

## Sorption of Cr<sup>VI</sup> ions from aqueous solutions using anion exchange resins

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### ABSTRACT

Batch and dynamic column experiments on anion exchangers with dimethylamin and trimethylammonium functional groups (Lewatit MonoPlus MP 64), DETA functional groups (Purolite A 830), trimethylammonium functional groups (Lewatit MP 500) and aminomethylglucitol functional groups (Purolite S 110) were performed. The influence of pH and coexisting ions on the efficiency of sorption of Cr was investigated. The ion exchange resin Lewatit MonoPlus MP 64 was also investigated for the effect of a flow rate on the column efficiency of sorption of Cr. Optimal pH for sorption of Cr<sup>VI</sup> using these ion exchange resins was found to be 3-4. The accompanying SO<sub>4</sub><sup>2-</sup> ions showed strongest negative influence on the sorption of Cr<sup>VI</sup>. At column dynamic experiments regeneration of ion exchange resin Purolite A 830 was unsuccessful. Anion exchanger Lewatit MonoPlus MP 64 is suitable for repeated sorption of Cr<sup>VI</sup> ions.

**Keywords:** sorption; chromium; aqueous solutions; ion exchangers

### INTRODUCTION

Chromium and its compounds are widely used in the industry. For example: elemental chromium is used for the production of alloy steels, chromium oxide as a coloring pigment and chromium trioxide for oxidation of organic substances<sup>1,2,3</sup>.

Toxicity of chromium compounds depends on their oxidation state. Metallic (elemental) and trivalent chromium compounds are virtually non-toxic. On the contrary all hexavalent chromium compounds (chromates) are mutagenic and carcinogenic<sup>4,5,6,7</sup>.

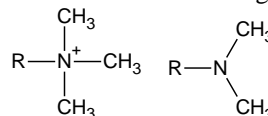
The aim of this work was to perform batch and dynamic column experiments with selected anion exchangers Lewatit MonoPlus MP 64, Purolite A 830, Lewatit MP 500 and Purolite S 110. The influence of pH and coexisting ions on the efficiency of sorption of Cr was studied. The effect of a flow rate on efficiency of sorption of Cr was also monitored on anion exchange resin Lewatit MonoPlus MP 64.

### EXPERIMENTAL

Ion exchangers used for the sorption of chromium ions:

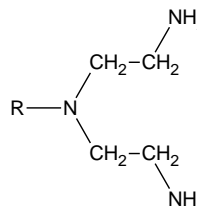
- a) Lewatit MonoPlus MP 64 (Fig. 1) - monodisperse, macroporous medium basic

anion exchanger with dimethylamine and trimethylammonium functional groups



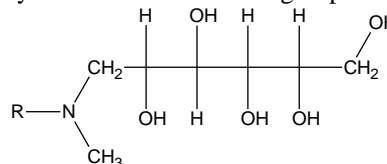
**Figure 1** Dimethylamine and trimethylammonium functional groups

- b) Purolite A 830 (Fig. 2) - weakly basic anion exchanger with DETA functional groups



**Figure 2** DETA functional groups

- c) Lewatit MP 500 - macroporous strongly basic (type I) anion exchanger with trimethylammonium functional groups



**Figure 3** Aminomethylglucitol functional groups

d) Purolite S 110 (Fig. 3) - selective sorbent for sorption of borates having aminomethylglucitol functional groups

All the exchangers were converted into chloride or hydrochloride form. Solution of NaOH of a concentration  $1 \text{ mol.L}^{-1}$  was used at first and subsequently HCl solution of the same concentration was used. For conditioning of the anion exchange resin Lewatit MonoPlus MP 64 solution NaCl + HCl ( $1.5 \text{ mol.L}^{-1}$  HCl +  $1 \text{ mol.L}^{-1}$  NaCl) was used.

Dynamic column experiments were carried out with 10 mL of resin, which was transferred to a glass column fitted at the bottom with the fritted glass. Uniform input flow rate of the solution into ion exchange column was secured by using a peristaltic pump. Dynamic column experiments were performed first with a model solution prepared from demineralized water and  $\text{Cr}^{\text{VI}}$ . The concentration of  $\text{Cr}^{\text{VI}}$  solution was always around  $5 \text{ mg.L}^{-1}$  ( $0.1 \text{ mmol.L}^{-1}$ ) and the input value of pH was not adjusted.

Further experiments were carried out with solutions simulating real conditions (groundwater contaminated with chromium), the concentration of Cr in the range of 3-8  $\text{mg.L}^{-1}$ , pH 7.5). Solutions for sorption were prepared from tap water (Table I) and  $\text{Cr}^{\text{VI}}$  concentrations ranged from 8.6 to 8.9  $\text{mg.L}^{-1}$  (from 0.165 to 0.171  $\text{mmol.L}^{-1}$ ). The pH value of the solutions (7.7 – 8.0) was not adjusted.

**Table I** Concentrations of selected ions in tap water (ICT Prague)

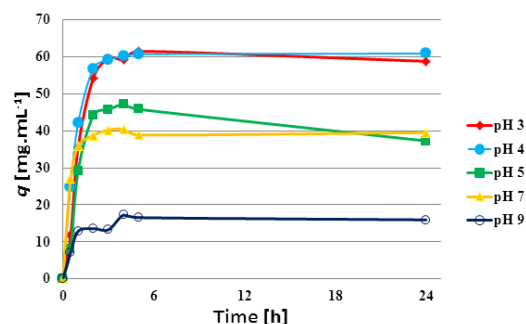
Ions	$\text{Fe}^{3+}$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$
$\rho$ [ $\text{mg.L}^{-1}$ ]	0.02	34.8	8.2	23.0	23.2	52.4

$\text{Cr}^{\text{VI}}$  concentration was determined by atomic absorption spectrometry on Varian SpetrAA 220. The detection limit of this device for chromium is  $0.05 \text{ mg.L}^{-1}$ .

## RESULTS AND DISCUSSION

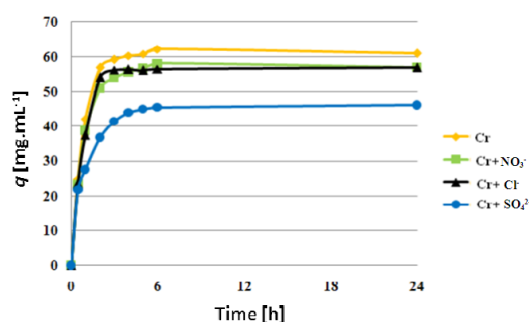
Batch experiments showed that the maximum sorption of  $\text{Cr}^{\text{VI}}$  by ion exchanger Purolite A 830 was reached at pH 3. Ion exchange resin Lewatit MP 64 MonoPlus reached the maximum sorption at pH 4 and reached very good results even at pH 3 (Fig. 4). The anion exchange resin Purolite S 110 and

Lewatit MP 500 also achieved the maximum sorption of  $\text{Cr}^{\text{VI}}$  at pH 4. Equilibrium was reached after 5-6 h of sorption at Lewatit MonoPlus MP 64 and Lewatit MP 500. At pH 5 partial desorption of  $\text{Cr}^{\text{VI}}$  occurred on Lewatit MonoPlus MP 64. The Purolite A 830 occurred at pH 9 to partial desorption of  $\text{Cr}^{\text{VI}}$  and at pH 3-5 the equilibrium was not achieved even after 24 h of sorption.

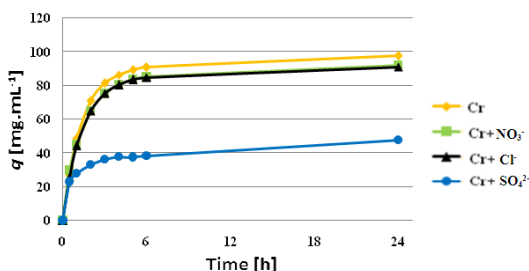


**Figure 4** Amount of captured  $\text{Cr}^{\text{VI}}$  to 1 mL resin Lewatit MonoPlus MP 64 in dependence on time and pH

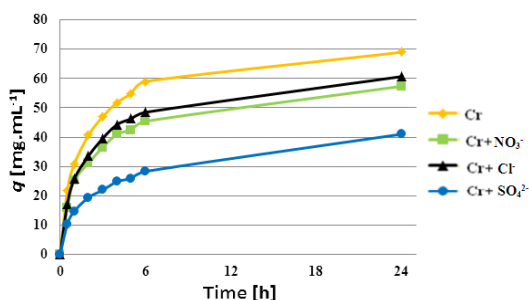
The influence of accompanying anions  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  on sorption efficiency of  $\text{Cr}^{\text{VI}}$  was examined. Molar concentration of  $\text{Cl}^-$  and  $\text{NO}_3^-$  was  $1.92 \text{ mmol.L}^{-1}$ , molar concentration of  $\text{SO}_4^{2-}$  was  $0.96 \text{ mmol.L}^{-1}$ . It was found that the greatest influence on the sorption of  $\text{Cr}^{\text{VI}}$  have  $\text{SO}_4^{2-}$  ions. In the presence of  $\text{SO}_4^{2-}$  ions at pH 4 the amount of captured  $\text{Cr}^{\text{VI}}$  decreased by 23.4 - 51.0 % (Fig. 5-8). The greatest deterioration selectivity to  $\text{Cr}^{\text{VI}}$  was at this pH on anion exchange resin Purolite A 830, high selectivity to  $\text{Cr}^{\text{VI}}$  has Lewatit MonoPlus MP 64.



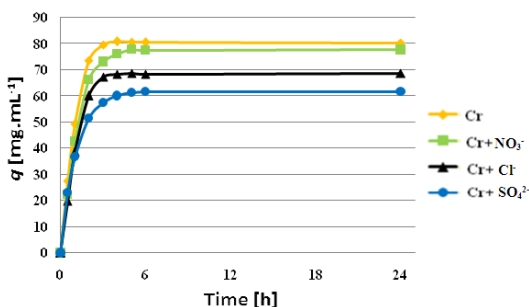
**Figure 5** Amount of captured  $\text{Cr}^{\text{VI}}$  to 1 mL resin Lewatit MonoPlus MP 64 in dependence on time and coexisting ions at pH 4



**Figure 6** Amount of captured  $\text{Cr}^{\text{VI}}$  on 1 mL resin Purolite A 830 in dependence on time and coexisting ions at pH 4

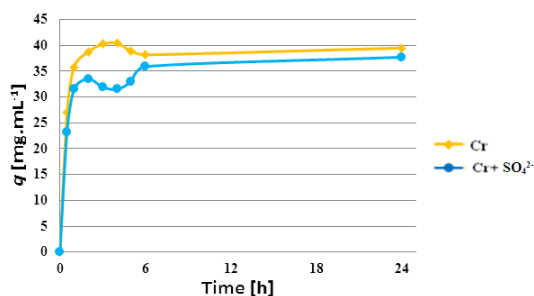


**Figure 7** Amount of captured  $\text{Cr}^{\text{VI}}$  to 1 mL resin Purolite S 110 in dependence on time and coexisting ions at pH 4

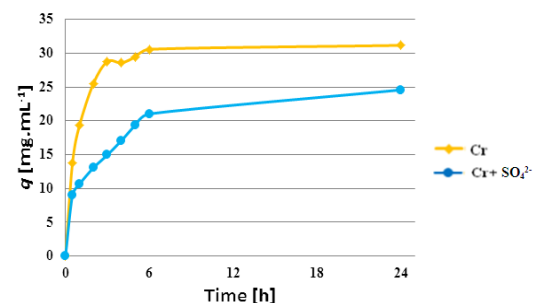


**Figure 8** Amount of captured  $\text{Cr}^{\text{VI}}$  to 1 mL resin Lewatit MP 500 in dependence on time and coexisting ions at pH 4

By increasing the pH of the input solution to 7 the adsorption capacity of ion exchangers was reduced, but the selectivity of the sorption of Cr increased (Fig. 9-10). It was probably caused by the presence of  $\text{Cr}^{\text{VI}}$  in aqueous solutions predominantly in the form of an anion  $\text{HCrO}_4^-$  at pH 4, whereas at pH 7 the  $\text{CrO}_4^{2-}$  form predominates. At both values of pH  $\text{S}^{\text{VI}}$  occurs in the form of  $\text{SO}_4^{2-}$ . Exchangers generally prefer multivalent ions rather than bivalent and monovalent. For this reason by increasing the pH to 7 competitiveness of chromate ions with sulphate ions increased. The presence of  $\text{Cl}^-$  and  $\text{NO}_3^-$  ions had little impact on sorption of  $\text{Cr}^{\text{VI}}$  by ion exchangers Lewatit MonoPlus MP 64 and Purolite A 830.

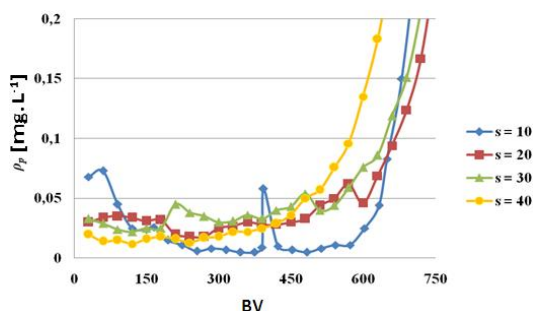


**Figure 9** Amount of captured  $\text{Cr}^{\text{VI}}$  to 1 mL resin Lewatit MonoPlus MP 64 in dependence on time and coexisting ions at pH 7



**Figure 10** Amount of captured  $\text{Cr}^{\text{VI}}$  to 1 mL resin Purolite S 110 in dependence on time and coexisting ions at pH 7

Ion exchange resin Lewatit MonoPlus MP 64 achieved excellent results at the flow rate of  $s = 10$  BV/h (Fig. 11), there was also the smallest continuous penetration of Cr at the outlet of the column. When  $s = 20$  and  $30$  BV/h similar results were achieved. With  $\text{Cr}^{\text{VI}}$  input solution prepared from tap water and  $s = 10$  BV/h the maximum breakthrough capacity of the resin was  $5.12 \text{ mg.mL}^{-1}$ , which corresponds to  $23.84 \text{ mg.g}^{-1}$  of anion exchange resin in the free base form. Resin Purolite A 830 reached relatively good sorption capacity (Fig. 13), however, its regeneration has managed to displace only 30% of the captured Cr. The reason was probably quite strong interaction of  $\text{Cr}^{\text{VI}}$  on DETA functional group.



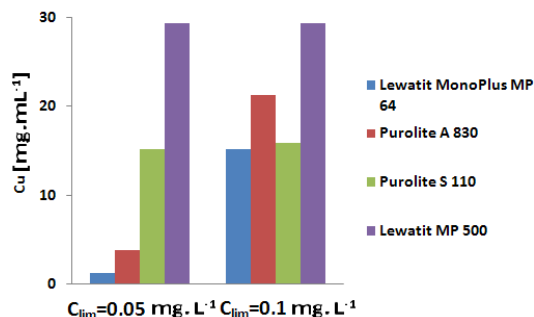
**Figure 11** Penetration of  $\text{Cr}^{\text{VI}}$  ions from tap water during the sorption phase on ionex Lewatit MonoPlus MP 64,  $s = 10, 20, 30, 40$  BV/h

Green color of Cr saturated Purolite S 110 resin (Fig. 12) suggests that aminomethylglucitol functional group probably reduces  $\text{Cr}^{\text{VI}}$  to  $\text{Cr}^{\text{III}}$ . For this reason it is possible to assume that Cr penetrating column is in the form of  $\text{Cr}^{\text{III}}$ . In column experiments with this resin there was relatively little ongoing leakage of Cr concentration at the outlet of the ion exchange column.

Breakthrough capacities of studied ion exchangers are graphically compared in Figure 13.



**Figure 12** Comparison of color ion-exchange columns after sorption  $\text{Cr}^{\text{VI}}$ . A - resin with trimethylammonium functional groups, B - resin with aminomethylglucitol functional groups



**Figure 13** Breakthrough capacities of ion exchangers at zero cycles with sorption solutions of  $\text{Cr}^{\text{VI}}$  prepared from demineralized water related to various chromium concentration limits at output of the ion exchange column

## CONCLUSIONS

Optimum pH for sorption of  $\text{Cr}^{\text{VI}}$  on studied ion exchangers was found to be between 3 and 4. Sorption of  $\text{Cr}^{\text{VI}}$  was most negatively influenced by  $\text{SO}_4^{2-}$  ions compared with  $\text{Cl}^-$  and  $\text{NO}_3^-$ . Lewatit MonoPlus MP 64 (dimethylamin and trimethylammonium functional groups) was shown to be suitable for repeated sorption of  $\text{Cr}^{\text{VI}}$ . Anion exchangers Purolite S 110 (aminomethylglucitol functional groups) had high breakthrough capacity, but recovery ratio was only 87 %. Regeneration of ion exchange resin Purolite A 830 (DETA functional groups) was unsuccessful.

## ACKNOWLEDGEMENTS

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