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Selective Sorption of Metal Oxoanions from Dilute Solution by Chemicaly Modified Brown Seaweed *Ascophyllum Nodosum*

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Abstract: Two samples of chemically modified seaweed Ascophyllum nodosum (NS-1 and DS-1) were used for selective removal of metal (W, Mo, V, Ge, and Sb) oxoanions. All experiments were carried out by dynamic column sorption. The effects of pH, the concentration of the accompanying anions in the feed solution, and the effect of the flow rate were studied. Tungstate, molybdate, and vanadate were adsorbed extensively. Sorption of Sb(III) anion was notable but the sorption capacity was very low and the desorption was difficult. Sorption of Ge(IV) oxoanion was negligible. Stability of the NS-1 and DS-1 sorbents was limited by, 20 and 25 sorption cycles, respectively.

Keywords: Biosorption, metal oxoanions, seaweed

INTRODUCTION

It is now generally accepted that certain natural polymers derived from biomass serve similarly as synthetic ion-exchange resins or even chelating resins for the removal of toxic metal cations or for the recovery of some valuable ions (1–4). Many studies presented the application of natural cation-exchange biopolymers to the sorption of heavy metals from

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aqueous solutions. They are summarized in review articles (5–7). Studies of selective sorption of metal-oxoanions such as As(V), As(III), W(VI), Mo(VI), V(V), Se(IV), Se(VI), Ge(IV), etc. by biopolymers exist, but many of them are concerned with the sorption of arsenic only (8–15), sorption experiments involving other metal-oxoanions (16–26) are rarely published.

Metal-oxoanions such as As(V), As(III), W(VI), Mo(VI), V(V), Se(IV), Se(VI), Ge(IV) etc. are among the most commonly encountered and difficult to treat environmental pollutants. They are introduced into the environment during mining, refining of ores, combustion of fossil fuels, industrial processes, and the disposal of industrial and domestic wastes. Metal–oxoanions are conventionally recovered by liquid-liquid extraction (27–29), ion-exchange by standard strongly or weakly basic anion exchange resin (30,31), ion-exchange by chelating resin (8,25,32–36), flocculation by Fe^{3+} salts (37), nanofiltration, and ultra filtration (38,39).

It is known (40–43) that low molecular weight substances containing diol-groupings in an appropriate steric conformation form complexes with some metal-oxoanions. These hydroxycompounds can form two kinds of the coordination diol- or polyol- complexes with metal-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 (Table 1) for particular oxoanions to form diol (polyol) complexes was determined (44).

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 the conformation of OH-groups as a selective sorbent.

Table 1. Optimal pH for form of complexes

	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

Ascophyllum nodosum (45) is a brown seaweed closely related to Fucus. It forms single bladders centrally in long, flattened, strap-like fronds. The fronds hand downwards draping sheltered intertidal rocks. Many fronds grow from the base and the plant generally regenerates new fronds from the base when one of the larger fronds is damaged. There is evidence that clumps of Ascophyllum can be over 400 years old and even older.

Ascophyllum is utilized as a source for the production of alginic acid by extraction of alginic acid, a polysaccharide used in foods and in biotechnology.

Seaweed contains a heterogeneous mixture (46) of different polysaccharides (Fig. 1) as alginic acid (20–25%), mannitol (5–10%), cellulose, chitosan, etc.

These polysaccharides contain –OH groups in different configurations and conformations. Some of them can form poly-ol-complexes with metal anions (W, Mo, V, Ge, Sb, As). This process is one of the mechanisms to remove these anions from water. Starting seaweed was cross-linked to prevent losses of soluble active components and enhance mechanical properties of the adsorbent. A negative charge of the ionized carboxyl groups, which hinders chelate formation by electrostatic repulsion of evenly charged oxoanions, was eliminated by esterification.

The main aim of this study was the testing of modified biosorbents containing alginic acid for the selective removal of metal oxoanions from dilute water solutions and for the treatment of contaminated wastewaters.

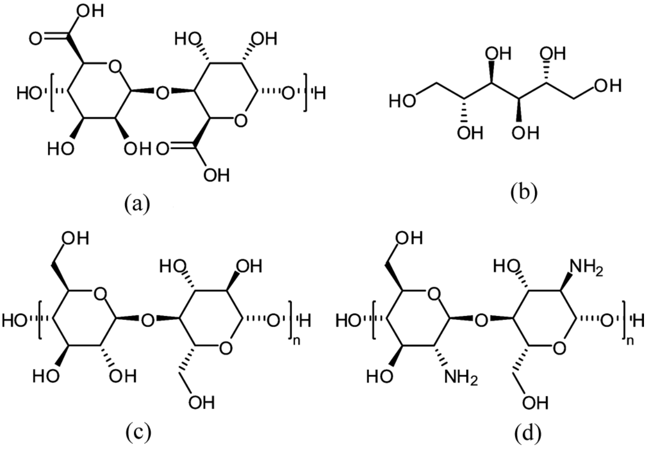

Figure 1. Structure of a) alginic acid, b) mannitol, c) cellulose, d) chitosan.

EXPERIMENTAL

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 flow rate of 3 or 6 BV/h. Fractions of filtrate were collected and metal concentrations were analyzed with the ICP-OES technique.

For the preparation of test solutions, $Na_2WO_4 \cdot 2H_2O$, NH_4VO_3, $Na_2MoO_4 \cdot 2H_2O$, GeO_2, and Sb_2O_3 of analytical grade purity were used. The solutions were freshly prepared before use, the initial concentration of metal was 0.5 or 1.0 mg/L, and the concentration of accompanying anions (Cl^-, SO_4^{2-}) was 100 or 500 mg/L. The experimental pH values were ranging from 3.5 to 10. All sorbents were regenerated with 0.1 mol/L NaOH solution after sorption of oxoanions W(VI), Mo(VI) and V(V), or with 0.5 mol/L HCl solution after sorption of Ge(IV) and Sb(III). Before every sorption run of W(VI), Mo(VI), and V(V) the sorbent was conditioned by 0.5 mol/L HCl solution, to keep all OH-groups and also carboxylic groups in the hydrogen form.

It was very important to keep the concentration of NaOH solution below 0.1 mol/L to prevent the degradation of the sorbent. If it was used higher concentrations of NaOH solution may cause a dealgination process.

For the sorption run the limiting breakthrough concentration was 0.1 mg/L of metal. The sorption capacities of the sorbent were calculated according to the equation:

Sorption capacity = (volume at the breakthrough point × mass concentration)/volume of the sorbent [mg Me/L of sorbent], resp. [mmol-Me/L of sorbent].

Preparation of Sorbents

For the preparation of chemically modified sorbents seaweed Ascophyllum nodosum seaweeds supplied by ISP Alginates UK Ltd. (47) were used on March 2001.

As the seaweed biomass particles were not mechanically and chemically stable enough for the column operation, it was necessary to improve their properties. Chemical crosslinking and esterification contributed to the elimination of those problems.

Two different samples of chemically modified seaweed Ascophyllum nodosum were used:

Natural Seaweed Crosslinked with Hexamethylenediamine (NS-1)

1. Esterification: 20 g of dry seaweed whit 270 mL of methanol and 10 mL HCl (35%, p.a.) was heated under reflux condenser for five days.
2. Crosslinking: 8 g of estrificated seaweed with 1.5 g of hexamethylendiamine was carried out for 12 hours in shaker at room temperature.

Carboxylic groups were partially eliminated by chemical modification. Amino groups were also introduced to the sorbent during reaction with hexamethylendiamine. They can function as anion-exchange sites. The sorbent contains –OH, residual $-COO^-$, and amino groups.

Dealginated Seaweed Crosslinked with Epichlorhydrin (DS-1)

61.2 g dealginated seaweed ground coarsely on coffee mill, was swelled under stirring for 30 min and then sonicated for 5 min in 800 ml mixture aceton – water (1:1, v/v). Liquid was filtered off and to solid in 240 mL aceton – water (1:1, v/v) was added under stirring first 50 mL 5 M NaOH (250 mmol) and after 10 min 24 g (259 mmol) 1-chlor-2,3-epoxypropane. Heating at 50°C continued for an additional 15 hours. The product was thoroughly washed with aceton-water and water.

20 g of dry crosslinked matrix with 270 ml of methanol and 10 mL HCl (35%, p.a.) was boiled under a reflux condenser for five days.

The matrix of sorbents are in the form of particles with different shape and size. Thus, it is possible that the sorption does not proceed uniformly.

RESULTS AND DISCUSSION

Sorption of Tungstate

The influence of pH on the W(VI) oxoanion sorption is shown in the Fig. 2 and Table 2. The concentration of W(VI) in the feed solution was 1 mg/L and the concentration of accompanying anions (Cl^-, SO_4^{2-}) was 100 mg/L. The sorption capacity of W(VI) anion at the pH of 3.5 was better on sorbent DS-1, where the sorption capacity was 1057.6 mg/L, on sorbent NS-1 was only 55.9 mg/L. At the pH of 5.5 the breakthrough capacity decreased to 775.2 mg/L (DS-1) and increased to 464.2 mg/L (NS-1). These results for the sorbent DS-1 indicate that the tungsten's chelates are more stable in the acidic pH range, where W is present in the form of isopolyanions (48) $W_{12}O_{41}^{10-}$ or $H_2\,W_{12}O_{40}^{6-}$. In these polyanions there are much more reactive sites (W–O bonds) to form

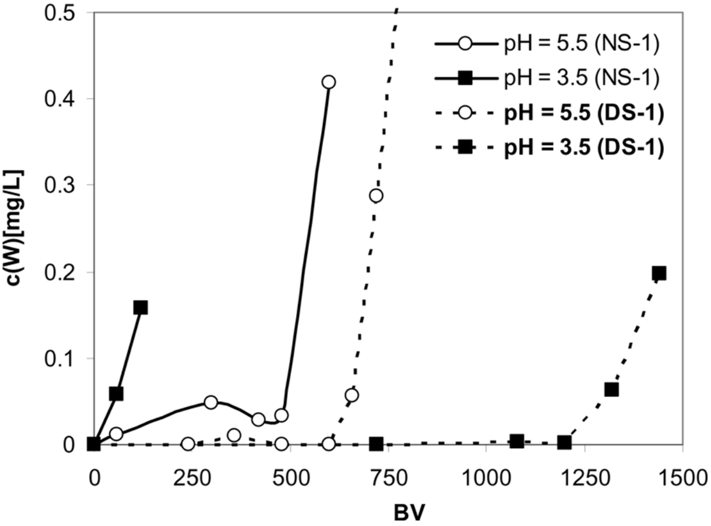

Figure 2. The history of W-sorption – Effect of pH.

polyolcomplexes with saccharide OH-groups, compared to a simple WO_4^{2-} anion, which is present in the neutral and alkaline environment. In the case of NS-1 we can say that its functional groups are less accessible to isopolyanions and so simple WO_4^{2-} anion (pH = 5.5–6) is better for separation from water solution.

When the concentration of sulfates and chlorides in the feed solution was increased from 100 mg/L to 500 mg/L at pH = 5.5 (Fig. 3) the sorption capacity of NS-1 decreased from 464.2 mg/L to 441.1 mg/L (by 5%), the sorption capacity of DS-1 decreased by 44% (from 775.2 mg/L only

Table 2. The comparison of breakthrough capacities for W-oxoanions

c(Me) [mg/L]	c(Cl$^-$) [mg/L]	c(SO$_4^{2-}$) [mg/L]	pH	s [m^3 . m^{-3}. h^{-1}]	Sorption capacity [mg/L]	
					NS-1	DS-1
0.5	100	100	3.5	3	<5.0	1925.8
0.5	100	100	3.5	6	–	1970.0
1.0	100	100	3.5	3	26.6	–
1.0	100	100	3.5	6	55.9	1057.6
1.0	100	100	5.5	3	434.7	–
1.0	100	100	5.5	6	464.2	775.2
1.0	500	500	5.5	6	441.1	432.0
0.5	500	500	3.5	6	–	921.4

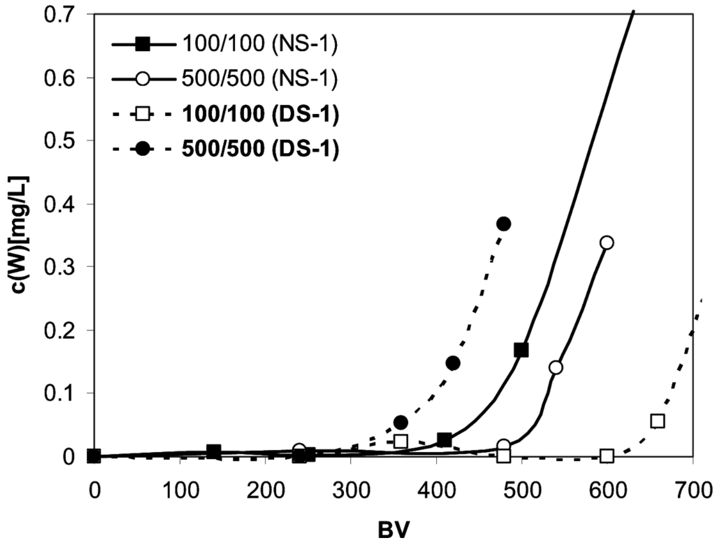

Figure 3. The history of W-sorption – Effect of accompanying anions (pH = 5.5).

to 432 mg/L). At pH = 3.5, the sorption capacity of DS-1 decreased by 53% (from 1970 mg/L only to 921 mg/L) (Table 2). The sorption capacity of the sorbent DS-1 was higher than the capacity of the NS-1, but the selectivity of DS-1 was lower than that of NS-1.

The effect of the flow rate was studied at the specific flow rates 3 BV/h and 6 BV/h. In the case of the sorbent NS-1 (Table 2) the difference between the sorption capacity at s = 3 BV/h and s = 6 BV/h (c(W) = 1 mg/L; c(Cl^-, $SO_4{}^{2-}$) = 100 mg/L; pH = 5.5), was only about 7%. This result shows that the kinetic of sorption was rather fast. As in the case of NS-1, the kinetic of the sorption by sorbent DS-1 between s = 3 BV/h and s = 6 BV/h (c(W) = 0.5 mg/L; c(Cl^-, SO_4^{2-}) = 100 mg/L; pH = 3.5) was similar. The sorption capacities were 1925 mg/L and 1970 mg/L, respectively.

The recovery of W(VI) oxoanion provided good yields, W was completely striped within 10 BV of the regeneration solution of 0.1 M NaOH. This high desorption efficiency enables the reuse of the sorbents.

Sorption of Molybdate

The influence of pH (Fig. 4) on the sorption was little different from tungstate sorption. At the concentration of Mo(VI) in the feed solution 1 mg/L and concentration of accompanying anions (Cl^-, SO_4^{2-})

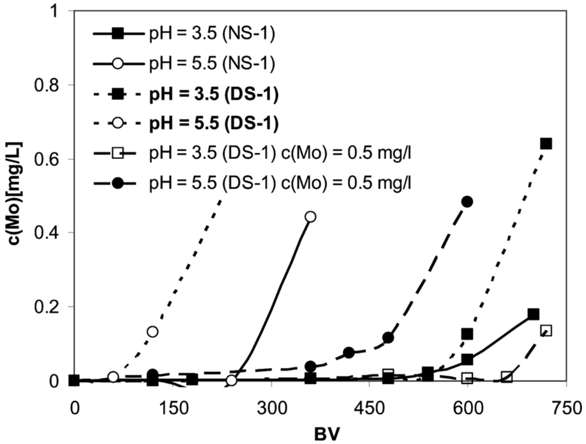

Figure 4. The history of Mo-sorption – Effect of pH.

100 mg/L the breakthrough capacity for sorbent NS-1 was 672.6 mg/L at pH of 3.5, at pH of 5.5 the capacity fall down to 274.9 mg/L (by 60%), the breakthrough capacities for DS-1 were 577.2 mg/L and 123.1 mg/L (by 78%), respectively. When the concentration of Mo was 0.5 mg/L

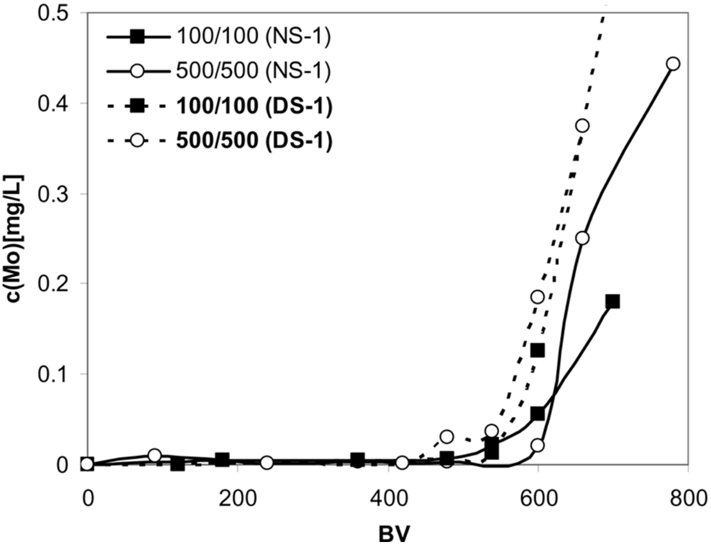

Figure 5. The history of Mo-sorption – Effect of accompanying anions (pH = 3.5).

the breakthrough capacities for DS-1 were 372.8 mg/L (pH = 3.5) and 270.3 mg/L (pH = 5.5). In this case the sorption capacities were higher at pH = 3.5 for both sorbents. This fact is very typical for the sorption of molybdate because the chelate of Mo-oxoanion is less stable than the W-chelate (42) and it is muchmore sensitive to the pH change.

The sorption capacities of molybdate oxoanion at concentrations of sulfates and chlorides 100 mg/L and 500 mg/L were similar (Fig. 5). The sorption capacity in the presence of 500 mg/L of the accompanying anions was 603.9 mg/L in the case of sorbent NS-1 and 584.6 mg/L in the case of sorbent DS-1. That means a decrease by 10% and 2%, respectively. It is possible to conclude, that both sorbents have high selectivity to the Mo oxoanion.

The effect of the flow rate was studied only in the case of the sorbent NS-1, when the specific flow rate was 3 BV/h or 6 BV/h (Table 3). The difference between the sorption capacities at s = 3 BV/h and s = 6 BV/h (c(Mo) = 0.5 mg/L; c(Cl^-, SO_4^{2-}) = 100 mg/L; pH = 3.5) was only about 5%. This result shows that the kinetic of the sorption was optimal.

The recovery of the molybdate oxoanion was similar to the recovery of W(VI). Mo(VI) was completely striped within 10 BV of the regeneration solution of 0.1 M NaOH.

Sorption of Vanatate

Sorption of V(V) oxoanion by sorbent NS-1 was successful only for one full sorption cycle, c(V) = 0.5 mg/L; c(Cl^-, SO_4^{2-}) = 100 mg/L; pH = 3.5; s = 3 BV/h, the sorption capacity was 731.4 mg/L. The next cycles were not completed because this type of chemical modification of brown seaweed Ascophyllum nodosum was not chemically stable in the solution of NaOH, which was used for the desorption of V(V), After 20 desorption cycles the particles of the sorbent were severely degraded and it was not possible to use the sorbent NS-1 for column separation.

Table 3. The comparison of breakthrough capacities for Mo-oxoanions

c (Me) [mg/L]	c(Cl^-) [mg/L]	c(SO_4^{2-}) [mg/L]	pH	s [$m^3 \cdot m^{-3} \cdot h^{-1}$]	Sorption capacity [mg/L]	
					NS-1	DS-1
0.5	100	100	3.5	3	459.0	———
0.5	100	100	3.5	6	439.0	372.8
1.0	100	100	3.5	6	672.6	577.2
1.0	100	100	5.5	6	274.9	123.1
1.0	500	500	3.5	6	603.9	584.6

In the case of sorbent DS-1 the degradation of particles was slower than in the case of NS-1, and it was possible to study sorption of V(V) oxoanion more in details.

The influence of pH (Fig. 6 and Table 4) on the sorption was little different in the cases of tungstate and molybdate sorption. At the concentration of V(V) in the feed solution 1 mg/L and concentration of accompanying anions (Cl^-, SO_4^{2-}) 100 mg/L, the breakthrough capacity in case of sorbent DS-1 was 260.6 mg/L at pH of 3.5, at pH of 5.5 the capacity was similar 285.5 mg/L (about 10% difference), when the concentration of accompanying anions (Cl^-, SO_4^{2-}) was 500 mg/L the sorption at pH = 3.5 was not successful and at pH = 5.5 the breakthrough capacity was 318.7 mg/L. When the concentration of the V anion decreased to 0.5 mg/L (c(Cl^-, SO_4^{2-}) = 500 mg/L; pH = 5.5) the breakthrough capacity was 259 mg/L. In this case the optimal pH value for the sorption of V oxoanions was pH = 5.5.

The sorption capacities of the vanadate oxoanion were similar for both the concentration of accompanying anions (Fig. 6). When the concentration of the sulfates and the chlorides was 100 mg/L the breakthrough capacity was 285.2 mg/L, when the concentration of Cl^-, SO_4^{2-} was 500 mg/L the sorption capacity was 318.7 mg/L (increase by 12%).

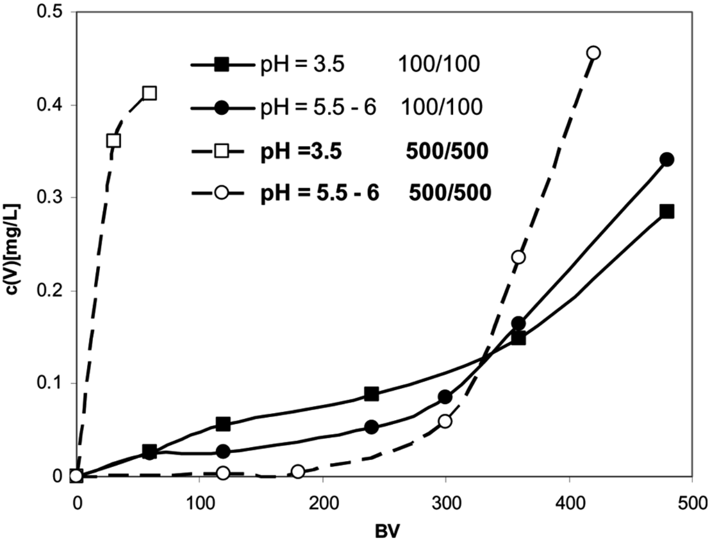

Figure 6. The history of V-sorption – Effect of pH and accompanying anions (DS-1).

Table 4. The comparison of breakthrough capacities for V-oxoanions

c(Me) [mg/L]	c(Cl^-) [mg/L]	c(SO_4^{2-}) [mg/L]	pH	s [$m^3 \cdot m^{-3}$ .h^{-1}]	Sorption capacity [mg/L] NS-1	Sorption capacity [mg/L] DS-1
0.5	100	100	3.5	3	731.4	–
1.0	100	100	3.5	6	–	260.6
1.0	100	100	5.5	6	–	285.2
1.0	500	500	5.5	6	–	318.7
0.5	500	500	5.5	6	–	259.0

The recovery of vanadate oxoanion provided good yields, as in the cases of W and Mo. Vanadate was completely striped within 10 BV of the regeneration solution of 0.1 M NaOH.

Sorption of Antimonate(III) and Germanante Oxoanions

For the oxoanion of Sb(III) the sorbent NS-1 was used. The first experiment at the concentration of Sb(III) anion 1 mg/L, c(Cl^-, SO_4^{2-}) = 100 mg/L, pH = 6 and s = 6 BV/h the breakthrough capacity was 85.6 mg/L. The desorption of Sb(III) was problematic. Two stage regeneration had to be used (10 BV 0.2 M HCl and 10 BV 0.1 M NaOH) to enable the successful consequent sorption run. The breakthrough capacity at experiment number 4 increased to 123.4 mg/L (increase by 44%).

In the case of Ge(IV) oxoanion the sorbent DS-1 was used, but Ge(IV) broke through within the first fractions of outlet solution.

CONCLUSIONS

The chemically modified brown seaweed Ascophyllun nodosum biosorbents NS-1 and DS-1 are suitable to remove tungstate, molybdate, and vanadate oxoanions from water. The matrix of the sorbents was not sufficently stable in the NaOH solution. Therefore, NaOH concentration of 0.1 mol/L was used for the desorption of V(V), W(VI), and Mo(VI) oxoanions. The application of these sorbents for the column separation was limited to 20–25 sorption cycles.

When the feed solution contains only a low concentration (100 mg/L) of the accompanying anions (sulfates and chlorides) the best results for tungstate sorption were obtained with sorbent DS-1. The sorption capacity was 1970 mg/L (pH = 3.5). In the case of the sorbent NS-1, the highest sorption capacity was 464 mg/L at pH = 5.5. The increase of the flow rate from 3 to 6 BV/h did not have any negative effect on the sorption. In the case of DS-1 a decrease of sorption capacity was observed, when the concentration of the accompanying anions increased form 100 mg/L to 500 mg/L. It is possible, that the sulfate oxoanion is a competitive anion for the tungstate oxoanion.

The best results for the molybdate sorption were obtained at pH of the feed solution 3.5. The sorption capacities were 672.6 mg/L and 577.2 mg/L in the case of the sorbent NS-1 and DS-1, respectively. The increase of the flow rate from 3 to 6 BV/h did not have any negative effect, similarly to the effect of increased concentration of the accompanying anions.

Sorption of the vanadate anion was also possible. The optimal pH value for the sorption of V oxoanions was pH = 5.5. The sorbent DS-1 had good selectivity for the sorption of vanadate, and the effect of the concentration of the accompanying anions was negligible.

Sb(III) oxoanion was removed, but the special type of regeneration had to be used. The sorption capacities were about 100 mg/L.

Sorption of Ge(IV) oxoanion was not successful under the studied conditions.

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