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Sorption of Germanium (IV) on Resin Having Methyl-amino-glucitol Moiety

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ABSTRACT

This work deals with selective removal of Ge oxoanions from contaminated water resources by synthetic resin having 1-deoxy-1-(methylamino)-D-glucitol functional groups on poly(styrene-co-divinylbenzene) matrix. During dynamic column experiments, the following general criteria were studied: comparison of germanium sorption on the sorbent in protonated and free base forms, optimal pH-range for sorption and the effect of concentration of germanium and accompanying anions on breakthrough capacity.

The optimal pH range for sorption of germanium oxoanions onto the studied resin is 6-9. For selective uptake of germanium oxoanions sorbent must be in the free base form. Effective desorption of germanium oxoanions was achieved with 7 BV of 1 mol.L^{-1} HCl.

Keywords: germanate; methyl-amino-glucitol resin; sorption

INTRODUCTION

The toxicity of germanium is considered to be low. However, some germanium compounds show nephrotoxicity[1].

In strongly alkaline[2,3,4] environment germanium is present in the solution as GeO_3^{2-} ion. At pH 6.9 to 9.4 germanium is sorbed in the form of the pentagermanate ions $Ge_5O_{11}^{2-}$.

Germanium is recovered from aqueous solutions by such methods as sorption on ion exchange resin, solvent extraction, precipitation, evaporation and flotation.

Sorption of germanium was studied on silica gel[5] and cation exchange resins[6]. Sorption of germanium from alkaline solutions was studied on anion exchange resin[2].

For selective removal of germanium compounds, formation of complexes with saccharides[7] is used. Thus, removal of germanium (IV) was studied such as on biosorbents[8], chitosan[9,10], branched-saccharide chitosan derivatives[11] and 2,3-dihydroxypropyl chitosan resin[12]. Polymeric sorbents (Wofatit MK-51[13,14], Diaion CRB 02[15,16], Purolite S-108[4] and Purolite D-4123[17]) having 1-deoxy-1-(methylamino)-D-glucitol functional groups on poly(styrene-co-divinylbenzene) (PS/DVB) matrix are commercially available. This group of sorbents was designed for the removal of boron oxoanions[18]. The functional -OH groups of these sorbents form a very stable mononuclear complex with Ge oxoanions[5]. The optimal pH range[15] to form polyol complexes between hydroxycompounds and germanium oxoanion is pH 6-12.

EXPERIMENTAL

This work was concerned with sorption and desorption of germanium oxoanions on resin having 1-deoxy-1-(methylamino)-D-glucitol on PS/DVB matrix Purolite D-4123. It has total N-capacity 1.2 mol.L^{-1} and particle size of 18-50 mesh. Its structure is shown in Figure 1.

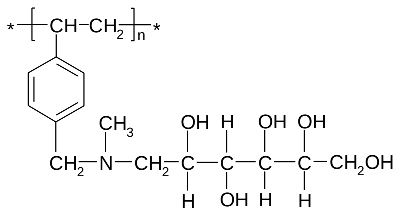

Figure 1 *Structure of Purolite D-4123 resin*

All presented results were obtained by dynamic column experiments that were carried out using synthetic metal solution containing 5, 10 or 20 $mg.L^{-1}$ of germanium ion and 100, 250, 500 or 1000 $mg.L^{-1}$ of accompanying anions (chlorides and sulfates). Germanium (IV) solutions were prepared from germanium dioxide. Solutions of sulfates and chlorides were prepared from their sodium salts. The specific flow rate of solution was s = 6 $BV.h^{-1}$. Column inner diameter was 12 mm, bed volume was 30 mL and bed height was 26.5 mm.

Effluent fractions were collected by fraction collector and concentrations of germanium were analyzed by ICP-OES technique (Perkin Elmer Optima 2000DV).

The sorption run was terminated at germanium breakthrough concentration 0.1 $mg.L^{-1}$.

RESULTS AND DISCUSSION

Comparison of free base and protonated form

The resin with 1-deoxy-1-(methylamino)-D-glucitol functional groups can be used in the protonated form or in the free base form. Effective form for the removal of germanium (IV) is free base form, which the suitable pH for complex formation with functional group is pH 6-12. For the sorbent protonated form, pH of effluent would decrease below pH 4 rendering the conditions unsuitable for formation of polyol complexes. Sorbent in free base form effectively removed germanium from loading solution containing 5 $mg.L^{-1}$ of Ge (Figure 2).

Germanium breakthrough capacities were 0.18 $g.L^{-1}$ and 11.58 $g.L^{-1}$ for the sorbent in protonated and free base form, respectively.

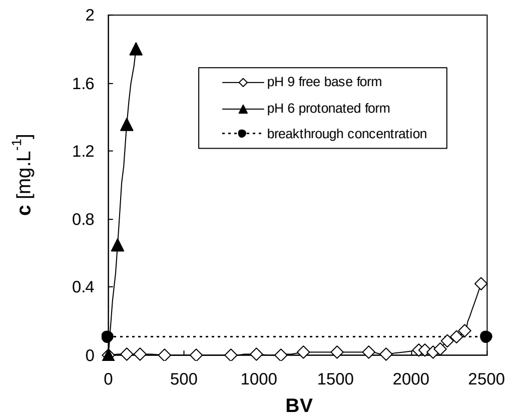

Figure 2 *Sorption of germanium onto free base and protonated form of Purolite D-4123 (Ge = 5 $mg.L^{-1}$, Cl^- = 100$mg.L^{-1}$, SO_4^{2-} = 100$mg.L^{-1}$)*

Effect of Ge concentration on breakthrough capacity

Experimental results shown that the highest breakthrough capacities were obtained with germanium loading concentration of 20 $mg.L^{-1}$. With increasing concentration of germanium in the loading solution in the range of 5-20 $mg.L^{-1}$, breakthrough capacities increased.

The maximum increase of 13% was achieved with loading concentrations of chloride and sulfate 1000 $mg.L^{-1}$ at pH 9, as can be seen in Figure 3.

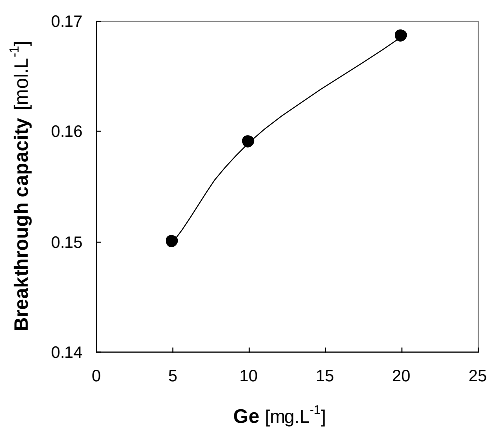

Figure 3 *Effect of germanium concentration on germanium breakthrough capacity (pH 9; Cl^- = 1000 $mg.L^{-1}$, SO_4^{2-} = 1000 $mg.L^{-1}$)*

Effect of pH on germanium breakthrough capacity

Germanium uptake efficiency depends on complex formation between germanium oxoanion and 1-deoxy-1-(methylamino)-D-glucitol functional group which is greatly affected by pH. Thus, breakthrough capacities in the pH range 6 – 11 were ranging from 0.13 to 0.16 mol.L^{-1}

The highest breakthrough capacities were obtained at pH 9 of the loading solution. Removal of germanium at pH 6 is slightly lower (Figure 4).

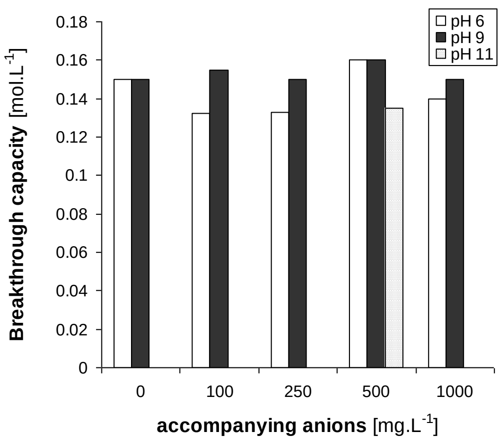

Figure 4 *Effect of pH on germanium breakthrough capacity (Ge = 5 mg.L^{-1})*

Effect of accompanying anions on germanium breakthrough capacity

Figure 5 shows removal of 5 mg.L^{-1} germanium from solution containing 100-1000 mg.L^{-1} accompanying anions (chlorides and sulfates). As may be seen, only very small differences in germanium uptake were observed within this concentration range.

Breakthrough capacities, corresponding to the breakthrough concentration of 0.1 mg.L^{-1}, were in the range of 0.14 to 0.16 mol.L^{-1}. These values correspond to the processing of 2040 to 2330 BV of germanate loading solution containing accompanying anions.

Germanium leakage was very low. With breakthrough concentration lowered to 0.01 mg.L^{-1}, at least 1740 BV of loading solution was processed in all the cases.

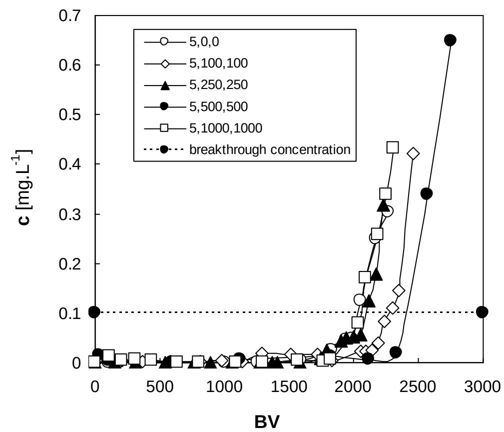

Figure 5 *Effect of accompanying anions on germanium breakthrough capacity (pH 9)*

Desorption efficiency

Desorption of germanium oxoanions was carried out by 7BV of 1 mol.L^{-1} HCl. Desorption was effective at specific flow rate of 3 BV.h^{-1}. Sorbent conditioning was performed with 7 BV of 1 mol.L^{-1} NaOH.

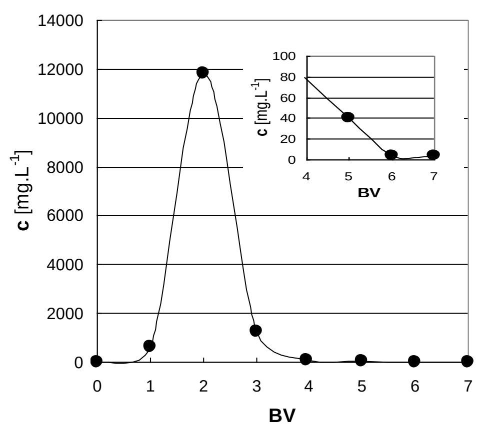

Figure 6 *Desorption curve after sorption of germanium on sorbent in free base form*

Desorption efficiency of germanium from sorbent was higher than 99%. Desorption curve of Purolite D 4123, shown in Figure 6, is sharp for 1.0 mol.L^{-1} HCl. Residual concentration of germanium in the range 6-7 BV fall below 10 mg.L^{-1}.

CONCLUSIONS

Dynamic column experiments have shown that the resin having 1-deoxy-1-methylamino-D glucitol functional group is able to selectively remove germanium oxoanions from solution containing 5-20 $mg.L^{-1}$ of germanium and 100-1000 $mg.L^{-1}$ of accompanying anions (chlorides and sulfates) down to concentrations lower than 0.1 $mg.L^{-1}$.

Sorption of germanium oxoanions is effective only on the sorbent in the free base form with the optimal pH range being 6-9.

Germanium oxoanions can be effectively desorbed with 7BV of 1 $mol.L^{-1}$ HCl.

ACKNOWLEDGEMENT

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REFERENCES

1) Schauss, A.G *Renal Failure*, **13**(1) (1991) 1 - 4
2) *Chirkst D.E.*, Chistyakov A.A., Cheremisina O.V., Zhadovskii I.T., *Russian Journal of Applied Chemistry,* **81** (2008) 38-41
3) Klikorka J., Hájek B., Votinský J., General and Inorganic Chemistry, Praha 1989
4) Jurečková, K., M.S.Thesis, ICT Prague, 2005
5) Lievens P., Hoste J., *Analytica Chimica Acta* **70** (1974) 462-464
6) Shostak F.T., Klimenko I.A., Sharova A.K. Chufarova *I.G. Izv. Sib. Otd. Akad. Nauk*, **8** (1960) 69-74
7) Bartušek M., *Chemické listy*, **73** (1979) 1036-1048
8) Mištová E., Parschová H., Jelínek L.,Matějka Z., Plichta Z., Beneš M., *Separation Science and Technology*, **43** (2008) 3168- 3182
9) Matějka Z., Parschová H., Ruszová P., Jelínek L., Houserová P., Mištová E., Beneš M., Hrubý M., Fundamentals and Applications of Anion Separations, Eds. B.A.Moyer and R.P.Singh, Kluwer Academic /Plenum Publishers, New York, 2004
10) Inukai Y., Kaida Y., Yasuda S., *Analytica Chimica Acta* **343** (1997) 275-279
11) Inukai Y., Kaida Y., Yasuda S., *Analytical Sciences* **13** (1997) 221-224
12) Inukai Y., Chinen T., Matsuda T., Kaida Y., Yasuda S., *Analytica Chimica Acta* **371** (1998) 187-193
13) Schilde U., Uhlemann E., *Reactive Polymers* **20** (1993) 181-188
14) Schilde U., Kraudelt H., Uhlemann E., *Reactive Polymers* **22** (1994) 101-106
15) Yasuda s., Kawazu K., *Bunseki Kagaku* **37** (1988) 67-71
16) Yasuda S. Kawazu K., *Separation Science and Technology*, **26**(9) (1991) 1273-1277
17) Parschová H., Matějka Z., Mištová E., *Separation Science and Technology,* **43** (5) (2008) 1208- 1220
18) Schilde U., Uhlemann E., *Reactive Polymers*, **18**, (1992) 155-158