certain contribution of the intraparticle diffusion step. That fact is in well accordance with the data on kinetics modelling.

## CONCLUSIONS

The fluorine adsorption kinetics on modified with aluminosilicate diatomite DMA was modelled. Three models of defluoridation kinetics were used to fit the experimental results of adsorption fluorine onto diatomite: the pseudo-first order model of Lagergren, the pseudo-second order model and intraparticle diffusion model. Kinetics studies revealed that the adsorption of fluorine followed the second-order rate model, complimented by intra particle diffusion kinetics. So, we can conclude that the kinetic model of the pseudo second order is the most adequate to describe the experimental kinetic curves (this model provides an excellent fitting of the calculated and experimental with correlation coefficient 0.9983). This means that the chemical interaction between the active centres on the surface and in pores of diatomite and fluoride ions from the bulk solution may be predominant and limiting step of the adsorption rate in the system under consideration.

The dominant mechanism of fluoride removal appeared to be a chemisorptive ligand exchange reaction involving the formation of inner-sphere complexation of fluoride with DMA.

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