BREAKTHROUGH ANALYSIS OF FLUORINE REMOVAL IN FIXED BED ADSORPTION COLUMN USING MODIFIED DIATOMITE

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Rezumat. În această se prezintă modelarea dinamicii sorbţiei fluorului pe diatomit modificat cu compuşii aluminiului (DMA). S-a demonstrat că duratele de lucru a stratului sorbentului faţă de fluor determinate experimental la diferite înălţimi ai coloanei, fluxului de apă şi concentraţie iniţială a fluorului şi cele calculate pe baza modelului dinamicii Shilov, ţinând cont de curbele de străpungere până la punctul de rupere ale lor, se află intr-o concordanţă satisfăcătoare. Ecuaţiile analitice ale modelului obţinute pot fi folosite pentru prezicerea formei şi construirea curbelor de reţinere a fluorului în condiţiile dinamice, întocmirea regimului de sorbţie, calculul capacităţii dinamice maxime a sorbentului necesare pentru construirea aparatelor de adsorbţie.

Cuvinte cheie: dinamica, modelarea, fluor, adsorbția, diatomit**.**

Abstract. The modeling of the dynamics of fluorine absorption on diatomite modified with aluminum compounds (DMA) was carried out. It has been shown that breakthrough curves of fluorine adsorption onto DMA experimentally determined at various column heights, solution flow rates and the fluorine initial concentrations and calculated on the base of Shilov model are in satisfactory agreement. The equations obtained from analytical model can be used to predict the shape and construction the fluorine retention curves in dynamic conditions, and to calculate the parameters necessary for an adsorption apparatus design.
Keywords: dynamics, modeling, fluorine, diatomite

1. INTRODUCTION

The water purification using adsorption method is a modern technology which is increasingly being applied in practice of fluorine removal from water in countries which are in the process of economic development. In practice using of adsorbents is carried out in adsorption columns - some kind of mass transfer devices for the separation of the impurity from the water.

Design of a column for adsorption starts with laboratory testing to establish the breakthrough curve [1]. At certain time intervals, the effluent from a column is sampled. Time zero is when the solution is applied to the column. At first, the adsorbent is fresh with all its adsorption sites. As time passes, some of the adsorption sites are used up, and concentration in the effluent rises. The shape of the graph (concentration vs. time) may vary considerably for different situations. Usually there is a long time before the effluent concentration rises sharply and then levels off. If all the sites were occupied, we would expect the inlet concentration and the outlet concentrations to become the same – the breakthrough. The breakthrough concentration is determined by the process specifications. This can be the allowable concentration. As to fluorine - its maximum allowable concentration in drinking water is 1.5mg/l.

Total capacity of sorbents which are to be used is properly appreciated only by analyzing of breakthrough curves of fluorine under dynamic conditions till sorbent saturation.

The experimental retention curves of fluorine and mass transfer of sorbate into the pores of sorbent particles can be described with different models of dynamics besides which are the most important models of Clark [2], Thomas [3], Nelson [4], and Shilov [5, 6].

Various low cost adsorbents have been studied for their applicability in treatment of different types of effluents. In this study the modified with aluminosilicate Moldavian diatomite was used as a batch column for fluorine adsorption; the obtained breakthrough curves of fluorine removal in fixed bed column experiments were modeled according to Shilov model.

In dynamic condition the total amount of adsorbed fluorine per adsorbent mass unit - 1g –is the follows:

$$a_{tot} = \frac{w}{m} \cdot \int_{t=0}^{t=t_{ep}} C_{ad} \cdot dt \qquad (1)$$

The integral is equal to the surface area under the curve retention of chlorine onto DMA– C_t / C_0 vs. t.

Amount of fluorine adsorbed up to breaking point (b. p.) is determing by the formula:

$$a_{p.r.} = \frac{w}{m} \cdot \int_{t=0}^{t=t_{p.r.}} C_{ad} \cdot dt \qquad (2),$$

where $C_{ad} = C_0\text{-}C_t$.

1.1. Shilov model of the sorption dynamics

To calculate the protective time of a sorption column *t* the Shilov dynamic equation can be used [5]:

$$t = K \cdot h - \tau_0 \qquad (3)$$

where *t* - time of the protective action of the adsorption column, min., *K* – the factor of the protective action, min/cm., *h* - height of the sorbent bed of the column, sm, τ_o- time of loss of the protective action, min.

Shilov model makes it possible to calculate the duration of effective work of the sorbent column (load) in parallel movement of the adsorption front.

2. EXPERIMENTAL PART

To investigate the fluorine adsorption dynamics the model NaF solution in which the content of the fluorine was 4.65 mg/l, which corresponds to the average fluorine content in the majority of underground water sources in Moldova was used. Experiments were carried out in dynamic mode in a glass column of 200 mm height and 15mm internal diameter. As a sorbent the granules with fraction -2.0 + 0.5 mm of modified with aluminum compounds diatomite (DMA) were used. Fluorine solution flow rate through a sorbent layer was 10 and 15 ml/min. The filtrate output from the column was collected in the flask at regular intervals and analyzed for fluorine content. To characterize the sorption capacity of DMA in dynamic conditions the Shilov equation of sorption dynamics was used, which reflects the impact of static and kinetic factors on the sorption of fluorine.

In preliminary experiments the kinetics and equilibrium of fluorine adsorption on DMA using separate samples of the sorbent were investigated. The fluorine concentration in the solution varied from 2 to 20 mg/l, pH-4.0 - 9.0, sorption duration from 0.5 to 360 minutes and sorbent mass from 0.05 to 0.1 g in 50ml of the solution. Adsorption experiments were performed in acetate buffer. The concentration of F was determined using selective fluorine electrode ECOM-F with the ionometer I 160M. The amount of adsorbed fluorine was calculated according to the formula:

$$a = (C_o - C_e)\, V / m \qquad (4)$$

where C_o and C_e are the initial and equilibrium concentration of fluorine, mg/l. *V* – the solution volume, l, *m* - the DMA sample mass, g. The optimal fluorine sorption pH F was in interval 4.5-5.5, the equilibrium time was established as 120 min. Sorption isotherms of F onto DMA were obtained, which have been processed using Langmuir and Freundlich models, the parameters of these models were determined. It was shown that the Freundlich model more correctly described the fluorine equilibrium sorption data - correlation coefficient, R^2 = 0.9845. Maximum adsorption capacity of F on DMA, a_m, was found to be 39.6 mgF/g at an initial concentration of fluoride 20 mgF/l.

Evaluation of fluorine adsorption in dynamic mode on DMA was carried out by the analysis of breakthrough curves i. e. the dependence of C_t/C_0 - the relative fluorine concentration in the filtrate on time -*t* (Fig. 1 is the typical breakthrough curve)

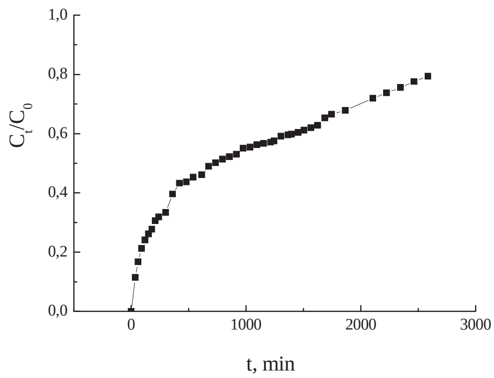


Fig.1 The breakthrough curve of fluorine adsorption on modified diatomite in dynamic condition.

3. RESULTS AND DISCUSSION

The experimental breakthrough curves in depending on the bed height are shown in Fig. 2

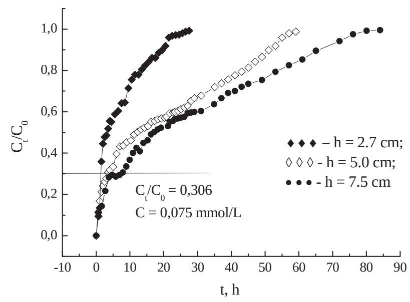


Fig. 2 Experimental breakthrough curves of fluorine sorption on DMA with bed volumes of treated water at different bed heights. C_0 = 0.245 mmolF/l; *v* = 10ml/min.

As can be seen from figure 2, all curves have a sharp rise at the beginning of the process turning into a less steep and then flat during the subsequent sorption time. The curves show a regular increase of the protective action of the sorbent layer with increasing layer height at constant fluoride concentration and the solution flow rate. This kind of curves indicates, apparently, the dominant external diffusion at early sorption stage which turns into the internal diffusion at the end of the process.

3.1 Modeling of breakthrough curves

To determine the mass transfer coefficient K_v and K -factor of protective action the Shilov extended dynamic equation of sorption has been used [6]:

$$t = K \cdot h - (K \cdot w / K_v) \cdot \ln (C_0 / C_t - 1) \qquad (5)$$

where w - volumetric flow rate divided by the cross section of the sorption apparatus, cm/min ($w = v / S$, v - cm^3/min, S - cross section of the column, cm^2, C_o and C_t - fluorine concentration at the beginning and at time t, mg/l, K_v - kinetic constant proportional of mass transfer rate of fluoride ions with the active sites on the surface of diatomite, 1/min.

a_m - maximum adsorption capacity has been determined by the formula:

$$a_m = K \cdot w \cdot C_0 \qquad (6)$$

To determine the parameters of equation (5) the latter has been given in a linear form:

$$\ln (C_0 / C_t - 1) = (K_v \cdot h / w) - (K_v / w \cdot K) \cdot t \ (7)$$

A plot of $\ln (C_0/C_t - 1)$ versus t is the straight line (Fig. 3), the slope of which corresponds to the $(K_v / w \cdot K)$, and the intercept is $(K_v \cdot h / w)$. From these two equations we find K and K_v.

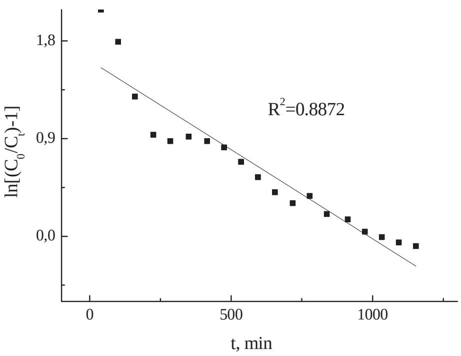


Fig.3. Breakthrough curve of fluorine adsorption on DMA in linear coordinates of Shilov equation, h = 7.5cm; v = 10 ml/min; C_F = 0.245 mmol/l

The intercept is equal to 1.619 and the slope of the curve is equal to 0.00164. Calculated from these data rate of the protective action - K and mass transfer coefficient K_v, are 179.8 min/cm and 1.220 1/min, respectively. Similar calculations of these parameters have been made for the heights 2.75 and 5.0 sm of the sorbent layer at the same solution rate and the initial concentration of fluoride (Table I).

Table I
The calculated parameters of the Shilov dynamic equation

N	h [cm]	K [min/cm]	K_v [1/min]	t_{exp} [min.]	t_{cal} [min.]	Δ [%]
1	2.75	67.10	0.908	90	82	8.8
2	5.0	195.80	1.330	210	195	7.1
3	7.5	179.85	1.220	475	484	1.9
4	5.0	118.17	2.505	150	135	10.0

Flow rate = 10 ml/min, C_0 = 0.245mmol/l

From the table it can also be seen that the coefficient of protective action K decreases with increasing of flow rate of the solution through the column from 10 to 15 ml/min. This is due, obviously, to the fact that at a given height of the column at the flow rate increasing the parallel movement regime of fluorine in the sorbent layer is not attained. Using the calculated parameters (K and K_v) we can find analytic expressions of equation (5) which allow to calculate the duration of sorbent bed effective work under dynamic conditions for given loading height and the initial fluorine concentration in the water, as well as its values before breakthrough of fluorine in the filtrate. As the table data show that the calculated protective action time t_{cal} are very close to the experimental data t_{exp}. detrmined before fluorine breakthrough in the filtrate (the relative error does not exceed 10%).

The obtained characteristics may be used to design the sorption apparatus.

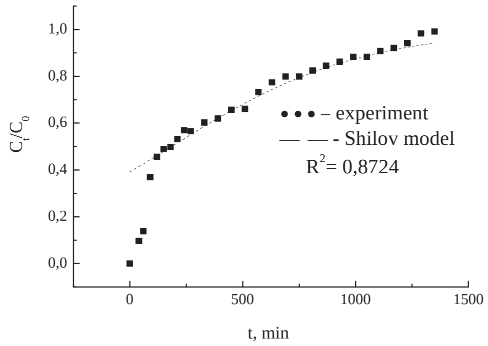
Evaluation of the applicability of Shilov dynamic model to describe the fluorine sorption regularities on modified diatomite DMA under dynamic conditions was carried out by comparison of the experimental breakthrough curves of fluorine adsorption with calculated by this model, as well as by the values of correlation coefficients - R^2. The expressions for calculation breakthrough curves C_t/C_0 vs. t in dynamic conditions are expressed by the following equations:

1. $C_t / C_0 = 1/(1+\exp(0.44 + 0.0046\ t))$ (8)
2. $C_t / C_0 = 1/(1+\exp(1.175 - 0.00183 \cdot t)$ (9)
3. $C_t / C_0 = 1/(1+\exp(1.619 - 0.00164 \cdot t)$ (10)

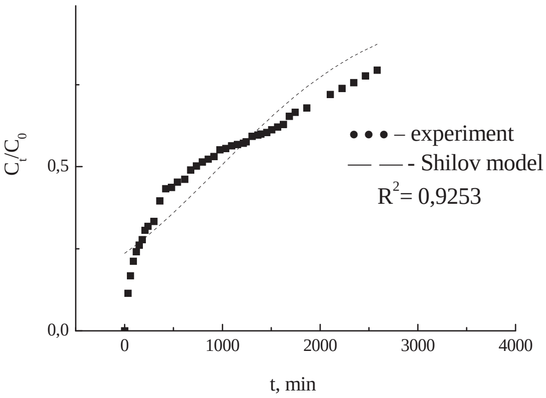
$$4. C_t / C_0 = 1/(1+\exp(1.477 - 0.0104 \cdot t)) \quad (11)$$

Numbers 1, 2, 3 and 4 in these equations correspond to the numbers in the table.

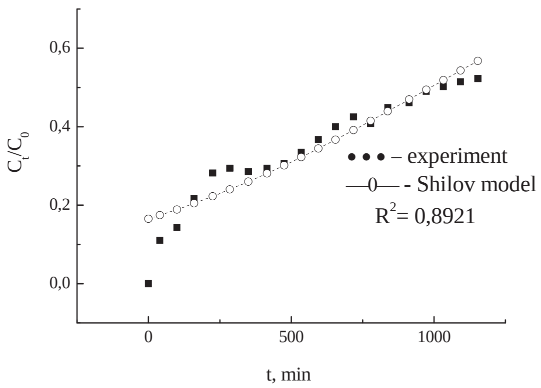
Figure 4 shows the experimental breakthrough curves of fluorine sorption on DMA and, for comparison - calculated by eq (8)-(11) of Shilov model for different dynamic conditions.



(a)



(b)



(c)

Fig. 4 Breakthrough curves of fluorine adsorption on DMA experimental and calculate, v = 10 ml/min, w= 5,662 cm/min, C_0 = 0.245 mmol/l

(a) h = 2.7cm; (b)- h = 5.0cm; (c) h = 7.5cm

The results presented show that the experimental breakthrough curves and calculated according Shilov model for all bed heights (2.75, 5.00 and 7.50 cm) under the same solution rates and the initial fluorine concentration are in satisfactory agreement - the correlation coefficients are within 0.8724 and 0.9253.

4. CONCLUSIONS

The analysis of breakthrough curves of fluorine adsorption on modified diatomite in dynamic mode has been performed.

The simulation of dynamics of fluorine adsorption on DMA using the extended dynamic equations Shilov has been carried out, the parameters of the equation have been calculated by which the analytical formulae of models have been obtained. It is shown that the correlation between the experimental breakthrough sorption curves and calculated by the Shilov model is good - the difference in the values of column service time does not exceed 10%. The results can be used in the design of adsorption devices.

Acknowledgments

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