Modeling of the kinetics of fluorine sorption onto modified trepel

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The application of kinetic models of pseudo first and second order for the description of experimental kinetic data related to the adsorption of fluorine ions on trepel modified by aluminum compounds (TMA) is discussed in this work. The pseudo-first-order kinetic model is expressed as [1]:

$$\frac{\mathrm{d}a_t}{\mathrm{d}t} = k_1(a_m - a_t) \tag{1}$$

Integrating within the boundary conditions $t = 0$ to $t = t$ and $a_t t = 0$ to $a_t = a_m$ gives the linearized form as

$$\ln(a_m - a_t) = \ln a_m - k_1 t \tag{2}$$

The pseudo-second order Mackay and Ho model [2] is expressed as

$$\frac{\mathrm{d}a_t}{\mathrm{d}t} = k_1(a_m - a_t)^2 \tag{3}$$

Rearranging and integrating Eq. (3) with respect to the boundary conditions $t = 0$ to $t = t$ and $a_t = 0$ to $a_t = a_m$ gives the linearized form as

$$\frac{t}{a_t} = \frac{1}{k_2}a_m^2 + \frac{t}{a_m} \tag{4}$$

where a_m and a_t[mmol/g] are the the amounts of fluoride ions adsorbed at equilibrium at time t, respectively; k_1[min^{-1}] is the pseudo-first-order rate constant and k_2[mmol/(g min] is the rate constant of the pseudo-second order kinetics.

Employing the linearized form of pseudo-first-order model ($\ln(am - at) = f(t)$, Eq. (2)) and linearized form of pseudo-second-order model (t/a_t, versus contact time (t), Eq. (4)) we determined the constants k_1, k_2, and a_m values using the slopes and intercept points of the linear plots. The results are illustrated in Table.1.

Table 1. The kinetic parameters of adsorption of fluorine ions onto TMA and correlation coefficients R2 of two kinetic models

Kinetic model	Parameters			
Pseudo 1	k_1 min^{-1}	a_{calc} mmol/g	a_{exp} mmol/g	R^2
	0.050	0.041	0.241	0.6303
Pseudo 2	k_2 mmolg^{-1}min^{-1}	a_{calc} mmol/g	a_{exp} mmol/g	R^2
	12.827	0.240	0.241	0.9999

Experimental conditions: $m = 0.2$g, $v = 50$ml, $T = 20\,°C$, $t = 120$min., $Co = 1.03$, mmolF/L The found rate constants of fluorine adsorption were used for calculation of the adsorption values of fluorine on TMA and for construction of kinetic curves. The correlation coefficients R^2 for the pseudo-first-order kinetic model is not high ($R^2 = 0.6303$), the determined values of a_m calculated from the equation (2) differ from the experimental values (Table 2). This indicates that adsorption of fluorine onto TMA does not follow the pseudo-first-order reaction model.

Table 2. Comparison of the experimental adsorption kinetics of fluorine ions on the trepel TMA sample with those calculated from the kinetic models

t, min	a_{exp} mmol/g	a_{calc} mmol/g by Eq. (4)	a_{calc} mmol/g by Eq. (2)	Relative error $\triangle$, %(Eq. (4)
1	0.194	0.182	0,001	6.0
2	0.216	0.208	0.023	2.3
3	0.223	0.218	0.034	4.0
5	0.229	0.227	0.054	5.7
10	0.234	0.234	0.095	6.0
20	0.236	0.238	0.015	4.7
30	0.238	0.239	0.187	3.0
60	0.239	0.240	0.0229	3.0
90	0.240	0.241	0.240	2.0
120	0.241	0.241	-	2.1

It can be seen from the Table 1 the R^2 for the pseudo-second-order kinetic model has the maximum value ($R^2 = 0.9999$) and a small relative error ($\triangle$,%), Table 2; this indicates that this model most accurately describes the experimental kinetic data on the fluorine adsorption on aluminum-modified trepel. The analytical expression is obtained for the pseudo-second-order equation, which has the following form:

$$a_t = \frac{0.744}{1 + 3.078t}$$

The equation makes it possible to calculate theoretically the values of fluorine adsorption to TMA for any time of the sorption process.

Bibliography

[1] G. Sujana, R. S. Thakur, and S. B. Rao, *Removal of fluoride from aqueous solution by using alum sludge*, Journal of Colloid and Interface Science, **206**(1998) 94–101

[2] G. McKay, Y.S. Ho, *Pseudo-second-order model for sorption processes*, Process Biochem. **34**(1999) 451–465.