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Removal of arsenic from aqueous solution containing hexafluoroarsenate

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ABSTRACT

Arsenic removal from aqueous solutions containing hexafluoroarsenate or arsenate by strong and weak base anion exchangers was studied by dynamic column tests that were carried out using solution containing arsenic and accompanying anions (chlorides, sulfates and fluorides). The specific flow rate of solution was 6 BV/h. Desorption of arsenic was carried out by 1 mol/L NaOH or 2 mol/L KSCN. All the studied anion exchangers performed well in the absence of accompanying anions. In the presence of chlorides and sulfates, studied exchangers showed high selectivity towards hexafluoroarsenate

Keywords: arsenic; hexafluoroarsenate; anion exchanger

INTRODUCTION

For the removal of arsenic from aqueous solutions, weakly basic anion exchangers or strongly basic anion exchangers[1], selective polymeric adsorbents[2] or sorbents[3-5] based on hydrated ferric oxide, titanium oxide[6] and cerium oxide[7] can be used. In the presence of accompanying anions, which are commonly found in streams (chlorides and sulfates), there is a significant decrease in the sorption capacity of the standard anion exchangers due to the competitive sorption. In such cases, it is advisable to use more selective inorganic sorbents based on hydrated ferric oxide[1].

Arsenic may be present in surface waters, mainly in the form arsenate, but also in the form hexafluoroarsenate. Hexafluoroarsenate usually originates from waste water in the glass industry[8] (production of crystal glass). The salts containing hexafluoroarsenate anion are also used as herbicides[9] and as electrolytes in lithium batteries[10]. For example, $KAsF_6$ is used as a pesticide[11] under various brand names (Hexaflurate, Nopalmate, TD-840). Hexafluoroarsenate shows completely different behavior than the arsenite or arsenate commonly occurring in waters. Standard methods for arsenic removal, such as the use of sorbents based on hydrated ferric oxide, are ineffective when arsenic occurs as hexafluoroarsenate.

If the analysis of aqueous solution containing arsenic shows presence of fluoride, it is possible that arsenic does not occur in solution as arsenate, but as hexafluoroarsenate. The hexafluoroarsenate anion[12] $[AsF_6]^-$ has been known in inorganic chemistry for a long time, and can be produced by addition of fluoride F^- to arsenic pentafluoride (AsF_5) or by reaction of arsenate with HF or CaF_2.

The possibility of removing arsenic in the form hexafluoroarsenate or arsenate in the presence of fluoride was tested on standard anion exchangers. This work also examined the effect of accompanying anions (chlorides, sulfates) on the removal of arsenic from aqueous solutions.

EXPERIMENTAL

This work was carried out using column dynamic experiments with 10 mL of resin. Weakly basic anion exchanger was used in the

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protonated form and strongly basic anion exchanger in chloride form. Lewatit MP 62 WS is a weakly basic, macroporous anion exchange resin with tertiary amine groups, hence of particularly low basicity. Its structure is shown in Figure 1.

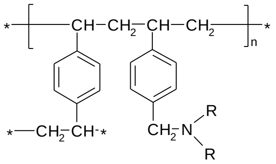

Figure 1: *Structure of Lewatit MP 62 WS*

Amberjet 4200 Cl is a uniform particle size, high quality, strong base type 1 anion exchanger (Fig. 2) designed for use in all general demineralization systems.

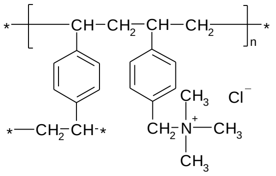

Figure 2: *Structure of Amberjet 4200 Cl*

Sorption was run at a specific flow rate *s* = 6 *BV*/h. Were tested model solutions containing arsenic in the form hydrogen arsenate (As = 5 mg/L) or hexafluoroarsenate (As = 5 mg/L). As the accompanying ions were selected, chlorides (100 - 1000 mg/L), sulfates (100 - 1000 mg/L) and fluorides (10 mg/L). The limit for calculating the concentration of breakthrough capacity was chosen to be 0.1 mg/L of arsenic.

To determine the concentration of arsenic optical emission spectrometry with inductively coupled plasma device for ICP-OES Optima 2000 DV was used.

RESULTS AND DISCUSSION

Sorption of arsenate

The removal of arsenic in the form of arsenate without the presence of accompanying anions by weak base anion exchanger in the protonated form was very effective (Fig. 3). According to the selectivity series of weakly basic resins, we can infer a high affinity of the resin to arsenate.

$OH^- > SO_4^{2-} > CrO_4^{2-} >$ citrate > tartare > $NO_3^- > AsO_4^{3-} > PO_4^{3-} > MoO_4^{2-} > CH_3COO^- > I^- = Br^- > Cl^- > F^-$

Almost identical results were obtained using a strong base anion exchanger in the chloride form (Fig. 4).

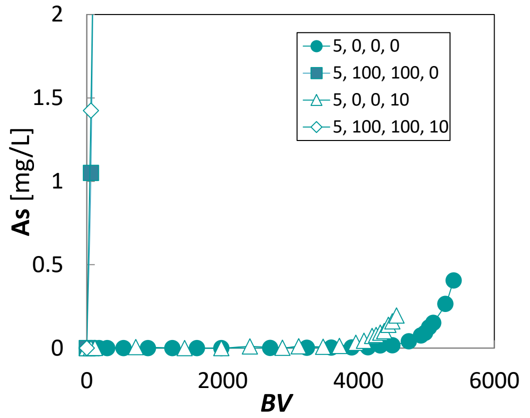

Figure 3: *Sorption of arsenate in the presence or absence of accompanying anions (chloride, sulfates and fluorides) on weak base anion exchanger (legend → e.g. 5, 100, 100, 10 → 5 = 5 mg/L of arsenic, 100 = 100 m/L of chlorides, 100 = 100 mg/L of sulfates, 10 = 10 mg/L of fluorides)*

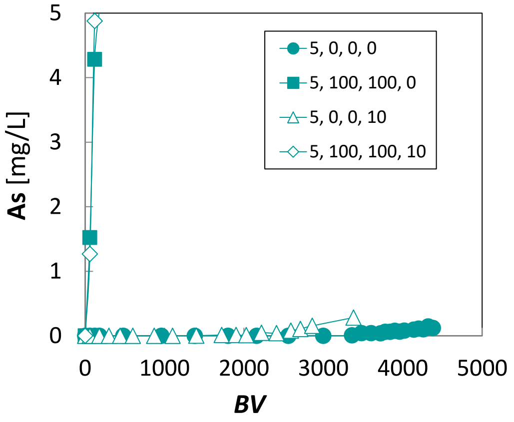

Figure 4: *Sorption of arsenate in the presence or absence of accompanying anions (chloride, sulfates, and fluorides) on strong base anion exchanger*

Sorption of hexafluoroarsenate

If the arsenic is presents in solution as hexafluoroarsenate, then it is a monovalent anion and low affinity to the resin is presumed. Weakly basic anion exchanger in the form of free base was ineffective in removing arsenic from hexafluoroarsenate solution.

$$\overline{R-NH_2} + AsF_6^- \rightarrow 0$$

Weakly basic anion exchanger in the protonated form (Fig. 5) removed arsenic in the hexafluoroarsenate form through ion exchange as follows:

$$\overline{R-N^+H_3Cl^-} + AsF_6^- \rightarrow \overline{R-N^+H_3AsF_6^-} + Cl^-$$

Hexafluoroarsenate has a high affinity for weakly basic anion exchangers and the adsorption efficiency of the sorption of arsenic in the form of hexafluoroarsenate was almost double the sorption of arsenic from arsenate solution. The selectivity of weakly basic anion exchanger on hexafluoroarsenate is high, because the addition of 100 mg/L of chlorides and sulfates in the hexafluoroarsenate solution did not affect the sorption efficiency of hexafluoroarsenate.

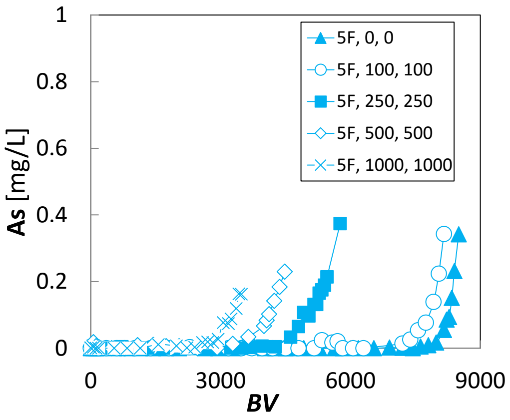

Figure 5: *Sorption of hexafluoroarsenate in the presence or absence of accompanying anions (chlorides and sulfates) on protonated weak base anion exchanger (legend → eg 5F, 100, 100 → 5 = 5 mg/L of arsenic, 100 = 100 mg/L of chlorides, 100 = 100 mg/L of sulfates)*

Sorption of hexafluoroarsenate in the presence or absence of accompanying anions (chlorides and sulfates) on a strong base anion exchanger was effective (Fig. 6). The removal of arsenic in the hexafluoroarsenate form by strongly basic anion exchanger in the chloride form proceeds as follows:

$$\overline{R-N^+(CH_3)_3Cl^-} + AsF_6^- \leftrightarrow \overline{R-N^+(CH_3)_3AsF_6^-} + Cl^-$$

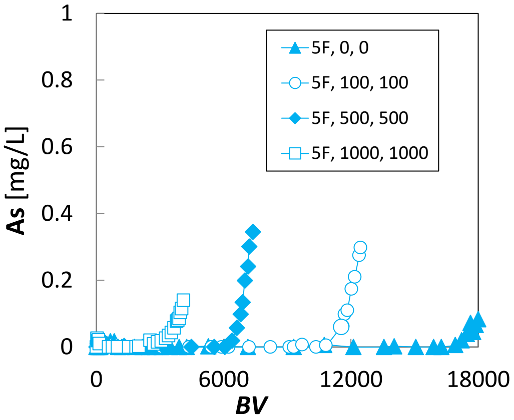

Figure 6: *Sorption of hexafluoroarsenate in the presence or absence of accompanying anions (chlorides and sulfates) on strong base anion exchanger in chloride form*

Desorption of hexafluoroarsenate

Desorption of hexafluoroarsenate was carried out by 10 BV of 1 mol/L NaOH on a weak base anion exchanger (Fig.7). 97 % of the arsenic was displaced during regeneration. Strong base anion exchanger (Fig.8) was regenerated by 35 *BV* of 2 mol/L KSCN because 1 mol/L NaCl was not effective. The first 10 *BV* of regeneration solution recovered about 82 % of arsenic. 98 % of the arsenic was displaced during regeneration. Desorption was carried out at a specific flow rate *s* = 3 *BV*/h.

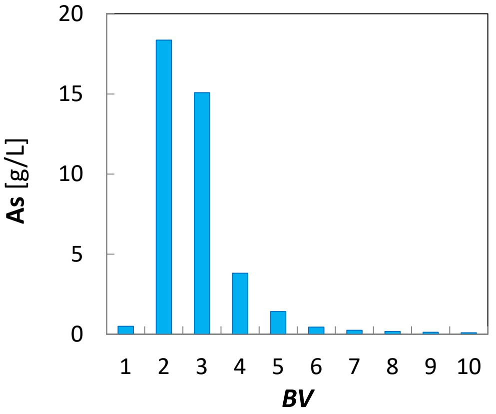

Figure 7: *Desorption of hexafluoroarsenate from weak base anion exchanger using 1 mol/L NaOH solution after sorption of hexafluoroarsenate (5 mg/L of arsenic)*

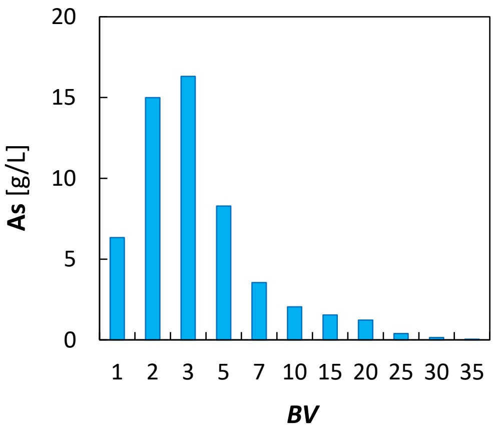

Figure 8: *Desorption of hexafluoroarsenate from strong base anion exchanger using 2 mol/L KSCN solution after sorption of hexafluoroarsenate (5 mg/L of arsenic)*

CONCLUSIONS

The standard strong and weak base anion exchangers can be efficiently used for removal of hexafluoroarsenate from aqueous solution in the presence of accompanying anions (chlorides and sulfates).

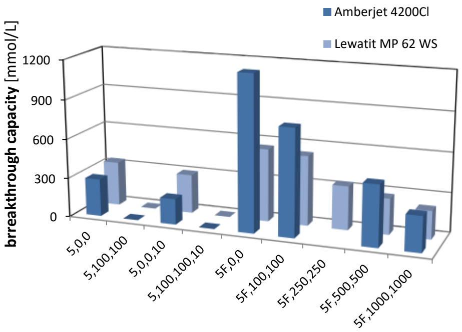

Figure 9: *Breakthrough capacities of arsenic from arsenate and AsF_6^- solutions on anion exchangers*

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