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7. Modification of diatomite with aluminum compounds and the possibility of its applying for water purification

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ABSTRACT. The paper investigates the possibility of applying of local modified diatomite (DMA) for different purposes. By modifying of the diatomite surface with a variety of active groups it is possibly giving it a selective properties with respect to a particular pollutant in the water, which must be removed. The structural and chemical surface modification method of diatomite surface with aluminum compounds to increase its adsorptive capacity with respect to fluorine has been used in the paper. The method consists of successive treatment of diatomite with sodium hydroxide solution under heating, aluminum salt and ammonia under constant agitation. Physic -chemical and adsorption-structural properties of the modified diatomite have been characterized using X-ray analysis method, DTA, FTIR, BET, chemical analysis. The selectivity of the synthesized sorbent has been tested by removing of fluoride from the model solution. The effect of the sorbent mass, pH, agitation speed, the initial concentration of the sodium fluoride solution and contact time of the solution with the sorbent have been investigated. Fluorine adsorption isotherms have been obtained, which were modeled by equations by Langmuir and Freundlich. The parameters of the equations have been calculated. Kinetic curves of sorption of fluoride on DMA have been constructed. The constants of adsorption velocity have been calculated, the coefficients of internal and external diffusion have been evaluated.

Key words: Diatomite, modification, adsorption, water purification, fluorine

INTRODUCTION

Diatomite (or diatomaceous earth) are mineral deposits of diatomaceous algae, which accumulated starting from the Miocene. Amorphous silica, a constituent of the diatom frustulae, is the main component of diatomite, although variable quantities of other materials (metal oxides, clays, salts (mainly carbonates) and organic matter) may also be present. The main components of silicone frustules are amorphous silicon hydrates with different water contents (opals, SiO2–nH2O). Diatomite has a large internal surface area and contains 80–90% cavity cells. This material with a microporous structure, where pores with a radius of 4–40 µm make 15% of the total pore volume, has an apparent density of about 30 g/dm^3. Diatomite is abundant in many areas of the world and has unique physical characteristics, such as high permeability and porosity (35-65%), small particle size, low thermal conductivity and density and high surface area. The properties of diatomite's surface, such as hydrophobia, solubility, charge, acidity, ion exchange and adsorption capabilities, are highly governed by the presence of water, which is partially structurally connected to the crystal mesh of the diatomite, forming active hydroxyl groups on it. By modifying of the diatomite surface with a variety of active groups it is possibly giving it selective properties with respect to a particular pollutant in the water, which must be removed [***2***]. Toxic substances, the fluoride ion first of all must be removed from tap and ground water. 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. World Health Organization (WHO) recommends it in the range of 0.1- 1.5mg/l. The problem of the removal of fluorine from drinking water is an urgent task for many regions of the world. Several methods have been tried to remove fluorides from water, namely, adsorption ([***6***]; [***17***]), ion exchange [***19***], precipitation [***18***], electrochemical [***10***] and membrane methods [***14***]. However these techniques are not in much use primarily because of their expensiveness, inefficiency or failure in mass scale application. In recent years, for removal of fluoride in the drinking water, attention of scientists have been devoted to the study of different types of low cost materials such as spent bleaching earth ([***3***], [***12***]), wollastonite and chine clay [***8***], Kaolinite and montmorillonite [***1***], laterite [***15***], zeolite [***4***], trepel [***20***], diatomite [***21***]. In the present report the natural material diatomite (D1) and the modified diatomite (DMA) have been tested as sorbents for fluorine removal.

MATERIALS AND METHODS

The local diatomite from locality Viscauti (region Orhei, Moldova) has been undergone to the structural chemical modification with aluminum compounds and denoted as DMA. A variety of methods, such as powder X-ray diffractometry, BET analysis, and DTA were used for the characterization of the DMA. The phase composition of the modified diatomite was identified by means of the diffractometric analysis with using a DRON-3M X-ray diffractometer with a CoK_α source of radiation, U/I = 30/30, measuring limits of 2.102–5, and the width of the slit of 1–1–1–0.25. The textural characteristics of the DMA i.e., the specific surface area, size and volume of the pores and their size distribution, were determined by using the BET method in compliance with the low-temperature adsorption of nitrogen (the area of a nitrogen molecule was assumed to be 0.162 nm^2) using an ASAP2000 micrometer device. The thermogravimetric analyses were performed using a Q1000 derivatograph.

The chemical structural modification of the initial material has been performed according to [***22***].

A sample of D1 (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.

Physical, chemical and structural properties of modified diatomite presented in ([***5***]; [***20***]).

To assess the ability of synthesized sorbent to remove fluorine from aqueous solution batch adsorption experiments were conducted. The adsorption experiments were carried out in an acetate buffer solution (1 M CH_3COONa + 0.5 M CH_3COOH) to exclude the influence of the medium pH on the fluorine adsorption. A 0.5 M Na_2SO_4 solution was added to maintain the ionic strength of the solution during adsorption [***5***]. A -0.2 mm fraction of the samples was used; the S : L relationship was 1 : 250. The adsorption process was performed with continuous stirring and control over the change in the fluorine concentration until a equilibrium was reached. A I -160M ion meter equipped with a fluorine-selective ELIS-131F electrode was used for the registration. The pH was determined with an accuracy of 0.05 pH and the content of fluorine ions with an accuracy of 0.01 mmol/l.

The data obtained in batch mode studies were used to calculate the equilibrium fluoride adsorptive quantity by using the following expression:

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

where:
a is the amount of adsorbed fluoride onto DMA per unit weight of the adsorbent in mmol/g;
V is the volume of solution treated in liter;
Co is the initial concentration of fluoride ion in mmol/l;
Ce is the residual fluoride ion concentration in mmol/l;
m is the mass of adsorbent in g/l.

Data of the amount of fluorine adsorbed by the DMA surface (a) vs equilibrium fluorine concentration in solution (Ce) presented graphically called the adsorption isotherm. **Fig. 1** presents the experimental adsorption isotherm of fluorine onto DMA.

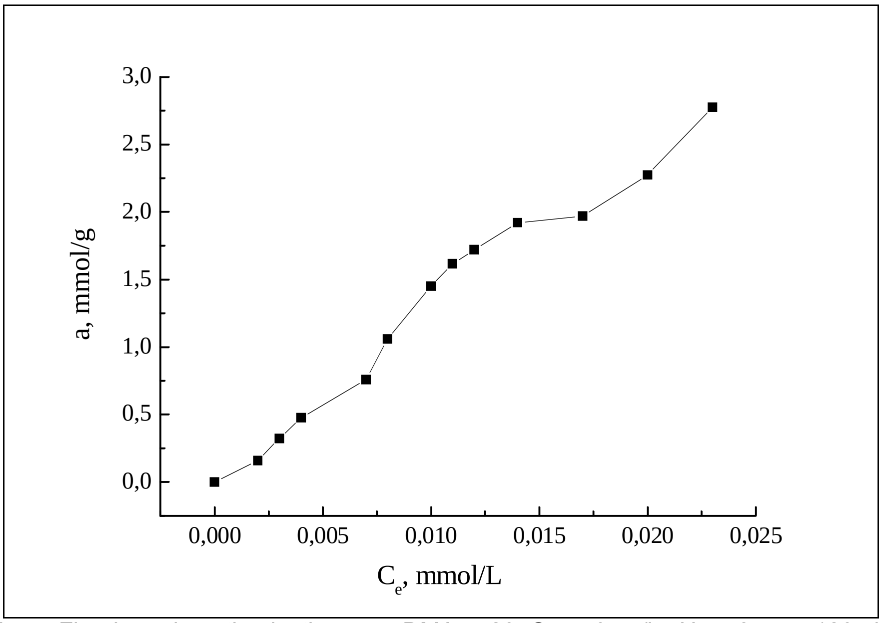

Fig. 1. Fluorine adsorption isotherm on DMA at 20oC. m=0.5g/l, pH=4, 85, τ = 120min.

For the analysis of isotherm data several adsorption models are usually used: Langmuir, Freundlich, Henry, BET etc. The non-linear method is a better way to obtain the isotherm parameters, an optimization routine to maximize the coefficient of determination R^2, between the experimental data and isotherms was used to compare the best fit of the isotherms [***11***]. The coefficient of determination R^2 is as follows:

$$R^2 = \frac{\Sigma(a_e - \overline{a_t})^2}{\Sigma(a_e - \overline{a_t})^2 + \Sigma(a_e - a_t)^2} \quad (2)$$

where:
a_t is the equilibrium capacity obtained by calculating from the model (mmol/g);
a_e is the experimental data of the equilibrium capacity (mmol/g);
$\bar{a}_t$ the average of a_t.

The analysis of the data using the Chi-square test χ^2 to confirm the best-fit isotherm for the sorption fluorine from aqueous system on DMA also was used. The mathematical statement of the Chi-square test basically the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models and can be given as [***9***]:

$$\chi^2 = \Sigma\ [(a_e - a_m)^2/a_m] \quad (3)$$

where:
a_m is the equilibrium capacity obtained by calculating from the model (mg/g);
a_e is experimental data of the equilibrium capacity (mg/g).

Small number of χ^2 indicates that data from the model is close to the experimental data. Whereas, large number of χ^2 indicates that data from the model is different from experimental data. In order to assess different isotherms and their ability to correlate with experimental results, the theoretical plots from each isotherm have been fitted with the experimental data for adsorption of fluorine on DMA.

RESULTS AND DISCUSSION

The initial diatomaceous earth contains SiO_2 - 60%, CaO - 11.7% Al_2O_3-4.8%, and also oxides of Mg, Fe, Na, K, diatomite main phases are quartz, amorphous silica, calcite, aragonite, kaolinite and montmorillonite present in small quantities.

The process of modification of diatomite leads to decomposition of calcite and aragonite phases and formation of a new one - aluminosilicate. During the diatomite treatment with NaOH at heating amorphous SiO_2 partially dissolved and in the second stage (interaction with a modifier) in volume and on the surface of diatomite formed aluminosilicates.

The initial sample and the modified diatomite are mixed structure mesoporous sorbents. The specific surface values calculated following BET equation are equal to 37.54 and 81.77 m^2/g, corresponding for the initial sample and modified. Thus specific surface of diatomite modified sample has changed 2 times higher than natural diatomite sample. Sorption pore volume vs of DMA samples is 0.105 cm^3/g and total pore volume V_Σ - 0.845 cm^3/g. Thus the volume of macropores for the DMA is 0.739 cm^3/g. For the initial diatomite sample this value is 0.492 cm^3/g.

Before carrying out the thermogravimetric analyses the samples were dried in the air and then heated at 110°C until achieving a steady mass. The samples treated in such a way were kept in a desiccator for their further use. Thermogravimetric analyses showed that on the raw diatomite sample DTA curve there are two endoefects: one in the 40-110^{0}C and the second - in the 750-820^{0}C temperature range with a minimum at 780^{0}C. First endoefect corresponds to physically adsorbed water removal, the second - decomposition of carbon minerals present in samples of natural diatomite. A shallow and wide exoefect on the DTA curve in the temperature range 280-380^{0}C is related to the start of combustion of organic substances. In the heating curves of the modified diatomite samples a clear and narrow endoefect also present in the temperature range 40-190^{0}C with a minimum at 120^{0}C, which corresponds to physically adsorbed water elimination and an exoefect in the temperature range 190-470^{0}C. The nature of these peaks is similar to those for unmodified samples. Qualitative changes in the composition of modified diatomite are confirmed by X-ray analysis and FTIR spectra: appearance of new reflexes on the diffractogram characteristic for aluminosilicates and vibration of groups Si—O—Al on the curves of infrared transmission spectra [***5***].

The adsorption isotherms of fluorine on DMA were analyzed by a regression analysis to fit the Freundlich [***7***] and Henry [***13***] models.

The Henry isotherm can be presented as (for solute adsorption):

$$a = K_H \cdot C_e \quad (4)$$

and the equality indicates that the fluorine adsorption value is directly proportional to its equilibrium concentration in bulk solution.

The Freundlich isotherm model assumes heterogeneous surface energies.

$$a = K_F \cdot C_e^{\,l/n} \quad (5)$$

In the equations above:
a – the amount of adsorbed substance per 1 g of sorbent at equilibrium;
C_e – equilibrium concentration of substance in solution;
K_F and n are parameters of Freundlich equation, they express adsorption capacity and intensity of interaction of adsorbate with the surface respectively. K_H and K_F equilibrium constants of the equations.

For fluorine adsorption equilibrium data interpretation the equations were used in linear form (for the Freundlich model):

$$\ln a = \ln K_F + \frac{1}{n}\ln C_e \quad (5)$$

The Henry K_H and Freundlich 1/n adsorption constants were calculated from slope of the linear plot of a vs C_e and lna vs lnC_e, but value of constant K_F – from intercept of the linear plot lna vs lnC_e.

In preliminary experiments on removing of fluorine from model solution with the help of DMA the optimal conditions have been determined: pH = 4.5 -5.5; τ = 120 min; m = 0.5g/l at which purification grade of water from fluorine was the highest.

In order to investigate the adsorption isotherm two equilibrium isotherms were analyzed – Henry and Freundlich. The adsorption isotherm of fluorine on modified diatomite sample based on experimental adsorption data for initial concentration of fluorine from 0.05 to 1.0 mmol/l is shown in **Fig. 1**. From the figure it is seen that the value of adsorption continuously increases with growth of equilibrium concentration of fluorine in solution. The shape of the isotherm assumes that it will be fitted to models Freundlich and Henry. These two models are discussed below.

The linear plots of a vs C_e (Henry) (**Fig. 2**) and lna vs lnC_e (Freundlich) (**Fig. 3**) have been applied for calculation of parameters of adsorption equations.

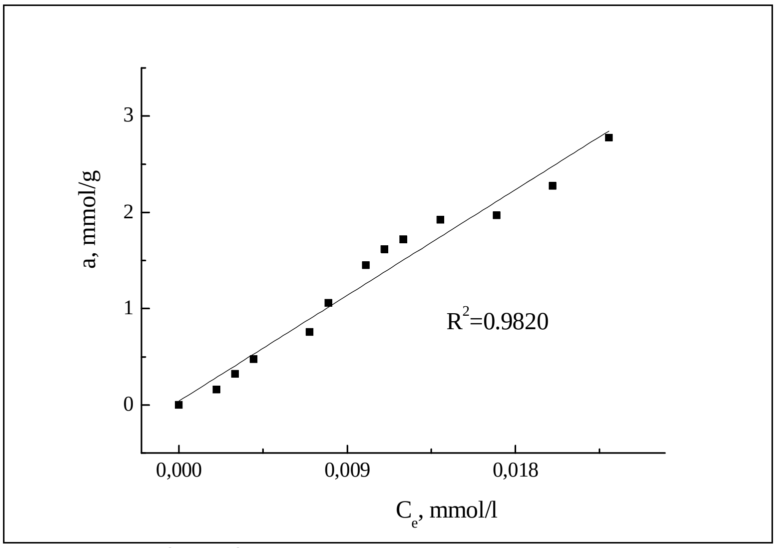

Fig. 2. Linear form of Henry isotherm. m=0.5g/l, pH=4, 85, τ = 120min.

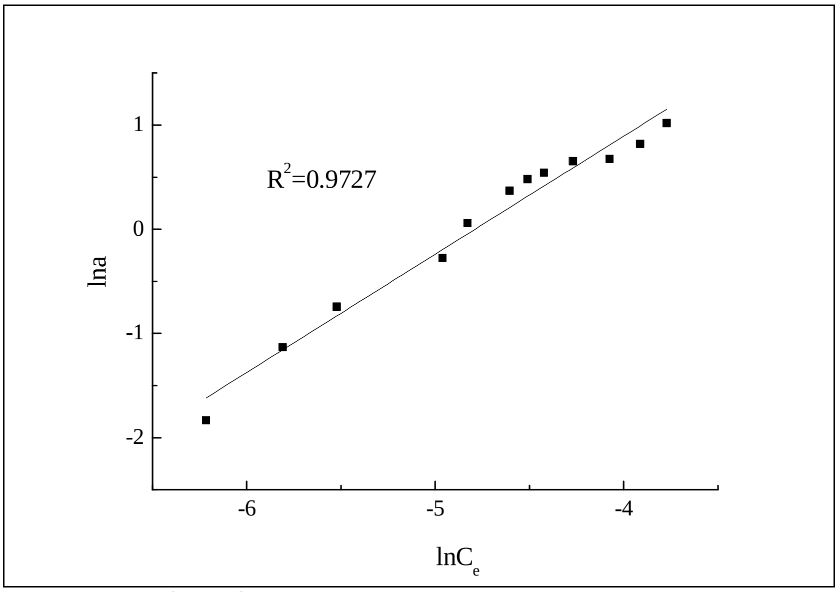

Fig. 3. Linear form of Freundlich isotherm. m=0.5g/l, pH=4, 85, τ = 120min.

Table 1

Parameters of Henry and Freundlich equations fluorine adsorption on DMA at pH 4,85, contact time 120min.

Model	Parameters			
Henry	K_H	a_m	R^2	χ^2
	121.927	2,98	0,9358	0.5124
Freundlich	K_F	1/n	R^2	χ^2
	229.39	1.134	0.9373	0.2986

Parameters of adsorption models evaluated from the isotherms together with the correlation coefficients R^2 and χ^2 are presented in **Table 1**.

Determination coefficients R^2 for Henry and Freundlich models indicate that the adsorption data of fluoride onto modified diatomite fitted well with both isotherm models because they are rather high and close, they are equal to 0.9358 and 0.9373. However Freundlich model better describes experimental data as its parameter value χ^2 is smaller than for Henry model (see **Table 1**). The value of Freundlich constant (n) is equal to 0,882 which indicates that adsorption process is favorable [***16***].

The calculated parameters of Henry and Freundlich equations were used for drawing of analytical expressions of these models which are given below:

$$a_F = 229.39 \cdot C_e^{1/n}$$

$$a_H = 121.927 \cdot C_e$$

Using these expressions, the adsorption capacity of the sorbent can be calculated for any fluorine initial concentration for the given system sorbent – water – fluorine.

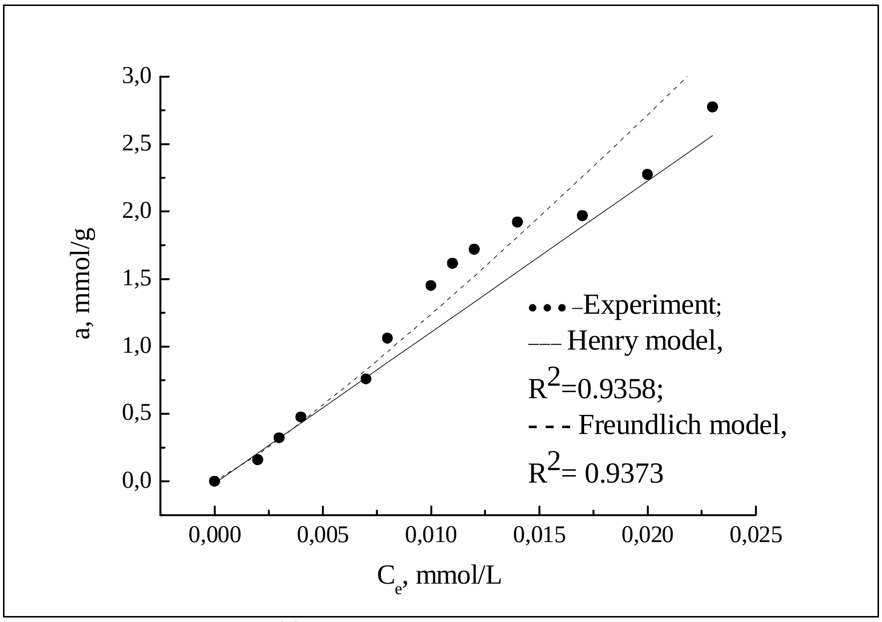

Fig.4. Comparison of the adsorption isotherms of fluoride on DMA, experimental and calculated according Freundlich and Henry models

In **Fig. 4** there are shown the experimental adsorption isotherms of fluoride on the modified diatomite and the isotherms, calculated by the models of Freundlich and Henry and for comparison they are plotted in the same graphs. From **Fig. 4** it is clear that the Freundlich model better describes the experimental results of adsorption of fluorine at DMA.

CONCLUSIONS

The physics-chemical, structural and adsorption properties of natural and modified diatomite from Moldova deposit have been studied. The adsorption equilibrium of fluorine from model solutions onto modified diatomite (DMA) has been investigated. A comparative study of the applicability of adsorption models of Henry and Freundlich to describe the experimental adsorption isotherms of fluoride on natural and modified diatomite has been carried out. The constants and parameters of these equations have been defined. Comparing the correlation coefficient R^2 and linear regression coefficient χ2 shows that the Freundlich model best describes the experimental data on the adsorption of fluoride with studied samples. This indicates that the adsorption of fluoride occurs on a heterogeneous surface and that the majority of active sites have different quantities of energy. High adsorption capacity for fluorine comparing to untreated diatomite and its low cost allow recommending the modified diatomite as promising sorbent for fluorine removal from water.

REZUMAT (SUMMARY IN ROMANIAN LANGUAGE). Lucrarea investighează posibilitatea de a aplica diatomitul local modificat (DMA) pentru înlăturarea fluorului din apă. Prin modificarea suprafeţei diatomitului cu diferite grupe active, este posibil de a atribui lui proprietăţi selective în ceea ce priveşte un anumit poluant în apă, care trebuie îndepărtat. În lucrare a fost utilizată metoda structural – chimică de modificare a suprafeţei diatomitului cu compuşii de aluminiu pentru a spori capacitatea de adsorbţie a lui în raport cu fluorul. Metoda constă în tratarea succesivă a diatomitului cu soluţie de hidroxid de sodiu la încălzire, sare de aluminiu şi amoniac la agitare constantă. Proprietăţile fizico – chimice, de adsorbţie şi structură ale diatomitului modificat au fost caracterizate cu ajutorul raze X, metodele de analiză DTA, FTIR, BET, analizei chimice. Selectivitatea adsorbantului sintetizat a fost testat prin eliminarea fluorului din soluţia apoasă model Au fost obţinute izotermele de sorbţie a fluorului,care au fost modelate prin ecuaţiile

ale lui Henry şi Freundlich. Au fost calculate parametrii acestor ecuaţii. S-a demonstrat că modelul lui Freundlich mai bine descrie datele experimentale de adsorbţie a fluorului pe diatomit modificat.

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