STUDY OF FLUORINE ADSORPTION ON MODIFIED TREPEL

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Abstract: In the paper a novel fluorine sorbent, modified trepel (TSM) has been investigated. For modification of natural trepel (TS) with the goal to make it more selective towards fluoride-ions we have used structural-chemical method which consists in introduction into the trepel matrix aluminum of that have a high affinity for adsorption of fluorine The modification of trepel was realized through surface modification treatments including NaOH treatment at heating, aluminum salt solution and ammonia solution interaction. For characterization of the original and modified trepel chemical, thermogravimetric, X-rays, structure and adsorption (BET) and FTIR analyses were used. Sorbent obtained was tested to remove fluoride from model solution with initial concentration of F^- up to 0.035mol/L. Fluorine removal degree has been evaluated as a function of pH, doze, contact time and initial fluorine solution concentration. Experimental adsorption isotherms (S:L=1:250; pH = 4,85; T=293K, 303K; time 120min) have been simulated by Langmuir and Freundlich adsorption models. It is shown that the Langmuir model better describes the experimental results of adsorption at 20^0C ($R^2 = 0{,}9973$), and the model of Freundlich - at 30^0C ($R^2 = 0{,}9742$). The presented results describe the obtained material on the base of trepel as a promising adsorbent for the removal of fluoride from water.

1. Introduction

Pure water is scarce and is not easily available to all. The quality of drinking water is very important for public safety and quality of life. Toxic substances, the fluoride ion firs of all must be removed from tap and ground water, because it causes teeth to become mottled. 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- 1.5ppm.

Several methods have been tried to remove fluorides from water, namely adsorption, precipitation, electrodialysis, ion exchange and reverse osmosis. Among these methods, adsorption is still one of the most extensively used methods for defluoridation of water.

In recent years, attention of scientists have been devoted to the study of different types of low cost materials such as spent bleaching earth [1.2], wollastonite and chine clay [3], bentonite and activated bentonite [4-6.], zeolite [7] and diatomite [8]

In the present report the natural material - trepel (TS) and the modified trepel (TSM) have been tested as sorbents for fluorine removal.

Adsorption isotherms

The adsorption isotherms generally used for the design of adsorption system. The Langmuir:

$$a = \frac{a_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \qquad (1)$$

and Freundlich:

$$a = K_F \cdot C_e^{\frac{1}{n}} \qquad (2)$$

equations are commonly used for describing the adsorption isotherm.

In these equations:

a and a_m - the amount of adsorbed substance at 1 g of sorbent at equilibrium and the adsorption capacity of the sorbent at saturation, C_e– equilibrium concentration of substance in solution. K_L, K_F -equilibrium constants of the equations of Langmuire and Freundlich; n - parameter of the equations of Freundlich. To the adsorption equilibrium data interpret both equations are used in linear form:

Langmuir model –

$$\frac{C_e}{a} = \frac{1}{K_L \cdot a_m} + \frac{C_e}{a_m} \qquad (3);$$

Freundlich model –

$$\ln a = \ln K_F + \frac{1}{n} \ln C_e \qquad (4);$$

The influence of isotherm shape is evaluated from r, a dimensionless constant [9], defined as

$$r = 1/(1 + K_L \cdot C_0) \qquad (5)$$

where K_L is the Langmuir constant and C_0 is the initial fluoride concentration. The parameter r indicates the shape of the isotherm accordingly:

r value	Type of isotherm
$r > 1$	Unfavorable
$r = 1$	Linear
$0 < r < 1$	Favorable
$r = 0$	Irreversible

Favorable adsorption is predicted in the present case from the r value (0.416 for TS and 0.162 for TSM at 293 K and initial fluorine concentration 1.03mmol/L).

2. Experimental

The starting trepel TS used in the present work was supplied from the deposits of Senatovka village in the Kamenka region in Moldova. The trepel samples initially have been dissipated into several fractions and for each of them adsorption capacity with respect to fluorine has been determined.

The chemical structural modification of the initial material has been performed according to [10].

A sample of TS (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. Trepel modified with aluminum compounds is denoted further as TSM.

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[11]. A -0.1 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 ionometer equipped with a fluorine-selective ELIS-131F electrode was used for the registration. The pH was determined with an accuracy of 0.05% and the content of fluorine ions with an accuracy of 0.1 mmol/L.

Kinetic experiments were performed to determine the time during which the equilibrium was reached.

For characterization of the initial trepel TS and the trepel modified by structural-chemical method TSM X-ray, thermogravimetric, and structure of adsorption (BET), chemical and FTIR analyses were used. It was established that the initial trepel contains SiO_2 – 81.05%, CaO – 1.84%, Al_2O_3-5.12%, and also oxides of Mg, Fe, Na, K, the trepel main phases are silica of different crystal modifications α – tridymite and β –cristobalite, kaolinite and montmorillonite present in small quantities.

In table 1 there are the data of adsorption capacity of initial trepel of different fractions

Table 1 Adsorption capacity of different fraction of TS. C_{in} = 0.875 mmol/L, pH 4,85, t=20^{0}C

Probe N	Particles dimension, mm	Adsorption, mmol/g
1	-0.50+0.315	0.022
2	-0.315+0.20	0.033
3	-0.20+0.10	0.038
4	-0.10+0.071	0.051
5	-0.071+0	0.062

As it is seen from the table adsorption value markedly increased for trepel particles less than 0.1 mm, this fraction has been used further in adsorption experiments.

BET analysis

The isotherms of the initial sample and the modified trepel are both of type IV by the classification of A.V. Kiseleov, i.e. samples are mixed structure mesoporous sorbents. A special feature of the isotherms is the presence of reversible hysterese. Both samples isotherms are satisfactorily described by the multimolecular adsorption model, specific surface values calculated following BET equation. Adsorption-structural characteristics calculated according BET model have been shown in table 2.

Table 2. Adsorption and structure characteristics of TS and TSM

Sample	Specific surface, S_{sp}, m^2/g	Adsorption pore volume, V_S, cm^3/g	Pore radius, r, Å
TS	72.15	0.197	28.4
TSM	54.08	0.292	65.2

As can be seen from the table the surface area of modified trepel decreases and the pore volume increases. Two opposite processes occur at the trepel modification – dissolution-precipitation of silica leading to the surface diminution and aluminosilicate formation which results to specific area enlargement and the result of these processes is specific area decreasing and pore volume increasing.

Thermogravimetry

The samples were dried in the air before carrying out the thermogravimetric analyses 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. The temperature of 110°C for drying the samples was chosen from the data of the thermogravimetric analyses.

There is one distinct endo effect present in the DTA curves both of the starting and modified trepel: in the temperature region from 60 to 140°C with the minimum at 120°C which corresponds to the removal of the physically adsorbed water. Besides in the modified trepel curve there is one more endo effect in the region 400-550 °C with the minimum at 480°C which we attributed to the removal of the crystallization water. There is also an exoeffect in the heating curve of TSM in the region 750-900 °C with the maximum at 800°C which may correspond to phase transition of α – tridymite and β – cristobalite into α-quartz according X-ray data.

Fluorine adsorption study

Effect of pH

The effect of initial pH of the fluoride solution on the amount of fluoride ions adsorbed was studied at pH values 4.5 – 8.5.

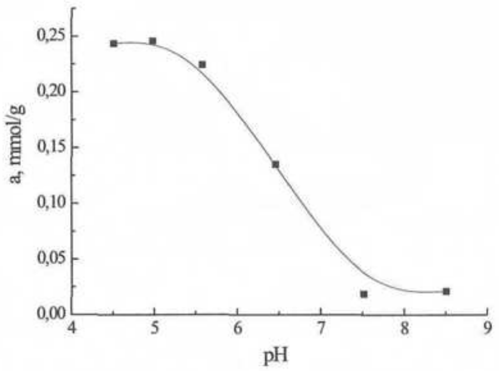

Fig. 1. Influence of solution pH on fluorine adsorption on TSM

The graph indicates that the adsorbent exhibits a defluoridation capacity in narrow range of pH – 4.5-5.5.. Hence, the defluoridation capacity of the adsorbent is appreciable in acidic range, at pH more than 5.5 the defluoridation capacity decreases sharply. This may be due to the competition between hydroxide and fluoride ions in this pH range.

Effect of adsorbent dosage

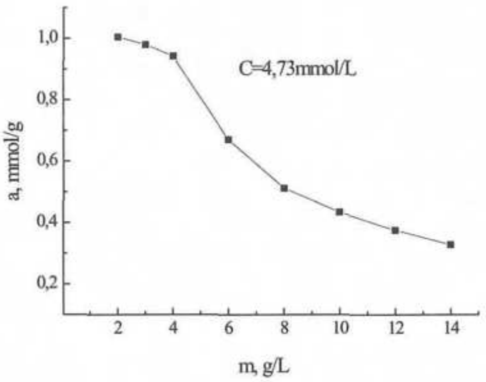

Fig. 2. Influence of adsorbent doze on the adsorption value of fluorine by TSM

Fig. 2 shows the amount of fluoride removed as a function of adsorbent dosages at 4.73mmol/ L of initial fluoride concentration and at 20⁰C. Adsorbent dosages was varied from 2 to 14 g/L and equilibrated for 120 min. From the result it is evident that optimum adsorbent dosage of 4 g/L is required for maximum fluoride. The binding ability of an adsorbent surface for an element can be determined from the distribution coefficient, K_d whichwas calculated as follows

$$K_d = C_S/C_e \qquad (6)$$

where C_S is the concentration of fluoride on the solid particles (mmol/g) and C_e is the equilibrium concentration in water (mmol/L).

The distribution coefficient K_d, increases with increasing of adsorbent dose which is depicted in Fig. 3. This increase trend in K_d value implies that the surface of TSM is heterogeneous in nature. The same regularity observed and at fluorine adsorption onto activated alumina coated with manganese dioxide. [12].

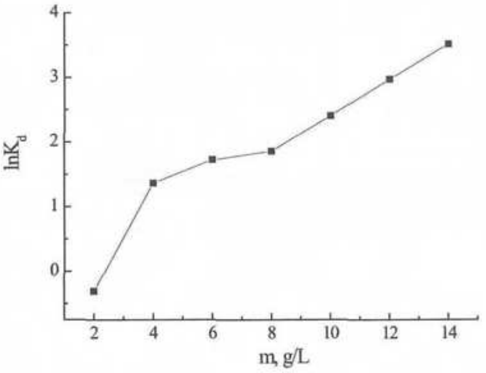

Fig. 3. Dependence of distribution coefficient on the adsorbent doze at adsorption of fluorine by TSM

Effect of contact time

Fig.4 exhibits the dependence of fluorine adsorption value on agitation time.

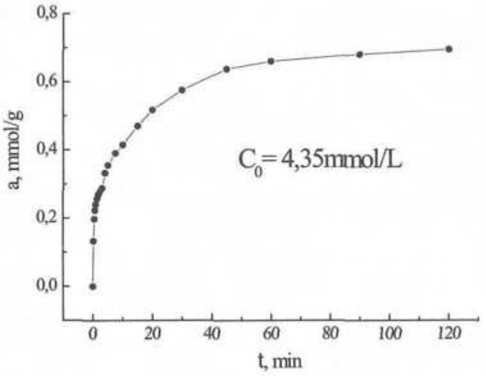

Fig. 4. Effect of agitation time on the adsorption value of fluorine by TSM

As can be seen in the figure, the main fluorine quantity (up to 80%) was adsorbed during 40 min of the process. The time needed to reach the equilibrium amounted to 120 min; the further contact of the fluorine solution and the absorbent did not lead to a substantial adsorption increase, therefore the time contact for all adsorption experiments was determined as 120 min.

Adsorption isotherms

Fig.4 shows the fluorine adsorption isotherms on TSM at 20 and 30⁰C.

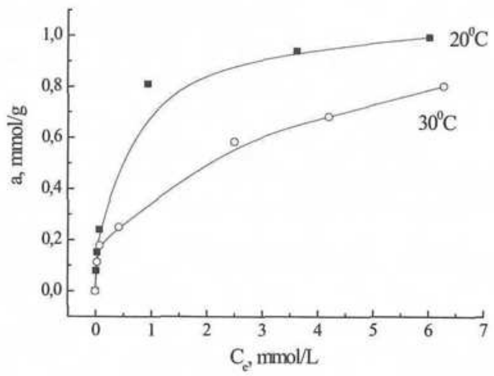

Fig. 4. Fluorine adsorption isotherms on TSM.

The graph indicates that the adsorption capacity decreased with temperature increasing.

Langmuir and Freundlich adsorption equations were applied to quantify the adsorption capacity of the chosen adsorbent for the removal of fluoride ions from water. The linear plots of *Ce/a* versus *C*e (Langmuir) and *lna* versus lnC_e (Freundlich) have been served for calculation of parameters of adsorption equations.

The values of isotherm constants and other statistical parameters presented in table 3.

Table 3. Parameters of Langmuir and Freundlich equations at fluorine adsorption on TSM. pH 4,85, contact time 120min.

Model	Parameters		
Langmuir	K_L	a_m	R^2
20^0C	7,6667	1,019	0,9973
30^0C	1,435	0,847	0,5868
Freundlich	K_F	1/n	R^2
20^0C	0,6710	0,379	0,5843
30^0C	0,3807	0,352	0,9742

The table data indicate the applicability of the Langmuir adsorption isotherm for experimental data description at 20^0C. However, the Freundlich model describes experimental data on fluorine adsorption on TSM better at 30^0C.

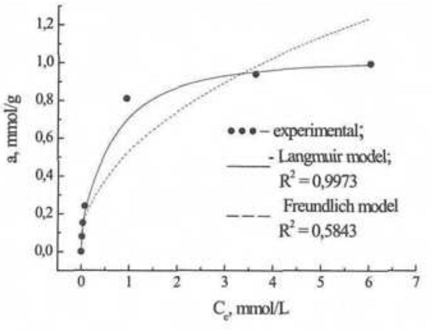

Fig.5 Fluorine adsorption isotherms on TSM at 20^0C.

Conclusion

The physic-chemical, structural and adsorption properties of natural and modified trepel from Senatovka (Moldova) deposit have been studied.

The adsorption equilibrium of fluorine from model solutions onto modified trepel (TSM) has been investigated.

The effect of fluorine adsorption conditions: adsorbent dose, solution pH and temperature, contact time and initial concentrations of fluorine on adsorption capacity of TSM have been determined.

Experimental data of fluorine adsorption on TSM have been simulated by Langmuir and Freundlich models.

It is shown that the Langmuir model describes experimental data at 20^0C, and Freundlich model – at 30^0C.

High adsorption capacity for fluorine comparing to untreated trepel, fast kinetics and low cost allow recommending the modified trepel TSM as promising sorbent for fluorine removal from water.

References

[1] Boukerroui A., Quali M.S., *J. Chem. Technol. Biotechnol.* 75, 773, 2000.

[2] Mahramanlioglu M., Kizilcikli I., Bicer I.O, Tuncay M., *J. Environ. Sci. Health* 35(2), 187, 2000.

[3]Gonzales-Pradas E., Villafranca-Sanchez M., Gallego-Campo A., Urena-Amate D.,. Socias-Viciana M.M, *J. Chem. Technol. Biotechnol.*,69, 173, 1997.

[4] Gonzales-Pradas E.,. Villafranca-Sanchez M, Valverde Garcia A., Socias-Viciana M., Bueno F., Rodriguez G., *J. Chem. Technol. Biotechnol.*, 42, 105, 1988.

[5].Gonzales-Pradas E, Villafranca-Sanchez M., Gallego-Campo A., Urena-Amate D., Perez F., *J. Chem. Technol. Biotechnol.* 74, 49, 1999.

[6] Kizilcikli I., Mahramanlioglu M., Sezer S., Tuncay M., *Chim. Acta Turcica,* 27, 37, 1999.

[7]. Chang H.L, Shih W.H., *Ind. Eng. Chem. Res.*, 37, 71, 1998.

[8] Zelentov V., Datko T., Dvornikova E. *Simpozion Internaţional "Mediul şi Industria"*, România, Bucureşti, 1, 213, 2005.

[9] Prasad M., Amritphale S.S., Saxena S.,. Chandra S.N, *Ind. Eng. Chem. Res.*, 39, 3034, 2000.

[10] Zelenţov V., Daţko T., Dvornikova E. *Brevet de invenţie* MD 3973C2. 2010-07-31.

[11] Zelenţov V., Daţko T., Dvornikova E., *Surface Engineering and Applied Electrochemistry,* 44(1), 64, 2008.

[12] Tripathy S. S., Raichur A. M., *Journal of Hazardous Materials,* 153, 1043, 2008