THERMODYNAMICS OF FLUORINE ADSORPTION ONTO MODIFIED TREPEL

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Abstract. The effect of temperature on the equilibrium adsorption of fluorine from aqueous solution using modified trepel was investigated. The equilibrium adsorption data were analyzed using widely applied isotherms; Langmuir and Freundlich isotherm. A nonlinear method was used for comparing the best fitting of the isotherms. Best fits were found to be Langmuir isotherm. Thermodynamic parameters, such as $\Delta G°$, $\Delta H°$, and $\Delta S°$, were calculated using adsorption equilibrium constant obtained from the Langmuir isotherm. Results suggested that the fluorine adsorption on modified trepel was a spontaneous and endothermic process.

Keywords: sorption; fluorine; modified trepel; thermodynamic parameters.

1. INTRODUCTION

Thermodynamics provides a practical tool for the estimation of the chemical states of adsorbent and solution in chemical industry applications. Such a fundamental approach relates to the chemical energy, chemical reactions, solubility of salts, and an important process parameter pH. Modern simulation methods combined with experiments provide a useful tool for the research and design of new processes as well as evaluating changes in the operational conditions of chemical processes. Thermodynamic functions (Gibbs free energy, enthalpy, and entropy) from solution thermodynamics provide a complete thermodynamic description of the system. The knowledge of the adsorbent and solution properties along with the results of the model calculations could be used for optimization of the adsorption process with respect to reaction time and temperature. The effect of solution temperature and the determination of the thermodynamic parameters of adsorption of fluorine onto aluminosilicate-modified trepel (TSM), such as free energy of adsorption, ΔG^o, enthalpy of adsorption, ΔH^o, entropy of adsorption, ΔS^o is important in understanding the adsorption mechanism[1-5].

Fluoride in drinking water is perhaps the only substance producing divergent health effects on the consumer depending upon their relative proportions. While a fluoride concentration in the range of 0.8 to 1.20 mg/l is considered to be beneficial, concentration higher than 1.5 mg/l are reported to be harmful to the teeth and bone structure of men and animals, therefore the problem of removal of excess of fluorine from drinking water is the actual and very important for many global regions.

Based on the nature of processes, the defluoridation techniques that have been employed so far are adsorption [6, 7] and ion exchange [8], precipitation [9], electrochemical method and membrane technique [10, 11]. However these techniques are not in much use primarily because of their expensiveness, inefficiency or failure in mass scale application. Therefore it is aimed to find a suitable low cost environmentally friendly method for removal of fluoride in the drinking water that could be used by common man.

The removal of fluorine excess from underground water is considered an important application of adsorption processes using a suitable adsorbent. There is continuously growing interest in using low cost, commercially available materials for the adsorption of fluorine [12, 13]. Trepel, a siliceous sedimentary rock available in abundance in various locations around the world, has received attention for its unique combination of physical and

chemical properties (such as high permeability, high porosity, small particle size, large surface area, low thermal conductivity and chemical inertness) and as low cost material for the removal of pollutants from wastewater [14]. Previous studies by the authors established that chemical modification of trepel, especially with aluminosilicate compounds, enhanced its fluorine removal capacity and its feasibility for large-scale application to the treatment of natural underground water with increased content of fluorine. Detailed information about the effect of this chemical modification can be found in [14]. A number of experimental parameters are usually considered in these studies, including the effect of agitation speed, particle size, adsorbent mass, initial adsorbate concentration, as well as solution temperature. This paper focuses on the effect of solution temperature on the equilibrium of fluorine removal from solution using aluminosilicate-modified trepel (TSM).

Adsorption reactions are normally endothermic; thus the extent of adsorption generally increases with increasing temperature. The change in the heat content of a system in which adsorption occurs, the total amount of heat evolved in the adsorption of a defined quantity of adsorbate on an adsorbent, is termed the heat of adsorption. When any spontaneous process occurs, there is a decrease in the Gibbs free energy. Further, there must also be a decrease in entropy because the molecules lose at least one degree of freedom when adsorbed [15].

The aim of this paper is therefore to consider the effect of solution temperature on the process of fluorine adsorption. The thermodynamic parameters of the process, such as adsorption free energy, enthalpy and entropy were determined.

2. EXPERIMENTAL MATERIALS AND METHODS

The local trepel with particle size (mm), %: -0.2+0.1 -18.7; -1+0.071 – 10.4; -0.071+0 – 71.9 has been undergone to the structural chemical modification with aluminum compounds and denoted as TSM. A variety of methods, such as powder X-ray diffractometry, BET analysis, and DTA were used for the characterization of the TSM. The phase composition of the modified trepel 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 TSM, 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.

2.1 Modification method

15 g of trepel 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.

2.2 Adsorption experiments

Batch adsorption experiments were conducted to examine time-dependent sorption behavior and the effects of temperature and solution pH on adsorption performance. Following a systematic process, the adsorption uptake capacity of F in batch system was studied in [14]. The data obtained in batch mode studies was used to calculate the equilibrium fluoride adsorptive quantity by using the following expression:

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

where a is the amount of adsorbed fluoride onto TSM per unit weight of the adsorbent in mmol/g, V is the volume of solution treated in liter, C_o is the initial concentration of fluoride ion in mmol/L, C_e is the residual fluoride ion concentration in mmol/L and m is the mass of adsorbent in g/L.

Adsorption studies were carried out at different conditions viz. contact time (1-180 min), pH (4-9), initial fluoride concentration (0.5 - 10 mmol/L), temperature (20, 30 and 40°C), and sorbent dosage (2 – 16 g/L).

The conditions of maximum fluoride removal from solution within studied concentrations interval are as follows: pH = 5.0±0.5; experiment duration – 120min; sorbent dose – 4g/L.

About 0.2 g of the adsorbent was mixed with 50 ml of a desired fluoride solution with known pH

and agitated in a mechanical shaker at 300 rpm at a regular interval of time. The solutions were filtered and collected for analysis and fluoride concentration in the solutions was determined.
Each determination is repeated three times and the results given were the average values.

It has been presented that 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 [4]. The coefficient of determination R^2 is as follows:

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

where a_t is the equilibrium capacity obtained by calculating from the model (mmol/g) and a_e is the experimental data of the equilibrium capacity (mmol/g), and $\overline{a_t}$ is the average of a_t.

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 TSM.

3. RESULTS AND DISCUSSION

Moldavian trepel consisting mainly of: (%) $Si0_2$ – 81,05, Al_2O_3 -5.12, Fe_20_3 - 1.34, MgO - 0.32, CaO - 1.84, Na_2O+K_2O-0.41, LOI -11.04 was used. The X-ray diffractometry showed the presence of different modification of silica: α, β-cristobalit, α-tridimit and α-quartz. Thermal analysis demonstrated the only one endoefect within the temperature range 60 – 140^{0}C with the minimum at 100^{0}C, which is connected to the elimination of physical adsorbed water. The absence of any other effects in the heating curve of the sample indicates about the stability of the SiO_2.
The TSM specific surface area, volume and effective size of the pores were determined as: 72.2 m^2/g; 0.292cm^3/g and 2.8nm [14].

3.2. Effect of temperature on equilibrium isotherm

The analysis of the isotherm data is important to develop an equation which accurately represents the results and could be used for design purposes. Defluoridation capacity of TSM was evaluated using the Langmuir [16], and Freundlich adsorption isotherms [17].
The adsorption isotherms were studied at 20, 30 and 40^{0}C.
In Fig. 1 there are the experimental data of fluorine adsorption on TSM at the various temperatures. The graph is plotted in the form of fluorine amount adsorbed per unit mass of TSM, *a*, against the concentration of fluorine remaining in solution, C_e.

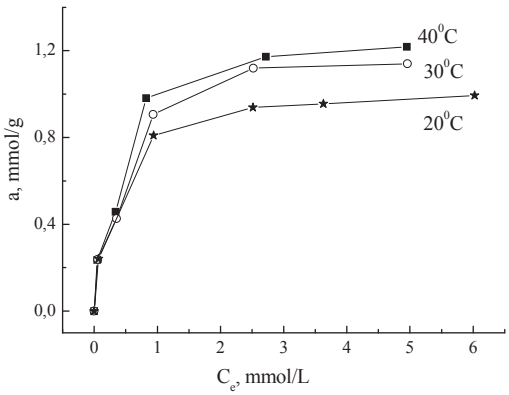

Fig. 1 Isotherms of fluorine adsorption onto TSM at solution temperatures 20, 30, and 40^{0}C

Fig. 1 shows that solution temperature increasing leads to the growth of fluorine adsorption on TSM. The increase in
adsorption values with temperature indicates a higher heat of adsorption with increasing temperature. It might be that stronger bonds are formed at higher temperatures supporting the fact that adsorption is endothermic.
The adsorption capacity of fluorine increases with temperature which is typical for the adsorption of electrolytes from their solution. When the system is in a state of equilibrium, the distribution of fluorine between the TSM and the fluorine solution is of fundamental importance in determining the maximum adsorption capacity of TSM for the fluorine from the isotherm.
Langmuir Isotherm
Langmuir equation which is valid for monolayer sorption onto a surface with a finite number of identical sites which are homogeneously distributed over the adsorbent surface is given by the equation [16]:

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

where *a* is the amount of fluoride adsorbed per unit weight of the sorbent (mmol/g), C_e is the equilibrium concentration of fluoride in solution (mmol/L), a_m is the amount of adsorbate at

complete monolayer coverage (mmol/g) and gives the maximum sorption capacity of sorbent and K_L (L/mg) is Langmuir isotherm constant that relates to the energy of adsorption. Langmuir isotherm constants, a_m and K_L were calculated from the slope and intercept of the linear plot of C_e/a vs C_e of linear equation of Langmuir model:

$$\frac{C_e}{a} = \frac{1}{K_L \cdot a_m} + \frac{C_e}{a_m} \qquad (4)$$

Freundlich Isotherm

The Freundlich isotherm is the earliest known relationship describing the adsorption isotherm [17]. This fairly satisfactory empirical isotherm can be used in adsorption from dilute solutions.

The ordinary adsorption isotherm is expressed by the following equation:

$$a = K_F \cdot C_e^{1/n} \qquad (5)$$

where C_e is the equilibrium concentration in the solution (mmol/L), a - the equilibrium adsorption capacity (mmol/g), K_F is the Freundlich equilibrium equation constant relating to the adsorption capacity, and $1/n$ are empirical constant, indicating the intensity of adsorbent-adsorbat interaction. Linear form of the Freundlich isotherm is as follows:

$$\ln a = \ln K_F + \frac{1}{n} \ln C_e \qquad (6)$$

The parameters K_F and $1/n$ were calculated from the slope and intercept on the linear graph in coordinates of equation (6).

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 onto TSM.

By using non-linear method there was no problem with transformation of non-linear isotherm equation to linear forms. The Langmuir and Freundlich isotherms constants are shown in Table 1.

Table 1 Parameters of Langmuir and Freundlich isotherm for the system TSM-fluorine aqueous solution

Langmuir, T, K	**K_L, L/mg**	**a_m, mmol/g**	**R^2**
293	2.55	1.10	0.9998
303	2.62	1.24	0.9918
313	2.92	1.31	0.9899
Freundlich, T, K	**K_F, L/g**	**$1/n$**	**R^2**
293	0.727	0,192	0,8425
303	0.819	0.250	0.8081
313	0.879	0.245	0.8103

The maximum adsorption capacity a_m, and the adsorption constant, K_L, of Langmuir model were found to increase from 1.04 to 1.22 mmol/g and 2.55 to 2.92 L/mg for an increase in the solution temperatures from 293 to 313 K, respectively. The increase in K_L values with temperature indicates a higher heat of adsorption with increasing temperature. It might be that stronger bonds are formed at higher temperatures supporting the fact that adsorption is endothermic. The Freundlich constants also increase with temperature growth that also indicates on the intensification of interaction between adsorbent and adsorbate. The values of R^2 are close to unity, which means that the isotherms are approaching the Langmuir model and not the Freundlich isotherm.

3.3. Thermodynamic studies

The standard free energy change (ΔG°), enthalpy change (ΔH^o) and entropy change (ΔS^o) are the main thermodynamic characteristics of any adsorption system in equilibrium. Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change, ΔG°, is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Both enthalpy and entropy factors must be considered in order to determine the Gibbs free energy of the process. The fundamental thermodynamic equation that relates all the three above parameters is the follows:

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (7)$$

Where ΔG° is the standard free energy change (KJ/mol), ΔH^o is the enthalpy change (KJ/mol), ΔS^o is the entropy change (KJ/mol·K), T is the absolute temperature (K).

Reactions occur spontaneously at a given temperature if ΔG° is a negative quantity. The free energy of adsorption, considering the adsorption equilibrium constant K is given by the following equation:

$$\Delta G^\circ = -RT \ln K \qquad (8)$$

Where R the universal gas constant (8.314 J/mol K), and K is the equilibrium constant. From equations (7) and (8) a relationship follows between $\ln K$ and T:

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{R} \cdot \frac{1}{T} \qquad (9)$$

The adsorption equilibrium constant, K_L, obtained from linearized Langmuir equation (4) was the base of calculation of ΔG°, and the values of ΔH° and ΔS° are determined from the slope and intercept of the linear plot of *lnK* vs inverse temperature, *1/T* (Fig. 3).

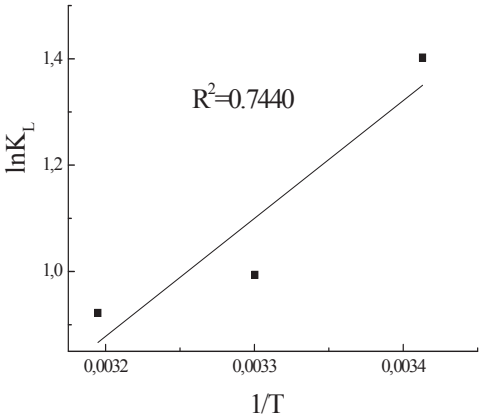

Fig. 3 Dependence $\ln K_L$ of the process of fluorine adsorption onto TSM on inverse solution temperature.

The calculated thermodynamic parameters for the adsorption process of fluorine onto TSM using the K_L from the Langmuir isotherm are shown in Table 2.

Table 2. Calculated thermodynamic constants of the fluorine adsorption on modified trepel.

T, K	*ln K_L*	*-ΔG, kJ/mol*	*ΔH, kJ/mol*	*ΔS, J/mol·K*
293	0.936	2.28	5.23	25.00
303	0.963	2.42		
313	1.072	2.79		

The values of ΔG° calculated using the K_L are found negative for the adsorption of fluorine onto TSM at all temperatures. The negative values confirm the feasibility of the process and the spontaneous nature of the adsorption.

The values of ΔG° were found to decrease -2.28 to -2.79 kJ/mol. The decrease in the value of ΔG° with an increase in temperature indicates that the adsorption process fluorine on TSM becomes more favorable at higher temperatures [1, 3, 4]. The values of ΔH° and ΔS° calculated from the plot of *lnK* versus *1/T* were given as 5.23 kJ/mol and 25.00 J/mol K, respectively. The value of ΔH° was positive, indicating that the adsorption reaction was endothermic. The adsorption energy reflects transfer of one mole of fluoride ion from the bulk solution to the interface. When this value in the range of 1-8 kJ/mol, adsorption can be regarded as a physical process, while its value from 8 to 16 kJ/mol corresponds to ion exchange, and when this magnitude is more than 16 kJ/mol, adsorption can be classified as chemical in nature [18, 19]. Since the enthalpy value of fluorine adsorption on TSM is 5.23kJ/mol, the mechanism of adsorption can be described in terms of physical interaction, for instance by electrostatic or Van-der-Vaals forces.

The positive value of ΔS° reflects the affinity of the TSM for the fluorine and also can indicate that the degree of disorder increases. Due to the fact that during fluorine adsorption on TSM there is a replacement by fluorine and release of hydroxyl groups (which have higher mobility than fluoride ions) from the sorbent surface into the bulk solution. Spontaneous and endothermic adsorption has also been reported for the system of fluorine on magnesia [1], magnesium titanate [3], methylene blue onto bentonite [4], and copper on Na–montmorillonite [20].

4. CONCLUSION

Trepel modified with aluminosilicate compounds (TSM) is able to adsorb fluorine from aqueous solutions. The removal of fluorine using TSM was a function of temperature. The adsorption capacity increased with increasing temperature. It is successful to use the coefficient of determination of the non-linear method for comparing the best fit of the Langmuir and Freundlich isotherms. The Langmuir isotherm had higher coefficients of determination than that of Freundlich isotherm so it is the better-fitting isotherm. Thermodynamic parameter, ΔG° could be calculated from adsorption equilibrium constant (K_L) obtained from Langmuir isotherm. The value of ΔH° and ΔS° could be obtained from the slop and intercept of the relationship between *lnK* and reaction inverse temperature, *1/T*. The negative values of ΔG° indicate the spontaneous nature of adsorption with a high preference of fluorine onto TSM. The value of ΔH° was positive, indicated that the adsorption reaction was endothermic. The positive value of ΔS° shows that increasing randomness at the solid/liquid interface during the adsorption of fluorine on modified trepel.

REFERENCES

[1] V. Aravind, and K. P Elango. - *Adsorption of fluoride onto magnesia – equilibrium and thermodynamics study*. Ind. J. Chem Tech., v.13, p. 476-483, (2006).

[2] M. Sarkar, A. Banerjee, P. P. Pramanick, A. R. Sarkar *Use of laterite for the removal of fluoride from contaminated drinking water*. Journal of Colloid and Interface Science, 302, 432–441, (2006)

[3] V. Gopal and K. P. Elango *Studies on defluoridation of water using magnesium titanate*. Ind. J.Chem Tech., 17, 28-33, (2010)

[4] S. Hong, Ch. Wen, J.He, F.Gan, Y.-S. Ho. *Adsorption thermodynamics of Methylene Blue onto bentonite.* Journal of Hazardous Materials, 167, 630–633, (2009)

[5] Z. Zawani; A. L. Chuah; S. Y. T. Choong, *Equilibrium, Kinetics and Thermodynamic Studies: Adsorption of Remazol Black 5 on the Palm Kernel Shell Activated Carbon (PKS-AC)* European Journal of Scientific Research, Vol. 37, 1, p. 67 (2009).

[6] S. S. Tripathy , A. M. Raichur *Abatement of fluoride from water using manganese dioxide-coated activated alumina*. Journal of Hazardous Materials, 153, 1043–105, (2008.)

[7] X. Fan, D.J. Parker, M.D. Smith. *Adsorption kinetics of fluoride on low cost materials*, Water Res. 37 4929–4937, (2003).

[8] K. Vaaramaa, J. Lehto, *Removal of metals and anions from drinking water by ion exchange*. Desalination, 155, 157–170, (2003)

[9] B.D. Turner, P. Binning, S.L.S. Stipp, *Fluoride removal by calcite: evidence for fluorite precipitation and surface adsorption*, Environ. Sci. Technol., 39, 9561–9568, (2005).

[10] M. Hichour, F. Persin, J. Molenat, J. Sandeaux, C.Gavach, *Fluoride removal from diluted solutions by Donnan dialysis with anion exchange membranes*, Desalination, 122, 53–62, (1999).

[11] T. Ruiz, F. Persin, M. Hichour, J. Sandeaux, *Modelisation of fluoride removal in Donnan dialysis*, J. Membr. Sci. 212 113–121, (2003).

[12] X. Fan, D.J. Parker, M.D. Smith *Adsorption kinetics of fluoride on low cost materials,* Water Research, 37, 4929–4937, (2003)

[13] M. Agarwal, K. Rai, R. Shrivastav, and S. Dass. *A study on fluoride sorption by montmorillonite and Kaolinite.* Water, Air, and Soil Pollution **141:** 247–261, (2002).

[14] V. I. Zelentsov, T. Ya. Datsko, and O. B. Brynza**.** *Study of fluorine adsorption on modified trepel.* International Congress ARA 37, 2013, Chisinau, Moldova, Proc. p. 562-565, (2013).

[15] A. L. Myers *Thermodynamics of Adsorption in Porous Materials,* AIChE Journal, January 2002 Vol. 48, No. 1, (2002).

[16] I., Langmuir *The constitution and fundamental properties of solids and liquids*, J. Am. Chem. Soc., 38, 2221, (1916)

[17] H.M.F. Freundlich. *Over the adsorption in solution*, J. Phys. Chem., A 57, 385, (1906).

[18] A.R. Cestari, E.F.S Vieira, G.S Vieira, L. E. Almeida, *Aggregation and adsorption of reactive dyes in the presence of an anionic surfactant on mesoporous aminopropyl silica*, J. Colloid Interf. Sci., 309(2), 402–411, (2007).

[19] C.A Basar, *Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared waste apricot*, J. Hazard. Mater. B, 135, 232–241, (2006).

[20] M. El-Batouti, O. M. Sadek and F. F. Assaad. *Kinetics and thermodynamics studies of copper exchange on Na–montmorillonite clay mineral.* Journal of Colloid and Interface Science, 259, 223–227, (2003).