ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 5, pp. 801−804. © Pleiades Publishing, Ltd., 2009.
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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Kinetics of Chromium(VI) Adsorption from Model Solutions on Iron Oxide

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Received February 8, 2008

Abstract—Adsorption of Cr(VI) on Fe_2O_3 from model solutions with various Cr(VI) concentrations was studied. The adsorption capacity was determined, the constants of chromium(VI) adsorption on iron(III) oxide for the pseudo-second-order model were calculated, and the diffusion coefficients for the process were evaluated.

DOI: 10.1134/S1070427209050097

Because of stringent requirements to the content of Cr(VI) in industrial wastewaters [1], active efforts are made to develop procedures for its removal. For example, Chang Jun-ling et al. [2] examined how pH, Cr(VI) concentration, sorption time, and dosage of activated carbon affect the adsorption power toward Cr(VI). The activated carbon tested in their study proved to be an excellent sorbent which could be readily regenerated. Channalov and Molebnov [3] examined the possibility of purifying chromium-containing solutions using as sorbents wastes from local industry (sawdust, lignin). The treatment was performed in the static mode. To increase the sorption capacity, the sawdust was modified with alkalis or acids. It was found that modification with 0.5% sulfuric acid or 0.5% sodium hydroxide was the most efficient. The chromium concentration was decreased in a six-step process to 0.1 mg l^{-1}. At pH 1–3, the sorption capacity of VION anion-exchange fibrous materials studied by Zverev et al. [4] was higher than that at higher pH values, which was attributed by the authors to protonation of weakly basic groups of the anion-exchange fibers.

In this study we examined the kinetics of Cr(VI) adsorption on Fe_2O_3 from model solutions with various Cr(VI) concentrations.

EXPERIMENTAL

Experiments were performed with simulated wastewater prepared by dissolving CrO_3 in water to obtain chromic acid. The Cr(VI) concentration was 25–150 mg l^{-1}. As adsorbent we used γ-Fe_2O_3 with a bulk density of 1.092 g cm^{-3}. Adsorption was performed under static conditions with stirring for 60 min. The amount of Fe_2O_3 (g) per 100 ml of H_2CrO_4 solution was varied from 0.1 to 14. The size of Fe_2O_3 granules was 1 mm. The content of Cr(VI) and Cr(III) present in the simulated wastewater simultaneously was determined photometrically [5]. All measurements were performed with a Spekol-211 spectrophotometer at λ = 320 nm, spectral band width of 15 nm, amplification coefficient of 200, and cell thickness of 10 mm. The solution temperature, 20°C, was maintained with an accuracy of ±2°C using a UTU-4 thermostat. The pH of solutions was adjusted with HCl (pH 2). The pH values of the simulated solutions were measured with an I-130 pH meter using glass and silver chloride electrode.

The adsorption kinetics was studied with the aim to obtain a model of the solute adsorption. Obviously, the adsorption depends on the time of contact of the adsorbent with the solution. The kinetics of the Cr(VI) adsorption on iron(III) oxide was analyzed using pseudo-first- and pseudo-second-order equations [6, 7] and also a kinetic model taking into account the diffusion inside adsorbent grains [8, 9]. The pseudo-first-order equation is as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t), \quad (1)$$

Table 1. Adsorption capacities q_t of iron(III) oxide and degrees of chromium(VI) recovery Y at various initial Cr(VI) concentrations c_0 (20°C, sorption time 1 h)

S/L ratio[a]	c_0, mg l^{-1}											
	25			50			100			150		
	c_t, mg l^{-1}	Y, %	q_t, mg g^{-1}	c_t, mg l^{-1}	Y, %	q_t, mg g^{-1}	c_t, mg l^{-1}	Y, %	q_t, mg g^{-1}	c_t, mg l^{-1}	Y, %	q_t, mg g^{-1}
0.1	20	18	4.6	41	18	9.1	83	17	16.6	129	14	20.8
0.2	14	43	5.4	28	44	11.0	57	45	21.5	104	31	23.1
0.5	11	56	2.8	20	59	5.9	37	63	12.6	71	53	15.8
2.0	0	100	1.3	12	76	1.9	17	83	4.2	49	67	5.1
4.0	–	–	–	7	86	1.1	11	89	2.2	39	74	2.8
6.0	–	–	–	0	100	0.8	6	94	1.6	29	80	2.0
8.0	–	–	–	–	–	–	4	96	1.2	24	84	1.6
10.0	–	–	–	–	–	–	2	99	1.0	13	92	1.4
12.0	–	–	–	–	–	–	0	100	0.8	2	99	1.2
14.0	–	–	–	–	–	–	–	–	–	0	100	1.1

[a] (S/L) Fe_2O_3 amount (g) per 100 ml of solution.

where q_e and q_t are the adsorption capacities of the adsorbent at equilibrium and by the time t, respectively (mg g^{-1}); k_1, pseudo-first-order rate constant of adsorption (l min^{-1}).

The pseudo-second-order rate equation of the adsorption [7] can be given as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2, \quad (2)$$

where k_2 is the pseudo-second-order rate constant of adsorption (g mg^{-1} min^{-1}).

The adequacy of the suggested model to the experimental data is characterized by the correlation coefficient R (it is close or equal to 1). The relatively high value of R indicates that the suggested model successfully describes the kinetics of the Cr(VI) adsorption. The experimental results of studying the adsorption kinetics are given in Tables 1 and 2.

Molecular diffusion controls the rate of the majority of mass exchange processes. Determination of the diffusion coefficient is very important for evaluation of mass exchange processes. The diffusion rate constant for the model of diffusion control of a finite volume [10] was determined by the equation

$$\frac{d(1-\omega\bar{X})}{dt} = \frac{-3\overline{VD}Kc_0^{1-z}\left(1-\omega\bar{X}\right)^{2-z}}{V\bar{r}^2\left\{1-\left[(1-\bar{X})+\bar{X}\left(\frac{\bar{r}_s}{\bar{r}}\right)^3\right]^{1/3}\right\}}, \quad (3)$$

where $\bar{X}$ is the degree of filling of the adsorption layer (fractions of unity); $\bar{r}_s$, mean radius of the adsorbent granule (mm); ω, ratio of the equilibrium adsorption capacity of the adsorbent to the initial amount of the adsorbent in the solution (fractions of unity); and c_0, initial concentration of the adsorbate in the solution (mg l^{-1}).

Using the dependences $\omega = [1 - (\bar{r}_s/\bar{r})^3]$ and $\bar{X}_0 = (\bar{r}_s/\bar{r})^3\bar{X}$, we obtained $\omega = (1 - \bar{X}_0/\bar{X})$ and made the corresponding substitution in Eq. (3). The subsequent transformations gave

$$\bar{X} = \left(\frac{18\overline{VD}\lambda}{V\bar{r}^2}\right)^{1/2} t^{1/2} + \bar{X}_0. \quad (4)$$

The plot of $\bar{X}$ vs. $t^{1/2}$ should be linear with the absolute term $\bar{X}_0$. With this fact taken into account, the equation can be written as follows:

$$\ln[1/(1-\bar{X}+\bar{X}_0)] - 3[1-(1-\bar{X}+\bar{X}_0)^{1/3}] = \frac{3\overline{VD}\lambda}{V\bar{r}^2}t. \quad (5)$$

According to this model, the dependence of $\ln[1/(1 - \bar{X} + X_0)] - 3[1 - (1 - \bar{X} + X_0)^{1/3}]$ on t should also be linear. The calculation results obtained with Eqs. (4) and (5) are given in Table 2. Equation (5) ensures smaller deviation between the calculated values (Table 2) and experimental data, and therefore it describes the adsorption of chromium(VI) on iron(III) oxide most adequately.

As the initial concentration of chromium(VI) solution is increased from 25 to 150 mg l^{-1}, the adsorption capacity for Cr(VI) increases from 4.6 to 20.8 mg g^{-1} (Table 1, for S/L = 0.1). This effect is due to an increase in the driving force of adsorption [11]. The pseudo-second-order kinetic model ensures high correlation coefficients between the experimental and calculated data (Table 2, $R_2 > 0.95$).

In our experiments, pH of solution was kept equal to 2 to attain 100% recovery of Cr(VI). In the simulated solution, chromium mainly exists in oxidation states +6 and +3. It is known [12] that the prevalent form of Cr(VI) at pH 2 is $HCrO_4^-$. This anion is preferentially adsorbed on iron oxide.

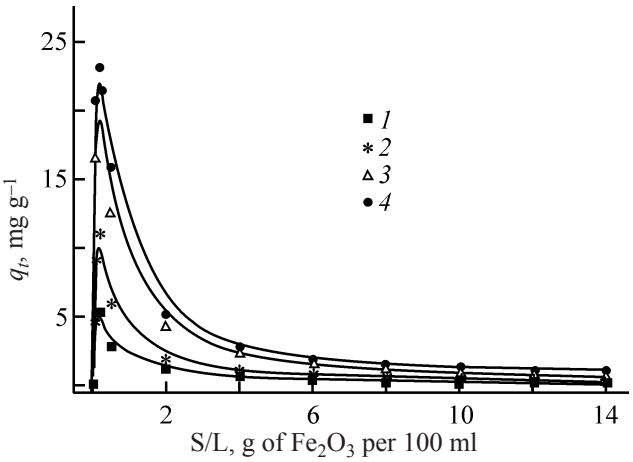
Table 2 shows that the constant h (mg g^{-1} min^{-1}) is higher at high initial concentrations of Cr(VI), especially at initial concentrations of 100 and 150 mg l^{-1}.

The mean value of the diffusion rate constant $\bar{D}\lambda$ for iron oxide as adsorbent decreases from 3.6×10^{-6} to 0.43×10^{-6} cm^2 s^{-1} (i.e., by a factor of ~9) with an increase in the sorbent amount from 0.1 to 8.0 g of Fe_2O_3 per 100 ml of solution.

The dependence of the degree of Cr(VI) adsorption on S/L at 20°C is shown in the figure. In this case, pH of the simulated solution was not kept constant using a buffer solution. The amount of the adsorbed Cr(VI) is maximal at S/L = 0.2 g of Fe_2O_3 per 100 ml of Cr(VI) solution at any initial Cr(VI) concentrations. This is due to the fact that introduction of iron oxide was accompanied by its hydrolysis and affected pH of the solution. Hydrolysis of Fe_2O_3 led to an increase in pH of the solution, which,

Table 2. Calculated rate and diffusion constants for the considered models of adsorption on Fe_2O_3 at various initial Cr(VI) concentrations

m_s Fe_2O_3, g	mg l^{-1}	Pseudo-second-order constants				Calculation of $\lambda D \times 10^6$, cm^2 s^{-1}, by indicated equation	
		$k_2 \times 10^{-3}$, g mg^{-1} min^{-1}	R^2	c_0, mg g^{-1}	h, mg g^{-1} min^{-1}	(4)	(5)
0.1	25	16	0.95	4.6	0.3	1.1	3.4
	50	18		9.1	1.5	1.9	7.1
	100	19		18.0	5.9	2.5	6.9
	150	22		21.0	9.3	2.9	3.2
0.2	25	33		5.4	0.96	0.6	2.1
	50	41		11.0	5.0	1.4	3.2
	100	109	0.99	21.5	50.4	3.1	11.3
	150	178		23.0	94.8	3.2	12.5
0.5	25	180		2.8	1.4	0.5	1.1
	50	144		5.9	5.1	0.7	1.9
	100	88		12.6	14.0	1.0	3.8
	150	83		15.8	20.8	1.1	4.1
2.0	25	255		1.3	0.4	0.2	0.9
	50	369		1.9	1.4	0.3	1.0
	100	260		4.2	4.6	0.5	1.3
	150	380		5.1	9.9	0.6	1.6
4.0	50	373		1.1	0.4	0.3	1.1
	100	2322		2.2	11.5	0.3	1.2
	150	3468	0.99	2.8	26.6	0.3	1.3
6.0	50	3255		0.8	2.3	0.2	0.9
	100	4967		1.6	12.1	0.2	1.5
	150	2187		2.0	8.8	0.2	1.1
8.0	100	2374		1.2	3.4	0.1	0.6
	150	2988		1.6	7.5	0.2	0.9
10.0	100	5637		1.0	5.5	—	—
	150	5556		1.4	10.6	—	—
12.0	100	76	1.0	0.8	0.1	—	—
	150	7507	0.99	1.2	11.4	—	—
14.0	150	9740		1.1	11.2	—	—



Degree of adsorption of Cr(VI) on Fe_2O_3 q_t as a function of the S/L ratio. 1 h, 20°C. Initial Cr(VI) concentration, mg l^{-1}: (*1*) 25, (*2*) 50, (*3*) 100, and (*4*) 150.

in turn, led to a decrease in the adsorption capacity of the adsorbent for Cr(VI). The adsorption capacity of the adsorbent for Cr(VI) for the chosen ratio increases from 5.4 to 23.1 mg g^{-1} with an increase in the initial Cr(VI) concentration from 25 to 150 mg l^{-1}. With a further increase in the amount of the sorbent, the adsorption capacity does not noticeably change, which is due to an increase in pH of the solution.

CONCLUSIONS

(1) The kinetics of Cr(VI) adsorption on Fe_2O_3 at various initial concentrations of the solution can be described by a pseudo-second-order rate equation. The pseudo-second-order rate constants increase from 0.016 to 9.740 g mg^{-1} min^{-1} with an increase in the Cr(VI) concentration. This fact indicates that the adsorption is diffusion-controlled.

(2) The maximal adsorption capacity of Fe_2O_3 for Cr(VI) is 23 mg g^{-1} at S/L = 0.2 g of Fe_2O_3 per 100 ml of solution. With an increase in the initial Cr(VI) concentration in the solution from 25 to 150 mg l^{-1}, the adsorption capacity increases from 4.6 to 23.0 mg g^{-1}.

(3) The mean diffusion rate constant $\bar{D}\lambda$ for iron oxide as adsorbent decreases from 3.6×10^{-6} to 0.43×10^{-6} cm^2 s^{-1} (i.e., by a factor of ~9) with an increase in S/L from 0.1 to 8.0 g of Fe_2O_3 per 100 ml of solution.

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