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Sorption of Chromium(VI) from Aqueous Solutions on AM-2b Anion Exchanger

L. A. Voropanova and E. Yu. Getoeva

North-Caucasus State Technological University, Vladikavkaz, North Ossetia, Russia

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Abstract—Sorption of chromium(VI) from a solution with the initial concentration of CrO_3 of up to 30 mg dm^{-3} on a commercial macroporous AM-2b anion exchanger pretreated by various methods was studied. The optimal conditions for efficient sorption were found.

Sorption of metal ions on a number of sorbents is largely influenced by the solution acidity. Sorption of Cr(VI) from solutions with various pH was studied in [1, 2]. It was shown that sorption is governed by the state of ions in the solutions, which, in turn, depends on pH. For example, at pH < 7 chromium(VI) solutions contain the $Cr_2O_7^{2-}$, $HCrO_4^-$, and CrO_4^{2-} ions, whereas at pH > 7 they contain the $HCrO_4^-$ and CrO_4^{2-} ions. In 0.5–2.0 N solutions of H_2SO_4 the $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ anions are formed. Polycondensation of CrO_4^{2-} anion in acidified aqueous solutions yields chromium(VI) isopolyanions:

$$nCrO_4^{2-} + 2(n - a)H^+ = Cr_nO_{3n+a}^{2a-} + (n - a)H_2O. \quad (1)$$

The final polycondensation products are hydrated polymeric oxides with the composition $(CrO_3)_n \cdot mH_2O$. All intermediates containing polyanions have some oxygen excess in comparison with the trioxide. The composition of these intermediates can be presented by the general formula $Cr_nO_{3n+a}^{2a-}$, where n is the number of chromium(VI) atoms in the anion and a is the excess of oxygen atoms in the polyanion relative to the trioxide [3]. At the same time, CrO_2^{2+} cations are known, for which $a < 0$. It was found [3] that a and n are integer quantities varying from –4 to 1 and from zero to infinity, respectively.

For studying chromium(VI) sorption, we used macroporous bifunctional AM-2b anion exchanger containing benzyldimethylamine and benzyldimethylammonium functional groups [4].

Sorption was carried out under static conditions with continuous stirring at a constant pH as in [5, 6]. The sorbent was saturated with 0.1 N solutions of H_2SO_4 or NaOH (SO_4^{2-} and OH^- forms) for 1 h or kept in distilled water (Cl^- form).

Data on sorption from solutions with the initial concentration C_{init} = 3000, 1500, and 1500 mg dm^{-3} recalculated on CrO_3 are given in Figs. 1a–1c for the AM-2b sorbent (weight 2 g) in the SO_4^{2-}, OH^-, and Cl^- forms, respectively.

For the anion exchanger in the SO_4^{2-} form in the range pH 2–12 the dependence of the residual concentration on solution pH passes through four minima: at pH 2, 4, 6, and 9. In this case, the exchange sorption capacity (ESC) in 20 min is 160, 170, 150, and 130 mg of sorbate per gram of sorbent, respectively.

For the anion exchanger in the OH^- form in the range pH 1–11 the dependence has three minima: at pH 1, 3, and 6 (Fig. 1b). The ESC is 130, 127, and 110 mg g^{-1}, respectively.

For the anion exchanger kept in water (Cl^- form) at pH 1–11 the best results were obtained at pH 2–6 and 9 (Fig. 1c). The ESC is 144 and 90 mg g^{-1}, respectively.

As seen from Fig. 1, the sorption depends on both pH and conditions of sorbent pretreatment, because it is determined by the state of chromium(VI) ions in the solution and the state of functional groups of the anion exchanger [1]. Probably, the sorption maximum at pH ≤ 4 is due to the formation of isopolychromates and to the increased degree of protonation of the amine groups of the anion exchanger [1]. The sorption at pH < 7 is governed by the formation of $Cr_2O_7^{2-}$ ions being the product of polymerization of monomers in the solution. The sorption maximum at pH 9 results from the ion exchange with CrO_4^{2-} anions and from complexation in the resin phase. The

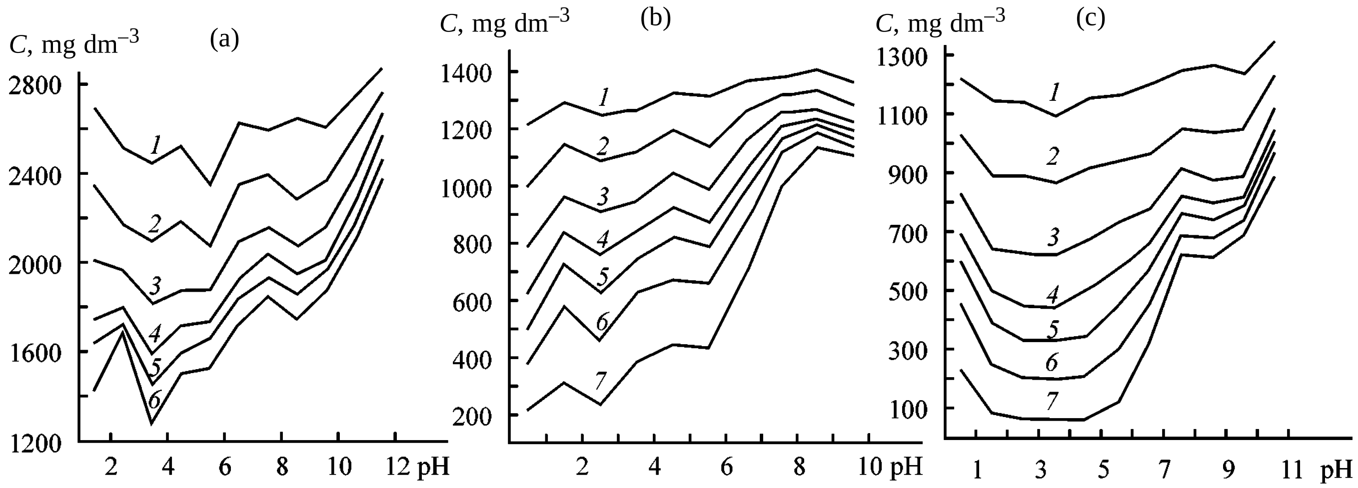

Fig. 1. Residual concentration of Cr(VI) ions *C* vs. solution pH at various times of sorption on AM-2b anion exchanger. Sorption time (min): (*1*) 2, (*2*) 5, (*3*) 10, (*4*) 15, (*5*) 20, (*6*) 30, and (*7*) 60. (a) SO_4^{2-} form, (b) OH^- form, and (c) preliminary treatment in water.

shift of the third maximum toward more acidic region (Fig. 1b) may be due to the fact that the low-basic groups of the AM-2b anion exchanger in the OH^- form loss virtually completely the exchange capability at pH ≥ 9.

The kinetic curves of Cr(VI) sorption on AM-2b anion exchanger kept in water at pH 4 are shown in Fig. 2.

Figure 3 demonstrates the isotherms of chromium(VI) sorption for the sorption time of 60 and 80 min, constructed from the data in Fig. 2.

As seen from Figs. 2 and 3, sorption increases with increasing time and initial solution concentration, which is due to polymerization.

By kinetic analysis of sorption using the substitution and graphical procedures [6], we determined the order *n* of the process with respect to the sorbate ($n = 2$):

$$-dC/d\tau = kC^n,$$

where *C* is the residual concentration of the sorbate in the solution, τ is the sorption time, and *k* is a constant.

The second order of the process suggests that the sorption process is kinetically controlled and is limited by chromium complex formation on the sorbent surface [6].

The sorption rate limited by complex formation is also governed by pH of the medium. Chromium(VI)-containing ions polymerize by polycondensation reaction (1) involving protons or hydroxide ions.

In the systems studied, the composition and struc-

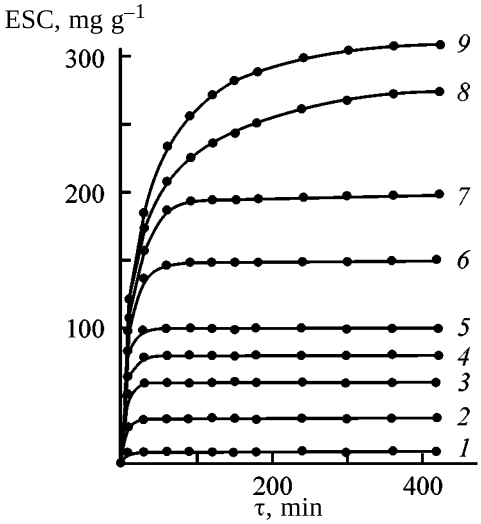

Fig. 2. Kinetic curves of Cr(VI) sorption on AM-2b anion exchanger kept in water at pH 4. (ESC) exchange sorption capacity. Initial concentration of CrO_3, mg dm^{-3}: (*1*) 100, (*2*) 340, (*3*) 600, (*4*) 800, (*5*) 1000, (*6*) 1500, (*7*) 2000, (*8*) 3000, and (*9*) 4000. The same for Fig. 3.

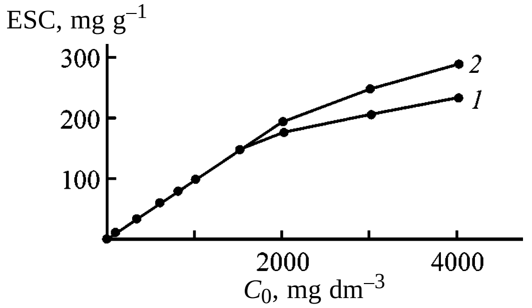

Fig. 3. Isotherms of chromium(VI) sorption for sorption times (*1*) 60 and (*2*) 180 min. (C_0) initial concentration of CrO_3.

ture of chromium(VI) isopolyanion of the composition Cr_nO_{3n+1} are governed by pH of the initial solution. However, reaction (1) is not in equilibrium but continues in the course of the ion-exchange process, which is confirmed experimentally by pH variations in the course of sorption.

Sorption can proceed by the reactions [7]

$$2RCl + CrO_4^{2-} = R_2CrO_4 + 2Cl^-,$$

$$mR_2CrO_4 + (n - m)CrO_4^{2-} + (n - 1)H^+$$
$$= R_{2m}Cr_nO_{3n+1}(OH)_{n-1},$$

$$2RCl + HCrO_4^- = R_2OHO_3Cr^+ + 2Cl^-, \text{ etc.}$$

Table 1. Kinetic analysis of chromium(VI) sorption at pH 4, performed by kinetic equations for gel and film using data of Fig. 2

C_0, mg dm^{-3}	Film kinetics		Gel kinetics	
	$K \times 10^2$	r*	$B \times 10^3$	r
340	21.18	0.9993	2.41	0.9952
600	21.32	0.9983	2.39	0.9969
800	15.28	0.9998	1.85	0.9987
1000	15.72	0.9943	2.05	0.9983
1500	8.29	0.9920	1.01	0.9967
2000	5.94	0.9969	0.63	0.9988
3000	2.31	0.9567	0.22	0.9852
4000	1.76	0.9618	0.16	0.9852

* (r) Correlation coefficient.

Table 2. Diffusion coefficient D at various times of contact τ of AM-2b anion exchanger with Cr(VI) solution at pH_{sorp} 4 as calculated from data of Fig. 2

τ, min	$B\tau$	$D \times 10^6$, cm^2 s^{-1}	τ, min	$B\tau$	$D \times 10^6$, cm^2 s^{-1}	τ, min	$B\tau$	$D \times 10^6$, cm^2 s^{-1}	τ, min	$B\tau$	$D \times 10^6$, cm^2 s^{-1}
C_0^* = 340 mg dm^{-3}			C_0 = 600 mg dm^{-3}			C_0 = 800 mg dm^{-3}			C_0 = 1000 mg dm^{-3}		
1	0.00097	1.2	1	0.00087	1.1	1	0.00034	0.4	1	0.000005	0.1
2	0.00128	1.6	2	0.00133	1.7	2	0.00056	0.7	2	0.000008	0.1
3	0.00154	1.9	3	0.00179	2.3	3	0.00075	1.0	3	0.00132	1.7
4	0.00171	2.2	4	0.00206	2.6	4	0.00101	1.3	4	0.00173	2.2
5	0.00188	2.4	5	0.00216	2.7	5	0.00125	1.6	5	0.00203	2.6
7	0.00236	3.2	7	0.00241	3.0	7	0.00167	2.1	6	0.00193	2.4
10	0.00283	3.3	10	0.00246	3.1	10	0.00186	2.3	7	0.00211	2.7
15	0.00294	3.7	15	0.00286	3.6	15	0.00199	2.5	8	0.00207	2.6
						20	0.00208	2.6	9	0.00219	2.8
						25	0.00216	2.7	10	0.00223	2.8
									15	0.00216	2.7
									20	0.00208	2.6
									25	0.00216	2.7
C_0 = 1500 mg dm^{-3}			C_0 = 2000 mg dm^{-3}			C_0 = 3000 mg dm^{-3}			C_0 = 4000 mg dm^{-3}		
1	0.00038	0.5	1	0.00045	0.6	1	0.00032	0.4	1	0.00013	0.2
2	0.00052	0.7	2	0.00053	0.7	2	0.00038	0.5	2	0.00027	0.3
3	0.00059	0.7	3	0.00052	0.7	3	0.00041	0.5	3	0.00026	0.3
4	0.00070	0.9	4	0.00054	0.7	4	0.00039	0.5	4	0.00026	0.3
5	0.00079	1.0	5	0.00054	0.7	5	0.00039	0.5	5	0.00025	0.3
6	0.00086	1.1	6	0.00056	0.7	6	0.00038	0.5	6	0.00024	0.3
7	0.00094	1.2	7	0.00058	0.7	7	0.00036	0.5	7	0.00023	0.3
8	0.00100	1.3	8	0.00058	0.7	8	0.00036	0.5	8	0.00022	0.3
9	0.00101	1.3	9	0.00061	0.8	9	0.00035	0.4	9	0.00023	0.3
10	0.00101	1.3	10	0.00062	0.8	10	0.00034	0.4	10	0.00022	0.3
15	0.00099	1.3	15	0.00061	0.8	15	0.00032	0.4	15	0.00020	0.3
20	0.00101	1.3	20	0.00058	0.7	20	0.00032	0.4	20	0.00019	0.2
25	0.00108	1.4	25	0.00060	0.8	25	0.00030	0.4	25	0.00019	0.2
30	0.00110	1.4	30	0.00059	0.8	30	0.00028	0.4	30	0.00020	0.3
40	0.00111	1.4	40	0.00062	0.8	40	0.00026	0.3	40	0.00019	0.2
50	0.00100	1.3	50	0.00064	0.8	50	0.00025	0.3	50	0.00019	0.2
60	0.00097	1.3	60	0.00065	0.8	60	0.00023	0.3	60	0.00018	0.2

* (C_0) Initial concentration of CrO_3 solution.

where R is the fixed polycation of the anion exchanger.

Further complexation may be associated with redox reactions, e.g.,

$$Cr^{6+} + 3e \rightarrow Cr^{3+} \text{ etc.}$$

The kinetic analysis of sorption was performed by kinetic equations for gel and film [8]. Table 1 shows that at a Cr(VI) concentration from 340 to 800 mg dm^{-3} the sorption is described by a kinetic equation for film, whereas at concentrations from 1000 to 4000 mg dm^{-3} it is described by a kinetic equation for gel.

The results of calculation of the diffusion coefficients D ($cm^2\ s^{-1}$) are given in Table 2 in relation to the time of contact of the anion exchanger with the solution containing different initial concentrations of Cr(VI) ions. The diffusion coefficient D is calculated by the equation

$$D = Br^2/\pi^2,$$

where r is the sorbent grain radius and B, the coefficient calculated from the tabulated data [9].

As seen from Table 2, the diffusion coefficient D decreases as the concentration C_0 of the initial solution grows. At $C_0 \geq 1000$ mg dm^{-3} D is approximately constant, irrespective of contact time.

From the equation

$$\log C_{\text{sorb}} = p \log C_{\text{s}} + \log(K/K_{\text{p}})$$

where p is the polymerization factor, $C_{\text{sorb}} = \text{ESC} \cdot M^{-1} V_{\text{sp}}^{-1}$ is the ion concentration in the sorbent (mol dm^{-3}), V_{sp} is the specific swelling of the sorbent ($cm^3\ g^{-1}$), C_{s} is the ion concentration in solution (mg dm^{-3}), K is the equilibrium constant, and K_{p} is the polymerization constant, we determined the polymerization factors p using the procedure described in [9].

C_{init}, mg dm^{-3}	p
800–1500	0.27
1925–4200	0.14

The difference in the values of the polymerization factor p indicates that over the initial concentration range studied the chromium(VI) complexes of various compositions are sorbed. With growing initial solution concentration the degree of polymerization of the complexes increases according to Eq. (1).

CONCLUSION

(1) The calculations of the diffusion coefficient and polymerization factor, along with the kinetic analysis, indicate that at higher concentrations of the sorbate the sorption process is kinetically controlled and is limited by chromium(VI) complex formation on the sorbent surface and by chromium(VI) polymerization in the solution and on the sorbent surface.

(2) Sorption of chromium(VI) from aqueous solution is optimal at acid treatment of the sorbent and pH 4: ESC 350 mg CrO_3 per gram of sorbent at the initial solution concentration $C_{\text{init}} \leq 4000$ mg CrO_3 dm^{-3}.

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