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Sorption of metal oxoanions by chemically modified alginic acid sorbents

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ABSTRACT

Chemically modified alginic acid was used as sorbent of metal oxoanions (W(VI), Mo(VI), Sb(III), V(V) and As(V)). All experiments were carried out in dynamic column sorption mode. Chemicall modifications such as esterification, crosslinking or granulation with PAN were important for the mechanical and chemical stability of prepared sorbents, but sorption of metal oxoanions was not very successful. The best results were achived with sorbent AA-2 – alginic acid crosslinked with diethylenetriamine and azide – for sorption of V(V) and Mo(VI). Sorbent AA-4 – which was crosslinked with epichlorohydrin could be used for sorption of W(VI) after conditioning with HCl. Sorbent AA-1 (granulated with PAN) needed to be conditioned with Fe^{3+} ions. Similarly, sorbent AA-4 could be used for As(V) sorption after the Fe^{3+} conditioning. In all the cases, the sorbents could not last many sorption-desorption cycles and the breakthrough capacities were not very high (hundreds of mg per L of sorbent). Price of sorbents prepared by modification of alginic acid was inadequate to their sorption ability.

Keywords: alginic acid; sorption; metal oxaonions; PAN

INTRODUCTION

Alginic acid is biopolymer found in marine algae and contains variable amounts of β-D-mannuronic (M) acid and α-L-guluronic(G) acid. These monomers can be organized in blocks of consecutive G-residues (G-blocks), consecutive M-residues (M-blocks), or alternating M and G (MG-blocks). The relative amount of each block-type varies between different alginates[1-3].

Alginic acid is biopolymer, which has many interesting properties, such as wound healing and ion-exchange ability (water treatment). It has already found applications in the food and pharmaceutical industries, in medical or environmental-friendly materials [4-9].

Alginic acid contains carboxylic groups, so it can be used as a weakly acidic cation exchanger. Therefore, many applications for heavy metal sorption are known [10-16].

It is known[17-20] that low molecular weight substances containing diol-groupings in an appropriate steric conformation form complexes with some metal and metalloid oxoanions. These hydroxycompounds can form two kinds of the coordination diol- or polyol- complexes with oxoanions:

1. mono-nuclear complexes (Ge, B, As(V));
2. bi (*or poly*)-nuclear complexes (V, W, Mo).

The complexation reactions between oxoanions and diol-compounds (diol-ligands) are pH-sensitive. Optimum pH-range (Tab. I) for particular oxoanions to form diol (polyol) complexes was determined[21].

The formation of these diol- or polyol-complexes can be utilized for the selective uptake of oxoanions from the water streams using a solid matrix containing these groupings with appropriate steric configuration and conformation of –OH groups.

Table I *Optimal pH for form of complexes*[21]

	Optimal pH
B(III)	7 – 11
Ge(IV)	6 – 12
As(III)	9 – 12
V(V)	2 – 7
Mo(VI)	1 – 6
W(VI)	1 – 6
As(V)	1 – 6

The main aim of this study was the testing of modified biosorbents based on alginic acid for the selective removal of metal oxoanions (As, Mo, V, W and Sb) from diluted water solutions and for the treatment of contaminated wastewaters.

EXPERIMENTAL

Sorption

All experiments were carried out in dynamic column sorption mode. The loading solution passed through the column (inner diameter 10 mm) containing 10 mL of sorbent with the specific flow rate of 3 or 6 BV/h. Fractions of filtrate were collected and metal concentrations were analyzed with ICP-OES technique (Perkin-Elmer Instruments - Optima 2000 DV).

For the preparation of test solutions, $Na_2WO_4 \cdot 2H_20$, NH_4VO_3, $Na_2MoO_4 \cdot 2H_2O$, Sb_3O_3 and $Na_3AsO_4 \cdot 12H_2O$ of analytical purity were used. The solutions were freshly prepared before the use, the initial concentration of metal was 0.5 or 1.0 mg/L and the concentrations of accompanying anions (Cl^-, SO_4^{2-}) were 100, 250 and 500 mg/L. The experimental pH values were ranging from 3.5 to 7.5. Regeneration and condition specifications are discussed in *Results and discussion* section.

For the sorption run, the limiting breakthrough concentration was 0.1 mg/L of metal. The sorption breakthrough capacities of the sorbent ***q*** were calculated according to the following equation (1):

$$q = \frac{V \cdot c_0}{V_0} \quad [\text{mg/L}] \qquad (1)$$

V…..volume at the breakthrough point [mL]
c_0…..metal concentration in the feed [mg/L]
V_0….volume of the sorbent in column [mL]

Sorbents preparation

For the sorption, four different modified sorbents based on alginic acid (Fig.1) were provided (see *Acknowledgement*).

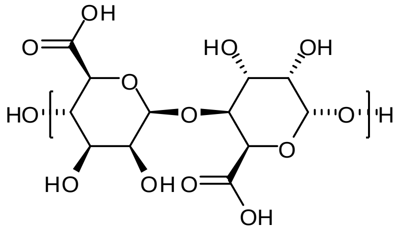

Figure 1: *Alginic acid*

Sorbent **AA-1** – Esterification process[22] was following: dry material matrix with methanol and H_2SO_4 (98%, p.a.) under reflux condenser was boiled for five hours. To dry matrix after esterification was added of 30 wt% NH_3 solution and reacted 4 days at the temperature of about 5°C. This material was granulated by method according to the one modification of the general procedure[23,24]. Fibrous polyacrylonitrile (PAN) was dissolved in dimethylsulfoxide and powdered esterification matrix was gradually added to PAN solution and suspension was carefully mixed. Homogeneous suspension was then dispersed into water bath. Coagulated beads were washed with distilled water and sieved. Swollen fraction with grain size 0.2 – 1.0 mm was separated and used without drying.

AA-2 – alginic acid was crosslinked with diethylentriamine and azide, following esterification process - dry material matrix with methanol and HCl (35%, p.a.) condenser was boiled under reflux for five days.

AA-3 – alginic acid was esterification by same process as sorbents AA-1 and AA-4. It was then crosslinked with hexamethylendiamine (shaking for 12 hours at room temperature).

AA-4 – alginic acid was crosslinked with epichlorhydrin[30], following esterification process.

RESULTS AND DISCUSSION

Sorbent AA-1

Sorbent AA-1 for sorption of Sb(III), W, Mo and V was used. All dynamic column sorption experiments were not successful. It is possible that, despite of the esterification, many carboxylic groups remained and obstructed the sorption these oxoanions.

When this sorbent was conditioned with Fe^{3+} ions, the sorption of oxoanions of Sb(III), W(VI) and V(V) was possible (Tab. II).

Table II *Sorption breakthrough capacities of sorbent AA-1*

	q_u [mg/L]	
	without Fe	with Fe
Sb(III)	0	244
W(VI)	0	285
V(V)	0	330

During the sorption cycle, concentration of Fe^{3+} in filtrate was under detection limit of AAS - SpetraAA 220, Varian - (0.01 mg/L). On the other hand, during the regeneration process, a great deal of Fe was lost. Consequently, sorbent was conditioned before every sorption. For conditioning, 6 BV of 0.04 mol/L $FeCl_3$ solution was used.

In the case of sorbent AA-1, it was determined that the observed sorption is purely due to the adsorption on Fe(III) oxides.

Sorbent AA-2

This sorbent was used for sorption of oxoanions of Mo(VI) and V(V). Before sorption sorbent was conditioned whit 4 BV of HCl solution with concentration of 0.5 mol/L.

Feed solution for dynamic column sorption of Mo(VI) contained 0.5 mg/L of Mo, pH was 3.5 and the flow rate 6 BV/h. Effect of concentration of accompanying anions (chlorides and sulfates) was studied. The best results (Fig.2) were obtained with concentration of 100 mg/L of both accompanying anions when the breakthrough capacity was 275 mg/L of the sorbent. Increasing the concentration of chlorides and sulfates to 250 mg/L and 500 mg/L resulted in the capacity decrease to 128 mg/L and 133 mg/L, respectively.

The influence of pH of feed solution on sorption of V(V) oxoanion was also studied. The concentration of V was 0.5 mg/L and *s* = 6 BV/h in all cases. The Fig. 3 shows that pH around 5.5 and 4.5 was optimal for sorption of V(V), with the breakthrough capacities 100 mg/L and 92 mg/L, respectively.

Because the effect of accompanying anions was strong, concentration of 100 mg/L of chlorides and sulfates was used for consequent sorption cycles.

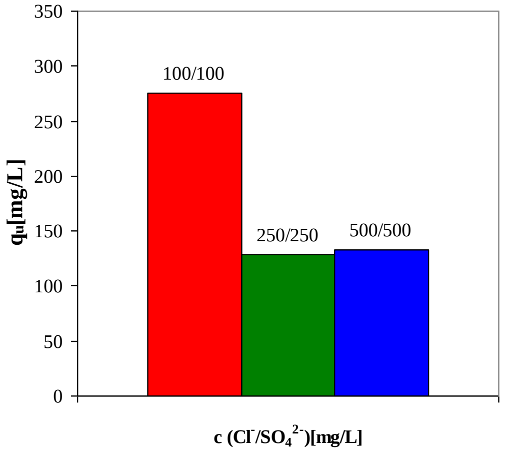

Figure 2: *Influence of accompanying anions on the breakthrough capacities of Mo(VI) on AA-2 (c(Mo) = 0.5 mg/L; pH = 3.5; s = 6 BV/h)*

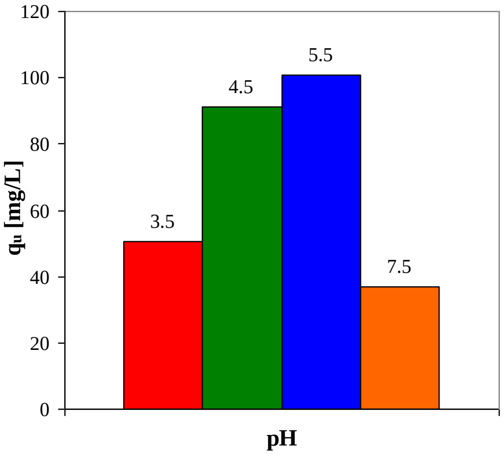

Figure 3: *Influence of feed solution pH on the breakthrough capacities of V(V) sorption by AA-2 (c(V) = 0.5 mg/L; c(Cl^-/SO_4^{2-}) = 100 mg/L; s = 6 BV/h)*

At pHs 3.5 and 7.5 capacities were 50 and 37 mg/L, respectively.

Regeneration of the sorbent whit 10 BV of 0.1 mol/L NaOH solution had good yield (about 97%) in all cases.

Sorbent AA-3

Sorbent AA-3 was used for sorption of W(VI), Mo (VI) and V(V). It was conditioned with 5 BV of 0.5 mol/L HCl solution before every sorption run.

Feed solution contained 0.5 mg/L of metal oxoanion and 100 mg/L of accommodation anions (Cl^- and SO_4^{2-}). The specific flow rate *s* was 6 BV/h. pH 3.5 was used for Mo and W and 5.5 for V sorption (Tab. III).

Table III *Sorption breakthrough capacities of sorbent AA-3*

	q_u [mg/L]
Mo(VI)	15.8
W(VI)	63.3
V(V)	19.6

Short sorption cycles and worst chemical and mechanical stability of sorbent AA-3 rendered this sorbent unsuitable for column sorption.

Sorbent AA-4

Also sorbent AA-4 had poor mechanical and chemical stability. During sorption, volume of sorbent increased twice.

Sorption of W(VI) oxoanion was better than in the case of sorbent AA-3. Breakthrough capacity was 137 mg/L (Tab. IV). However, sorption of Mo(VI) was not successful.

Table IV *Breakthrough capacities of AA-4*

	q_u [mg/L]
Mo(VI)	0
W(VI)	137

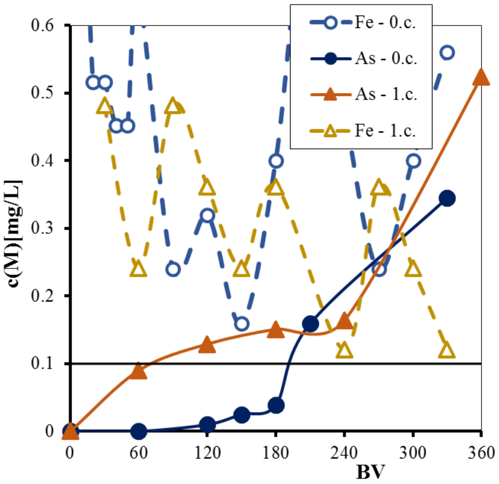

Figure 4: *Sorption of As(V) oxoanion onto sorbent AA-4, conditioned with Fe^{3+}; comparison of 0. cycle and 1. cycle (c(As) = 1 mg/L, c(Cl^-/SO_4^{2-}) = 100 mg/L , s = 3 BV/h and pH = 4)*

For the sorption of As(V) oxoanion, the sorbent was conditioned with 6 BV of 0.04 mol/L $FeCl_3$ solution. Breakthrough capacity for the solution containing 1 mg/L of As, 100 mg/L of both Cl^- and SO_4^{2-} at pH 4 was 245 mg/L.

However, both the sorption effluent and spent regeneration solution contained high concentration of Fe ions (Fig. 4 and Fig. 5) and before the subsequent sorption sorbent AA-4 had to be conditioned again. The breakthrough capacity was only 88 mg/L. The and regeneration yield of As was only 72%.

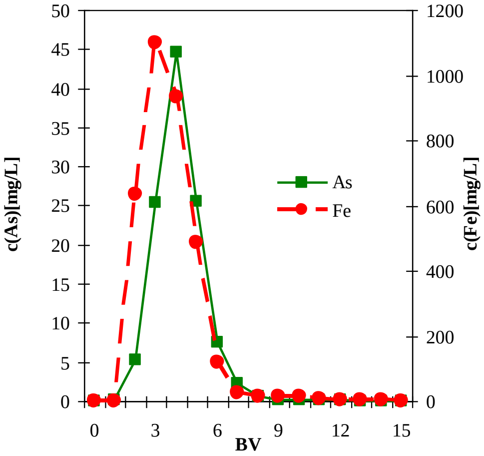

Figure 5: *Regeneration As from sorbent AA-4, conditioned with Fe^{3+}, with 10 BV 0.5 mol/L HCl.*

CONCLUSIONS

This study evaluated the applicability of four modified biosorbents based on alginic acid for the selective removal of metal oxoanions (As, Mo, V, W and Sb) by the column sorption.

Sorbent AA-1 (granulated with PAN) could be used only after conditioning with Fe^{3+}. Similarly, the sorbent AA-4 could be used for As(V) sorption after Fe^{3+} conditioning. Currently, there is a great number of sorbents based on iron oxides, which have much higher sorption capacity than the sorbents studied in this work[26-30].

Sorbents AA-2 and AA-3 could be used for sorption of V(V) and Mo(VI), but in both cases the sorbents did not last many sorption cycles and also the breakthrough capacities were not very high. Price of the studied sorbents is inadequate to their sorption ability.

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