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ADSORPTION MODELS FOR TREATMENT OF EXPERIMENTAL DATA ON REMOVAL FLUORINE FROM WATER BY OXIHYDROXIDESOF ALUMINUM

Veacheslav Zelentsov, Tatiana Datsko, Elena Dvornikova
Institute of Applied Physics of the Academy of Sciences of Moldova, Chişinău, Republic of Moldova
vzelen@yandex.ru

Abstract The adsorption of fluorine ions from aqueous solutions by oxihydroxides of aluminum was studied. The equilibrium sorption was explained by using the Lengmuire, Freundlich, Bet and Redlich-Peterson models of isotherms. The results obtained allow one to conclude that the mathematical model of adsorption Freundlich is the best for describing the measured experimental data, which testifies to the heterogeneity of the surface. The parameters of all equations of adsorption were calculated.

Keywords: adsorption models; equilibrium; aluminum oxihydroxides; fluorine adsorption isotherms; constants of the adsorption equations.
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1. INTRODUCTION

Experimental data on adsorption from solutions are, as a rule, presented in the form of dependence of the quantity of substance adsorbed on solid surface vs its equilibrium containing in solution - in form of adsorption isotherm [1 -5]. Adsorption isotherms are used for understanding the mechanism and quantifying the distribution of the adsorbate between the liquid phase and solid adsorbent phase at equilibrium during the adsorption process. For adsorption isotherms interpretation there are several empirical models, among them the most commonly used in sorption studies are the Langmuir [6], Freundlich [7], Redlich-Peterson [8] and BET (Brunauer - Emmett - Teller) [9] models. Langmuir model - a model based on the fact that on the surface of the sorbent is formed monomolecular layer of adsorbate, and all active sites are of equal energy and enthalpy of adsorption. Langmuir equation is as follows:

$$a = \frac{a_m K_L C_e}{1 + K_L C_e}. \tag{1}$$

Freundlich model is used to describe the adsorption on heterogeneous surfaces. Since the adsorption centers of the surface have different values of adsorption energy, the most active sorption centers with maximum energy are filled the first. Here

Freundlich equation is:

$$a = K_F C_e^{\frac{1}{n}}. \tag{2}$$

Redlich-Peterson model combines models of Freundlich and Langmuir and intends to describe in addition of the heterogeneity of the sorbent surface and a certain number of adsorption sites with the same adsorption potential. The equation by Redlich-Peterson is the following:

$$a = \frac{K_R C_e}{1 + \alpha C_e^{\beta}}. \tag{3}$$

BET model provides coverage of the surface with adsorbate multilayers, and as active sites have different energies, multilayers can be formed in different parts of the surface and may arise as to the completion of the monolayer, and after it. The equilibrium constant $K_B ET$ characterizes the interaction energy of the adsorbate with the surface of the adsorbent. The sign of this constant (positive or negative) indicates the applicability or inapplicability of this model to describe the adsorption in this system:

$$a = \frac{a_m K_{BET} C_e C_s}{(C_s - C_e)[C_s + (K_{BET} - 1)C_e]}. \tag{4}$$

In these equations:

- a and a_m - the amount of adsorbed substance at 1g of sorbent at equilibrium and the adsorption capacity of the sorbent at saturation;
- C_e and C_s - equilibrium and limiting concentration (its solubility at a given temperature) of substance in solution;
- K_L, K_F, K_R and K_{BET}-equilibrium constants of the equations of Langmuire, Freundlich, Redlich-Peterson and BET;
- n, α and β - parameters of the equations of Freundlich and Redlich-Peterson.

To the adsorption equilibrium data interpret all the equations are used in linear form:

- Langmuir model

$$\frac{C_e}{a} = \frac{1}{K_L a_m} + \frac{C_e}{a_m}; \tag{5}$$

- Freundlich model

$$\ln a = \ln K_F + \frac{1}{n} \ln C_e; \tag{6}$$

- BET model

$$\frac{C_e}{a(C_s - C_e)} = \frac{1}{a_m K_{BET}} + \frac{(K_{BET} - 1)C_e}{a_m K_{BET} C_s}; \tag{7}$$

- Redlich-Peterson model

$$\ln\left(\frac{K_R C_e}{a} - 1\right) = \ln \alpha + \beta \ln(C_e). \tag{8}$$

The equilibrium constants of the equations are calculated from the slope and the intersection of the line graph in the corresponding coordinates of linear equations (5)-(8): $\frac{C_e}{a}$ vs C_e, $\ln a$ vs $\ln C_e$, $\frac{C_e}{a(C_s - C_e)}$ vs $\frac{C_e}{C_s}$ and $\ln\left(\frac{K_R C_e}{a} - 1\right)$ vs $\ln(C_e)$.

2. MAIN RESULTS

This paper studies the equilibrium adsorption of fluoride ions in the Al_2O_3 - NaF system and clarifies the applicability of different models for interpreting experimental data on adsorption of fluoride - ion on aluminum oxihydroxides. All the above models have been applied for calculation of the isotherms of fluorine adsorption on aluminum oxihydroxides and the calculated isotherms have been compared with the experimental ones. For the absorption of fluorine from aqueous solutions were used 2 samples of aluminum oxyhydroxide A100 and A600. The first sample presents aluminum trihydrate containing 2.85 moles of water per 1 mole of Al_2O_3 ; A600 - consisting of a crystalline aluminum oxide γ-Al_2O_3 with composition of 0.09 mole H2O/mol Al_2O_3 . Adsorption of fluorine from solutions with initial concentration of 0.05 - 0.25 mol F / L was carried out in acetate buffer at optimum pH of 5.9. [10]. The amount of adsorbed fluoride was calculated by using the formula:

$$a = \frac{(C_0 - C_e)V}{m}, \ mmol/g \tag{9}$$

where C_0 and C_e - initial and equilibrium concentration of fluoride in solution, mmol / L; V - volume of initial solution, l; m - mass of the sample sorbent, g. The fluoride adsorption isotherms are shown in Fig. 1. The figure shows that for small (2-5mmol / L) concentrations of fluorine (the initial parts of the isotherms), the adsorption is almost directly proportional to the concentration of fluoride and there is a sharp rise of the curves. This indicates a strong interaction of the adsorbate with the surface of the adsorbent. With increasing concentration of fluoride in the solution the degree

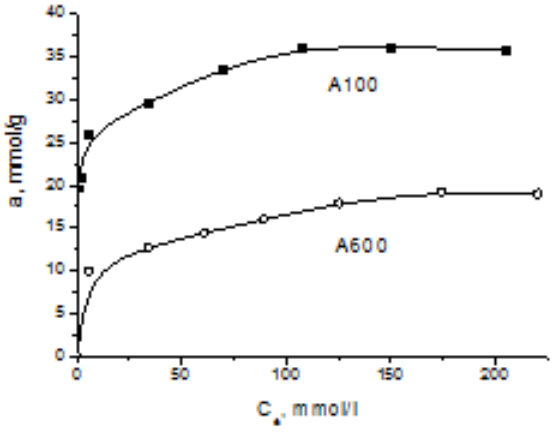

Fig. 1. Adsorption isotherms of fluorine on aluminum oxihydroxides

of its extraction increases. With further growth of the concentration of fluoride in the solution curves almost reach saturation. Comparison of sorption isotherms for samples A100 and A600 shows that the isotherm of the first sample is located higher than the second, indicating a greater affinity of fluoride ions to hydroxide than aluminum oxide. Plots designed on the base of linear equations (5)-(8) are shown in Fig. 2 It should be noted that in contrast to equations of models (1), (2), (4), which contains two parameters, equation of model (3) - Redlich-Peterson has 3 constants, and therefore it is impossible to use its linear form to determine the constants. In this case, we used a procedure to maximize [11]. Linear forms of the isotherms of (5) - (8) express the minimum deviation between the experimental equilibrium adsorption data and theoretical calculations.

It is important to note that the data for A100 and A600 fit well on straight lines (Fig. 2a, b, c, d), which serves as proof that the models can be used to describe the sorption of fluoride by these samples. The calculated values of the constants of equations and correlation coefficients R^2 are presented in the table. The data in the table show that Freundlich model (highest R^2 = 0.9935 and 0.9961 for A100 and A600, respectively) fits best for description of fluoride sorption on the studied samples. According to this model, adsorption occurs on heterogeneous surfaces and active sites have different values of adsorption energy. Langmuir model, which assumes homogeneity, including energy, the surface gives the minimum value of R^2, which may serve as confirmation of the applicability of the Freundlich model.

On the adequacy of the description of the adsorption of fluoride on the samples A100 and A600 the models are arranged in the following order:

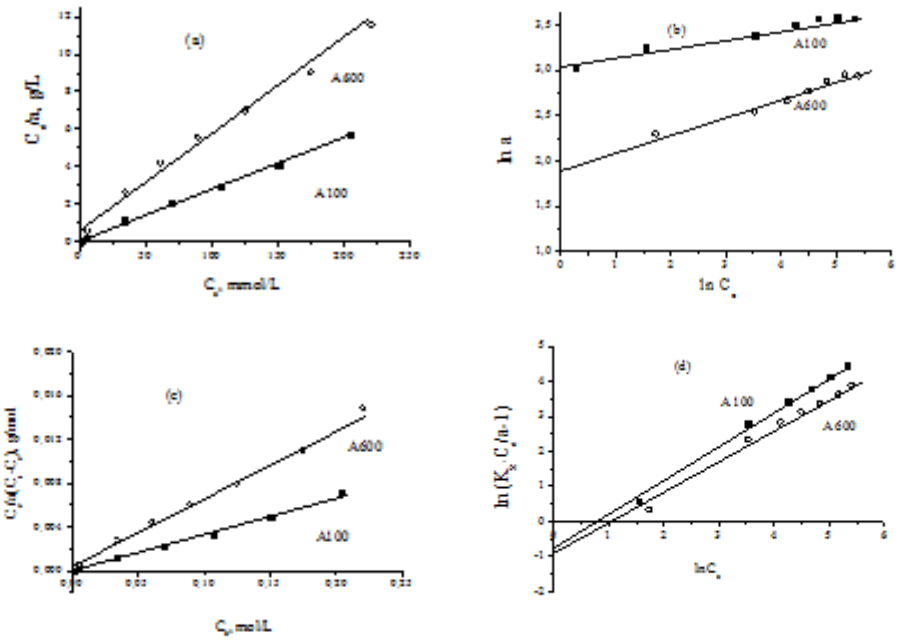

Fig. 2. Adsorption isotherms of fluorine on A100 and A600 in coordinates of linearized equations: (a) - Langmuir; (b) - Freundlich; (c) - BET; (d) - Redlich-Peterson

Table 1 The parameters of Lengmuire, Freundlich, BET and Redlich-Peterson equations at the adsorption of fluorine on aluminum oxihydroxides

sample	Lengmuire model			Freundlich model		
	K_L, L/mmol	a_m, mmol/g	R^2	K_F, (mmol/g)·(L/mmol)$^{1/n}$	$1/n$	R^2
A100	0.230	36.23	0.8981	20.90	0.116	0.9935
A600	0.065	19.60	0.9607	6.65	0.201	0.9961
sample	BET model			Redlich-Peterson model			
	K_{BET}, g/mmol	a_m, mmol/g	R^2	K_R, L/g	α	β, L/mmol	R^2
A100	9.239	30.80	0.9702	15.40	0.527	0.945	0.9876
A600	0.151	15.60	0.9886	4.31	0.520	0.854	0.9948

Adsorption model	Freundlich	> Redlich-Peterson >	BET >	Langmuire
A100, R^2	0.9935	0.9876	0.9702	0.8981
A600, R^2	0.9961	0.9948	0.9886	0.9607

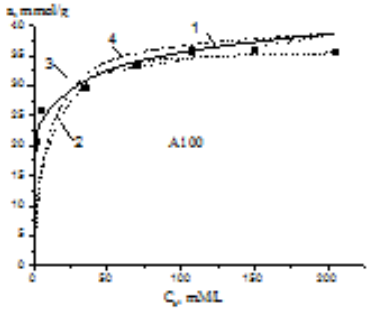

Fig. 3. Experimental adsorption isotherm -of fluorine on A100 (dots) and calculated according the models: 1- Freundlich; 2 - Lengmuire; 3 - BET; 4 - Redlich-Peterson

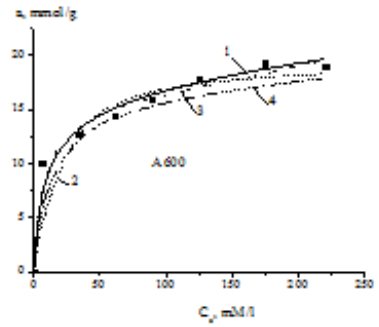

Fig. 4. Experimental adsorption isotherm -of fluorine on A600 (dots) and calculated according the models: 1- Freundlich; 2 - Langmuir; 3 - BET; 4 - Redlich-Peterson.

Fig. 3 and 4 show the experimental adsorption isotherms of fluoride on the sample A100 and A600 and the isotherms, calculated by the models of Langmuir, Freundlich, Redlich - Peterson and BET for comparison which are plotted in the same graphs.

From the figures it is clear that the Freundlich model best describes the experimental results.

3. CONCLUSIONS

A comparative study of the applicability of adsorption models of Langmuir, Freundlich, BET, and Redlich-Peterson to describe the experimental adsorption isotherms of fluoride on 2 samples of aluminum oxihydroxides, (A100) -hydroxide and (A600)

-alumina has been carried out. The constants and parameters of these equations have been defined. Comparing the regression coefficients R2 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.

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