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## H<sup>+</sup>/Cr<sup>3+</sup> ION EXCHANGE ON STRONGLY ACID RESIN

There are presented the results of investigations concerning the effect of sulfuric acid and chromium(III) concentrations on the kinetics, equilibrium and dynamics of the H<sup>+</sup>/Cr<sup>3+</sup> ion exchange on the strongly acidic cation exchanger Wofatit KS-10.

It has been found out that acidity of the solution and initial concentration of chromium(III) have no significant effect on the exchange kinetics. The exchange dynamics is not significantly affected by hydraulic load and counter-ion effect within the ranges studied. Sorption of chromium(III) from model solutions is virtually complete under dynamic conditions. The operating exchange capacity of Wofatit KS-10 is constant during successive cycles and averages 1.26 val/dm<sup>3</sup>.

Our investigations have shown applicability of ion exchange method to the recovery of Cr(III) from acid water solutions.

### 1. INTRODUCTION

Acid wastewaters containing chromium(III) and (VI) are produced in industrial plants during chemical and electrochemical treatment of metals, in tanning industry during light organic synthesis, etc. The wastewaters have hitherto been treated chemically, i.e. chromium(IV) ions have been reduced to chromium(III) ions and then converted into insoluble chromic hydroxide by means of a strong base. After partial dehydration, this sediment is usually stored on waste dumps, where it threatens the environment because of elution of toxic chromium by the rain water [1]. Wastewater containing high concentrations of chromium(III) or mixtures of chromates and salts of chromium(III) can sometimes be oxidized electrochemically to chromium(VI) and the product can be recycled to the technological process [2].

One of the methods for treating diluted wastewater containing chromium is ion exchange. Sorption of chromates of slight concentrations on anion exchangers does not present any serious technological difficulties [3], while the literature data on chromium(III) sorption from acid wastewater often indicates only partial recovery of the metal. It is par-

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ticularly difficult to remove chromium by the ion exchanger method when wastewaters contain considerable quantities of sodium sulfate [4] and organic substances [5]. These components are often present in tannery wastewater and wastewater produced during the light organic synthesis.

## 2. OBJECTIVES AND RANGE OF INVESTIGATIONS

The aim of the investigations carried out was to determine the effect of sulfuric acid and chromium(III) concentrations on the kinetics, equilibrium and dynamics of the  $H^+/Cr^{3+}$  ion exchange on the strongly acidic cation exchanger, Wofatit KS-10 produced in Germany. The total exchange capacity determined amounted to 5.45 mval/g of dry ion exchanger (1.94 mval/cm<sup>3</sup>).

Water solutions of chromium nitrate of concentrations of 10–550 mval/dm<sup>3</sup> and solutions of sulfuric acid of concentrations of 0–1000 mval/dm<sup>3</sup> containing ~100 mval/dm<sup>3</sup> of chromium(III) were used. The solutions were prepared from deionized water of an electrical conductivity  $\leq 5 \mu\text{s/cm}$  and analytically pure reagents. Concentration of chromium(III) was determined spectrophotometrically according to the method described by HERMANOWICZ [6]. All the measurements were carried out at a constant temperature of 40°C (313 K).

## 3. KINETICS AND EQUILIBRIUM OF ION EXCHANGE

Kinetics and equilibrium of ion exchange were investigated statically in a 1000 cm<sup>3</sup> beaker placed in the thermostatic system and equipped with an electromagnetic stirrer ensuring intensive stirring of the solution and the ion exchanger.

The air-dry ion exchanger in the hydrogen form was weighed with an accuracy of  $\pm 0.1$  mg in small glass bulbs. Then 10 cm<sup>3</sup> of deionized water was introduced into the bulb whose tip was melted over a gas burner and the bulb was put aside for 24 hours. Such a procedure ensured entire swelling of the ion exchanger. The bulb with a swollen ion exchanger was put into a beaker with 200 cm<sup>3</sup> of the solution under investigation. When the constant temperature was reached, the bulb was broken and, at the same time, a stop watch was started. At definite intervals of time, samples of the solution for analysis were taken with a micropipette of 0.26 cm<sup>3</sup> capacity. The experiment was carried out until the equilibrium state was reached ( $\tau = 120$  min.).

All the experiments were performed at a constant ratio of

$$\frac{Z_c m_i}{C_0 V} = 1 \quad (1)$$

where:

$Z_c$  – total exchange capacity of the dry ion exchanger,

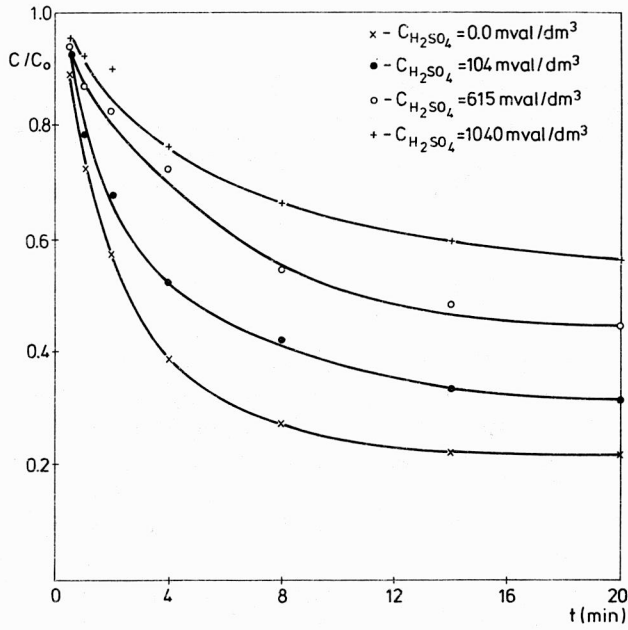


Fig. 1. Effect of  $H_2SO_4$  concentration on the rate of  $H^+/Cr^{3+}$  ion exchange

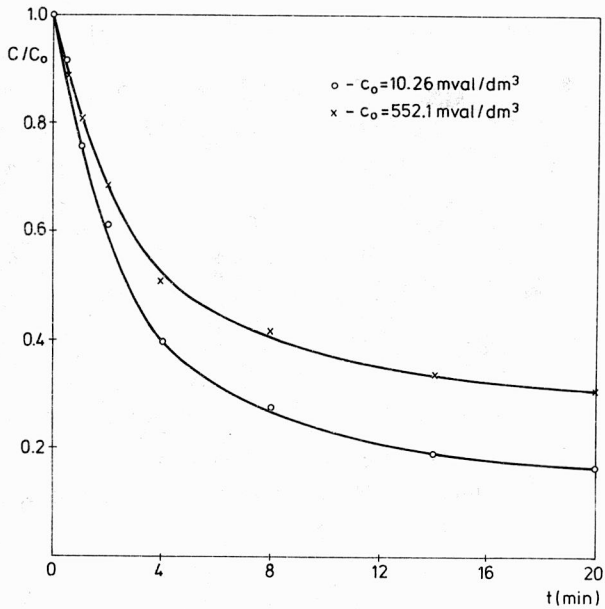


Fig. 2. Effect of  $Cr^{3+}$  concentration on the rate of  $H^+/Cr^{3+}$  ion exchange;  $C_{H_2SO_4} = 0$

$m_j^s$  – dry ion exchanger mass,

$C_0$  – initial concentration of chromium(III),

$V$  – volume of the solution investigated.

The experimental results have been presented graphically in figs. 1 and 2 in the form of curves  $C/C_0 = f(\tau)$ . An attempt was also made at mathematical interpretation of the data obtained. It turns out that these data can be described by the equation:

$$U = \frac{C_0 - C}{C_0 - C_r} = 1 - \exp(-k\tau) \quad (2)$$

where:

$U$  – degree of attaining the state of equilibrium,

$C_r$  – concentration of chromium(III) in the equilibrium state valid for  $U \leq 0.9$ .

The values of the constant  $k$  for different process conditions calculated from equation (2) by the least square method have been given in the table. As it results from the values of the constant  $k$ , the rate of ion exchange in the case of  $U \leq 0.9$  does not depend on the initial concentration of chromium(III) in the solution, and it decreases as the sulfuric acid concentration increases, this effect, however, is relatively small.

Table

Equilibrium and kinetics data of the ion exchange under investigation

$C_0$ (mval/dm <sup>3</sup> )	$C_{H_2SO_4}$ (mval/dm <sup>3</sup> )	$C_j^*$ (mval/g)	$C_r$ (mval/dm <sup>3</sup> )	$k$ (1/min)	$\lambda$
10.26	0	4.93	1.22	0.267	4038
100.4	0	4.29	21.6	0.270	199
552.1	0	4.42	147.0	0.276	30.0
102.6	104	3.81	32.7	0.268	116.5
102.6	615	3.08	46.0	0.216	67.0
102.6	1040	2.42	58.3	0.183	41.5

The table also presents equilibrium data of the ion exchange under investigation. Concentration of chromium(III) in the ion exchanger phase  $C_j^*$  was calculated with regard to the dry ion exchanger mass, while the distribution coefficient  $\lambda$  from the following equation:

$$\lambda = \frac{C_j^*}{C_r} \cdot 10^3. \quad (3)$$

The equilibrium concentration  $C_j^*$  varies to a slight degree only as the initial concentration of chromium(III) increases, and it decreases as the sulfuric acid concentration in the solution increases. These parameters significantly affect the values of the distribution coefficient  $\lambda$ . The kinetic and equilibrium experiments carried out have shown the possibility of effective sorption of chromium(III) from water acid solutions over a wide range of the concentrations of Cr(III) and sulfuric acid  $< 1 \text{ val/dm}^3$ .

#### 4. DYNAMICS OF $H^+/Cr^{3+}$ ION EXCHANGE

The dynamic investigation comprised:

determination of the effect of the sulfuric acid concentration and the hydraulic load ( $O_h$ ) on the dynamics of  $H^+/Cr^{3+}$  exchange,

investigation of the ion exchanger operation during 5 successive cycles of sorption and regeneration of chromium(III).

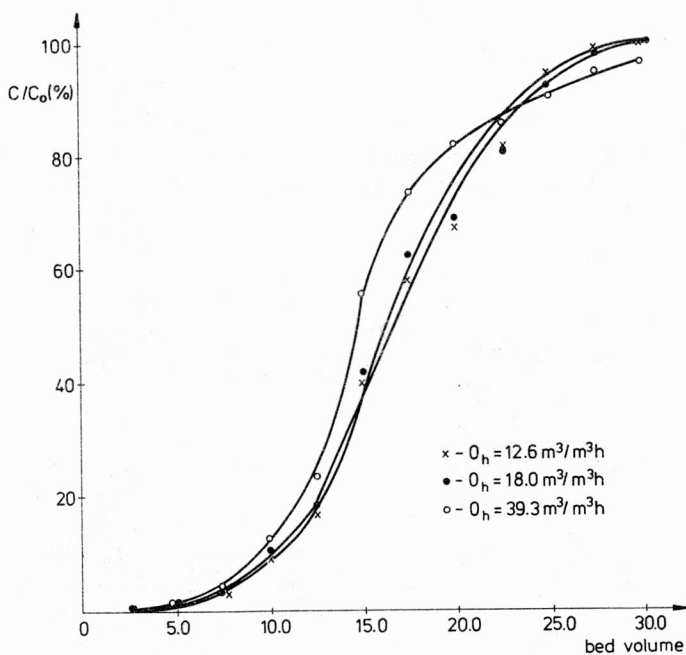


Fig. 3. Sorption of  $Cr^{3+}$  on cation exchanger Wofatit KS-10 under dynamic conditions. Effect of hydraulic load on exchange isoplanes;  $T = 313 \text{ K}$

The experiments were carried out in the flow column containing  $20 \text{ cm}^3$  of ion exchanger ( $100 \text{ cm}^3$  for investigations of the ion exchanger operation in the successive sorption-regeneration cycles). The dynamic exchange process was conducted until complete exhaustion of the bed.

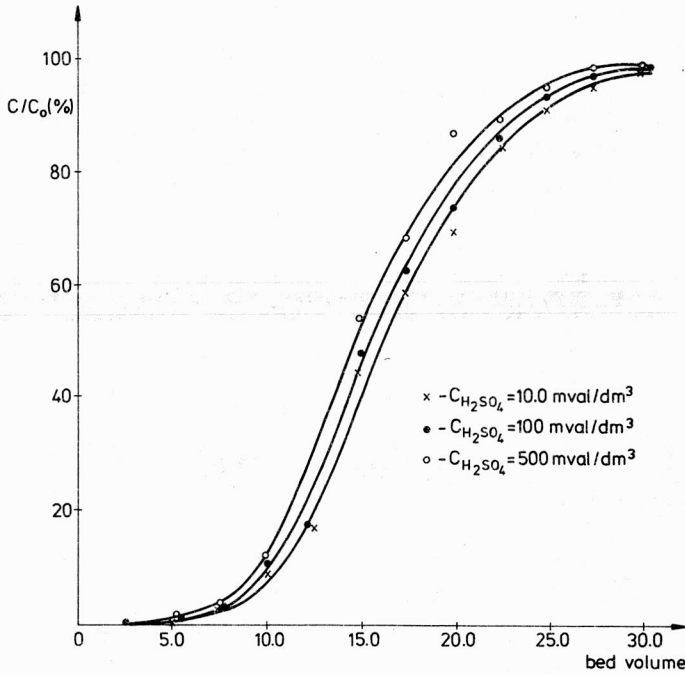


Fig. 4. Sorption of  $\text{Cr}^{3+}$  on cation exchanger Wofatit KS-10 under dynamic conditions. The influence of the counter-ion effect on exchange isoplanes;  $T = 313 \text{ K}$ ,  $O_b = 15.6 \text{ m}^3/\text{m}^3 \text{ h}$

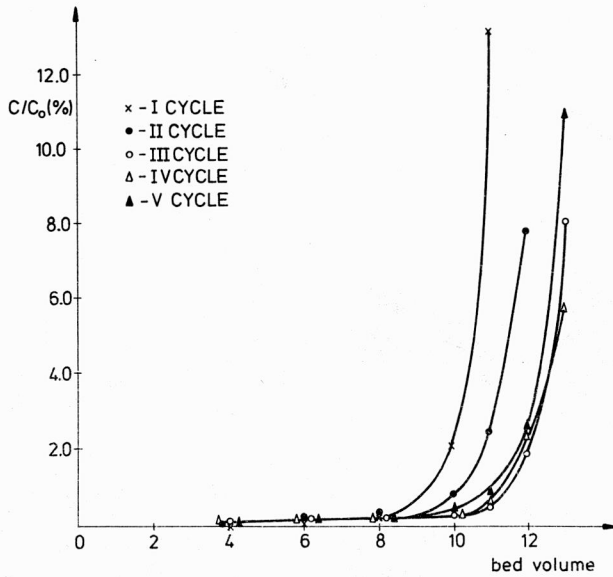


Fig. 5. Investigations of the ion exchanger operation during 5 cycles of sorption and regeneration of  $\text{Cr}^{3+}$ ;  $T = 313 \text{ K}$

The effect of the hydraulic load of the column on the dynamics of exchange was studied for  $O_h = 12.6, 18.0, 39.3 \text{ m}^3/\text{m}^3\text{h}$ , using water solutions of Cr(III) of a concentration of  $\sim 100 \text{ mval}/\text{dm}^3$ . The isoplanes obtained are shown in fig. 3.

The counter-ion effect (sulfuric acid concentration) was determined for the solutions containing  $\sim 100 \text{ mval}/\text{dm}^3$  of chromium and 10, 100 and 500  $\text{mval}/\text{dm}^3$  of sulfuric acid, respectively, at a column load  $O_h$  equal to  $15.6 \text{ m}^3/\text{m}^3\text{h}$ . The isoplanes obtained are presented in fig. 4.

To investigate the column operation in the successive sorption-regeneration cycles, a column containing  $100 \text{ cm}^3$  of ion exchanger was used and the process was conducted until the column breakthrough point was reached ( $C/C_0 = 0.05$ ). Chromium was absorbed from the solution of a concentration of  $100 \text{ mval}/\text{dm}^3$ , while the bed was regenerated with a 20% solution of sulfuric acid, considered to be the optimum [7]. The isoplanes obtained are shown in fig. 5.

It has been found that the hydraulic load and the acidity of the solution caused by  $\text{H}_2\text{SO}_4$  do not considerably affect the course of the exchange isoplanes. Over the studied ranges of the above parameters, the sorption process can be conducted effectively. The investigations of the ion exchanger operation performed during 5 successive cycles proved that stabilization of operation exchange capacity is established after 2 cycles on the level of  $1.26 \text{ val}/\text{dm}^3$ .

## 5. CONCLUSIONS

1. Acidity of the solution and initial concentration of chromium(III) have no significant effect on the  $H^+/Cr^{3+}$  exchange kinetics.
2. Investigations of the effect of hydraulic load and counter-ion effect on the  $H^+/Cr^{3+}$  exchange dynamics on Wofatit KS-10 indicate that the above parameters do not influence significantly the process over the ranges studied.
3. Under dynamic conditions, sorption of chromium(III) from model solutions is virtually complete. The operating exchange capacity of Wofatit KS-10 is constant during successive cycles and it averages  $1.26 \text{ val}/\text{dm}^3$ .

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WYMIANA JONOWA  $H^+/Cr^{3+}$  NA SILNIE KWAŚNYM KATIONICIE

Badano wpływ stężenia kwasu siarkowego i chromu(III) na kinetykę, równowagę i dynamikę wymiany jonowej  $H^+/Cr^{3+}$  na silnie kwaśnym kationicie typu Wofatit KS-10. Stwierdzono, że kwasowość roztworu i stężenie początkowe chromu(III) nie wpływają istotnie na kinetykę procesu, a dynamika wymiany w badanych zakresach nie zależy od obciążenia hydraulicznego i efektu przeciwjonowego. W warunkach dynamicznych sorpcja chromu(III) z roztworów modelowych jest praktycznie całkowita. Robocza zdolność wymienna kationitu podczas kolejnych cykli jest stała i wynosi średnio  $1,26 \text{ val/dm}^3$ .

Wykonane badania wykazały przydatność metody jonitowej do odzyskiwania Cr(III) z kwaśnych roztworów wodnych.

ИОННЫЙ ОБМЕН  $H^+/Cr^{3+}$  НА СИЛЬНОКИСЛОМ КАТИОНИТЕ

Исследовано влияние концентрации серной кислоты и хрома(III) на кинетику, равновесие и динамику ионного обмена  $H^+/Cr^{3+}$  на сильнокислом катионите типа Wofatit KS-10. Было установлено, что кислотность раствора и начальная концентрация хрома(III) не оказывают существенного влияния на кинетику процесса, а динамика обмена в исследуемых пределах не зависит от гидравлической нагрузки и противоионного эффекта. В динамических условиях сорбция хрома(III) из модельных растворов является практически полной. Рабочая обменная способность катионита во время очередных циклов является постоянной и составляет в среднем  $1,26 \text{ val/dm}^3$ .

Выполненные исследования обнаружили пригодность ионитового метода для восстановления Cr(III) из кислых водных растворов.