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ENVIRONMENTAL PROBLEMS OF CHEMISTRY AND TECHNOLOGY

Features of Cr(III) Cation-Exchange Recovery from Wash Water of Standard Chrome Plating

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Abstract—Features of treatment of the standard chrome plating wash water to remove Cr(III) with KU-1 cation exchanger in the H form were considered. The optimal conditions of Cr(III) recovery and ion exchanger regeneration were determined.

In [1, 2], a two-stage scheme of recovery and utilization of the main components of the standard chrome plating wash water was proposed. The scheme is based on the ion exchange followed by electrochemical treatment of chromium-containing eluates. The model and real wash waters with variable content of metal ions ($g\,l^{-1}$) were used: chromium(VI) (in the form of CrO_4^{2-} and $Cr_2O_7^{2-}$) up to 2.0, copper(II) up to 0.01, nickel(II) up to 0.01, and iron(III) up to 0.015. Along with chromium(VI) and the above foreign metal ions, wash water of standard chrome plating contains Cr(III). The chromium(VI) recovery from wash water by ion exchange was studied in [3, 4].

In this work we studied the features of Cr(III) ion-exchange recovery from wash water of standard chrome plating and determined its optimal parameters.

To recover Cr(III), we used a KU-1 cation exchanger in the H form, which was loaded into a column of 160 mm height and 18 mm inner diameter. The ratio of the cation exchanger bed height and column diameter was 9 : 1. The average diameter of ion exchanger grain was 2.5×10^{-3} m. Ion exchange was studied by both dynamic (with the concentration control at the ion-exchange column outlet) and static methods. The chromium(III) content was determined spectrophotometrically and by atomic absorption with SF-26 and S-115 spectrophotometers, respectively. The error of the above methods was 1.5–2.0%.

Ion exchange involves a series of successive stages of mass transfer over the interface controlled by hydrodynamic regime of the movement of the liquid phase [5]. Therefore, the efficiency of ion exchange should depend on the linear velocity of the flow of chromium-containing wash water. This is confirmed by ion-exchange output curves at various flow velocities (Fig. 1a) and ion-exchange characteristics (dynamic exchange capacity DEC and capacity up to breakthrough CB). DEC is the maximal mass of chromium(III) ions retained by 1 kg of swollen ion exchanger under the taken dynamic conditions of water flow. CB is the maximal mass of Cr(III) ions retained by 1 kg of ion exchanger up to appearance of Cr(III) in the eluate. The velocity of wash water flow *U* 3.25 $m\,h^{-1}$ corresponds to the absence of CB and insignificant decrease in DEC. At this and higher flow rate, CB cannot be determined quantitatively by the above method of analysis. Hence, only linear flow velocities lower than 3.25 $m\,h^{-1}$ are of practical interest. DEC and CB (Fig. 1b) are nonlinear functions of *U*: CB has a maximum at the flow velocity of 2.0 $m\,h^{-1}$, and DEC decreases with increasing *U*. The flow velocity of 2.0 m^{-1} is optimal, as it corresponds to high DEC value and maximal CB (31.6 and 10.6 g per kg of the resin, respectively).

The analysis of the ion-exchange kinetics with equations of diffusion kinetics suggests existence of the limiting stage of ion exchange. It is known [5] that at the metal concentration from 0.003 to 0.1 M ion exchange proceeds under conditions of mixed kinetics. The contribution of the internal diffusion constituent increases with increasing metal concentration. Since for these conditions the theory is not developed completely, to determine the limiting stage we used equations of internal diffusion kinetics for the case of simplest models (sphere, cylinder, plate) [6], which are as follows:

$$-\ln(1 - F) = Bt - \ln A, \quad (1)$$

where *A* and *B* are coefficients depending on the

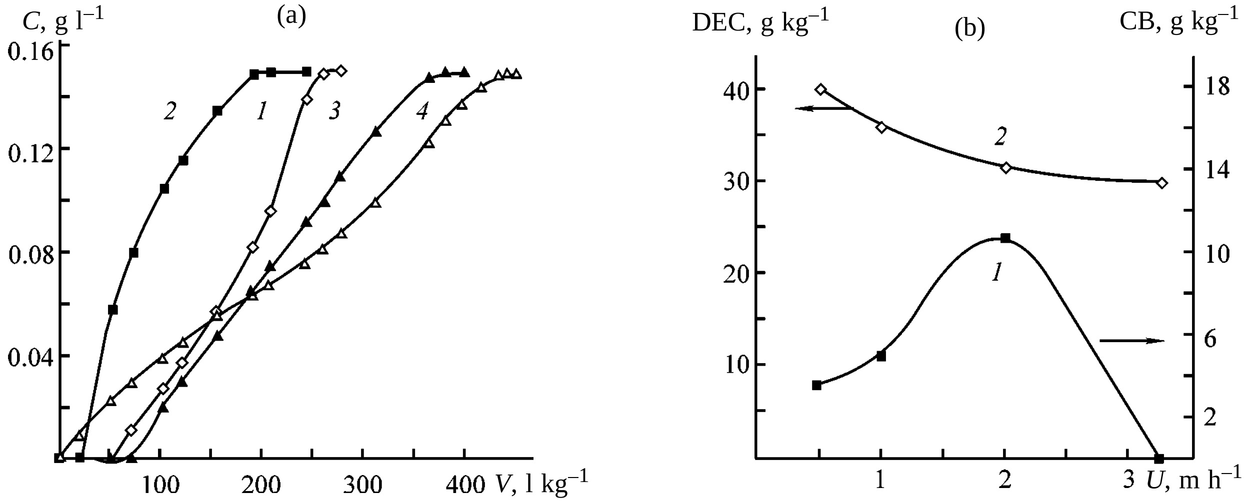

Fig. 1. Effect of (a) volume *V* and (b) flow velocity *U* of wash water on (a) the outlet concentration of Cr(III) *C* and (b) (*1*) CB and (*2*) DEC. Chromium(III) concentration 0.15 g l^{-1}; the same for Fig. 2. (a) Wash water flow velocity *U* (m h^{-1}): (*1*) 0.5, (*2*) 1.0, (*3*) 2.0, and (*4*) 3.25.

model taken, *F* is the exchange degree, and *t* is the exchange time.

The use of Eq. (1) is advisable at $F > 0.7$, because at high exchange degree the contribution of the internal diffusion constituent is very large. Coefficient *A* is the criterion of adequacy of the model taken and is 0.61, 0.69, and 0.81 for sphere, cylinder, and plate, respectively. In this case, the sphere model is the most acceptable. At high *F*, coefficient *B* can be determined from the slope of the $-\ln(1 - F)$–t dependences. Then, the apparent diffusion coefficient *D* can be calculated:

$$B = D\pi^2/R^2, \tag{2}$$

where *R* is the ion exchanger grain radius.

The value of *D* is 1.5×10^{-8} cm^2 s^{-1}. This value corresponds to the prevalence of the internal diffusion constituent and small contribution of the external diffusion. This allows explanation of the dependence of DEC on the velocity of wash water flow (Fig. 1b, curve *2*). At increased velocity, the contact time in the ion exchanger grain–liquid phase system becomes shorter, and hence, DEC decreases (especially strongly at the velocities higher than 3.25 m h^{-1}).

The effect of chromium(III) concentration in the wash water on the ion exchange dynamics was found at the wash water flow velocity of 2.0 m h^{-1} (Fig. 3a). With increasing metal ion concentration from 0.1 to 0.3 g l^{-1}, CB and DEC change (Fig. 3b), and their maxima are observed at a Cr(III) concentration of 0.15 g l^{-1}. Probably, such dependences are due to Cr(III) complexation in sulfate solutions. At the Cr(III) concentration increased to 0.15 g l^{-1} transfer of metal ion from the solution to the surface of the ion exchanger grain accelerates, and DEC and CB increase. At Cr(III) concentration higher than 0.15 g l^{-1}, the internal diffusion constituent becomes prevailing, and DEC and CB decrease. The apparent diffusion coefficient *D* was 3.5×10^{-8} cm^{2}s^{-1}. The effect of Cr(III) concentration was studied also for other velocities of wash water flow within the 0.1–6.25 m h^{-1} range. It was found that the shape of the DEC and CB dependences and the location of curve maxima are independent of the chromium(III) concentration. This is caused by a fairly narrow range in variation of the Cr(III) concentrations studied.

The above data on chromium(III) recovery show that fairly high wash water volume to breakthrough, maximal capacity to breakthrough (it amounts to 7.3, 10.6, 2.1, and 1.0 g per kg of the resin for concentra-

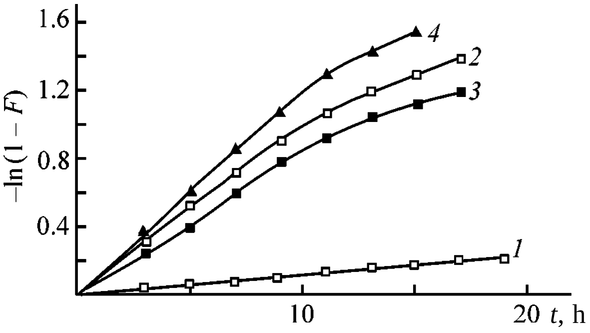

Fig. 2. Kinetics of Cr(III) sorption with KU-1 cation exchanger in the H form: (*F*) exchange degree and (*t*) time. Wash water flow rate *U* (m h^{-1}): (*1*) 0.5, (*2*) 1.0, (*3*) 2.0, and (*4*) 3.25.

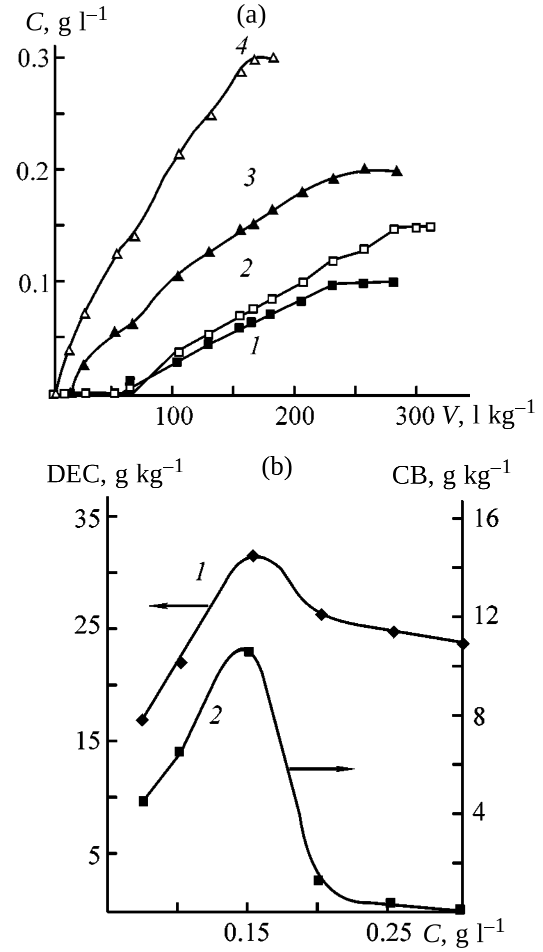

Fig. 3. Influence of wash water volume *V* and Cr(III) concentration *C* on (a) the outlet concentration of Cr(III) *C* and (b) (*1*) DEC and (*2*) CB. Wash water flow velocity 2.0 m h^{-1}. (a) Cr(III) concentration (g l^{-1}): (*1*) 0.1, (*2*) 0.15, (*3*) 0.2, and (*4*) 0.3.

tions of 0.1, 0.15, 0.2, and 0.3 g l^{-1}, respectively), and maximal DEC (31.6 g kg^{-1}) correspond to the Cr(III) concentration of 0.15 g l^{-1}.

Ion exchanger regeneration was performed with sulfuric acid solutions. We considered the effect of acid concentration and flow velocity of the solution on this process. The effect of acid concentration was studied by the static method. Cation exchanger was saturated with Cr(III) ions under the optimal conditions (0.15 g l^{-1}, 2 m h^{-1}) and then washed up to absence of trace amounts of Cr(III) in the eluate. Then, the resin was dried to the constant weight. The samples of solutions containing the same amount of H_2SO_4 and various amounts of water were added to the equal samples of the ion exchanger (4.0 g). The ratio of the cation exchanger to H_2SO_4 was 1 : 6.25 (by weight). The amount of Cr(III) recovered was determined by chemical analysis as a function of the time of cation exchanger contact with the solution. The data obtained are listed in the table.

Amount of chromium(III) recovered in regeneration

H_2SO_4, g l^{-1}	Amount of Cr(III), g, in indicated time, h				
	1	3	22	24	47
25.0	0.015	0.023	0.052	0.067	0.084
50.0	0.031	0.049	0.080	0.104	0.116
100.0	0.027	0.034	0.066	0.083	0.099
150.0	0.022	0.031	0.062	0.080	0.102
200.0	0.021	0.032	0.063	0.083	0.104
250.0	0.022	0.033	0.064	0.083	0.105

As seen, the best recovery is reached with 50.0 g l^{-1} H_2SO_4, which was used in the subsequent experiments.

We found that the maximal amount of the metal recovered corresponds to the flow velocity of sulfuric acid of 1.0 m h^{-1} (Fig. 4). This follows from comparison of the areas under the corresponding curves. At any volume of the sulfuric acid solution, the velocity of 1.0 m h^{-1} corresponds to the maximal amount of Cr(III) in the eluate, which is important for the further processing of the eluates into the commercial product. This result can be explained as follows. At the flow velocity of the H_2SO_4 solution below 1.0 m h^{-1}, the regeneration of the resin is controlled by mixed kinetics and at higher velocities, it is controlled by internal diffusion kinetics, which decreases the amount of recovered Cr(III).

The dependences of the recovery degree on the amount of sulfuric acid solution show that the maximal recovery is reached at a flow velocity of 1.0 m h^{-1} (98%), while for the velocities of 0.25, 0.5, and 2.0 m h^{-1} it was 64.4, 80.1, and 78.3%, respectively.

The volume of the acid solution required for complete regeneration was 43.12 l per kg of the resin [98% of chromium(III) recovery]. The 80% recovery of Cr(III) is reached on passing 7.2 l per kg of the resin. It is reasonable to maintain this level of the resin regeneration, because the additional volume of the acid required to reach the 98% recovery is unduly large. On the other hand, the incomplete regeneration degree should lower DEC and CB in the further use of the ion exchanger, which should be taken into consideration when designing the equipment for treatment of industrial wastewater.

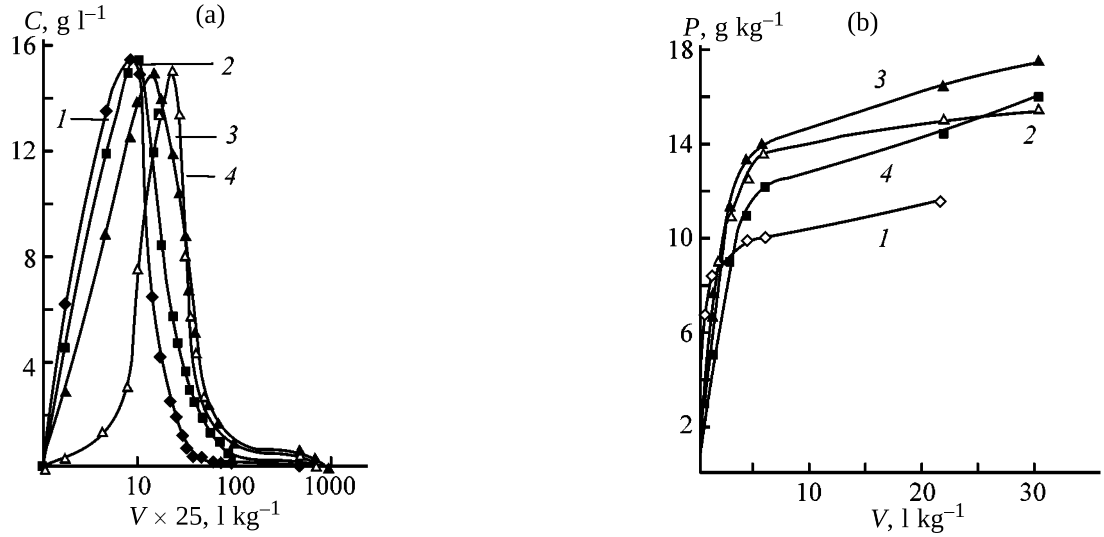

Fig. 4. Effect of the volume of the regenerating solution V on (a) the outlet concentration of Cr(III) C and (b) the amount of Cr(III) recovered P. Concentration of H_2SO_4 50 g l^{-1}. H_2SO_4 flow velocity (m h^{-1}): (*1*) 0.25, (*2*) 0.5, (*3*) 1.0, and (*4*) 2.0.

CONCLUSIONS

(1) Optimal parameters of Cr(III) cation exchange recovery from wash water of the standard chrome plating were determined: Cr(III) content in wash water 0.15 g l^{-1} and wash water flow velocity 2.0 m h^{-1}. Under these conditions, the dynamic exchange capacity and the cation exchanger capacity to breakthrough were 31.6 and 10.6 g per kg of the resin, respectively.

(2) It is advisable to regenerate the ion exchanger with 50 g l^{-1} sulfuric acid at the flow velocity of 1.0 m h^{-1} to recovery degree of 80%.

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