Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Sorption of Metal Oxoanions by Composite Biosorbents of Waste Material of Brown Seaweeds *Ascophyllum nodosum* and PAN

Eva Mištová[a]; Helena Parschová[a]; Luděk Jelínek[a]; Zděněk Matějka[a]; Ferdinand Šebesta[b]
[a] Institute of Chemical Technology, Department of Power Engineering, Prague, Czech Republic [b] Czech Technical University, Centre for Radiochemistry and Radiation Chemistry, Prague, Czech Republic

To cite this Article Mištová, Eva , Parschová, Helena , Jelínek, Luděk , Matějka, Zděněk and Šebesta, Ferdinand(2010) 'Sorption of Metal Oxoanions by Composite Biosorbents of Waste Material of Brown Seaweeds *Ascophyllum nodosum* and PAN', Separation Science and Technology, 45: 16, 2350 — 2355

To link to this Article: DOI: 10.1080/01496395.2010.484407

URL: http://dx.doi.org/10.1080/01496395.2010.484407

Separation Science and Technology, 45: 2350–2355, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.484407

Sorption of Metal Oxoanions by Composite Biosorbents of Waste Material of Brown Seaweeds *Ascophyllum nodosum* and PAN

Eva Mištová,[1] Helena Parschová,[1] Luděk Jelínek,[1] Zděněk Matějka,[1] and Ferdinand Šebesta[2]
[1]*Institute of Chemical Technology, Department of Power Engineering, Prague, Czech Republic*
[2]*Czech Technical University, Centre for Radiochemistry and Radiation Chemistry, Prague, Czech Republic*

Two different composite sorbents of chemically modified dealginaded seaweed *Ascophyllum nodosum* (DS-2 and DS-3) were used for the selective removal of metal (W, Mo, and V) oxoanions. All experiments were carried out by dynamic column sorption. The effects of the pH, flow rate and the concentration of the accompanying anions in the feed solution were studied. Sorption of tungstate, molybdate and vanadate anions was successful. The composite sorbents exhibited high stability during more than 25 sorption cycles.

Keywords brown seaweeds; composite biosorbent; metal oxoanion; PAN; sorption

INTRODUCTION

Of the many toxic metals that may be present as contaminants in natural waters and wastewaters, a few (like As, Cr(VI), Sb, etc.) occur as oxoanions. Biosorption is a potential alternative to the traditional treatment processes of the toxic metals removal (1). Removal of the oxoanions using biosorbents is not so common. However, the removal of As and Cr(VI) by biosorbens was thoroughly studied. For the removal of As(V) fungus *P. chrysogenum* (2), tea fungus *Pichia* and *Acetobacter* (3), methylated yeast biomass (4), seaweed *Sargassum hemiphyllum* (5), etc. were used. Bacteria *Escherichia coli* and *Zoogloea ramigera* were used for the removal of As(III), Cr(VI), Mo(VI), and W(VI) (6). Baker's yeast cells (*Saccharomyces cerevisiae*) (7) were used for the separation of Se(IV), Se(VI), Sb(III), and Sb(V). A study about the selective sorption of antimony by rice husk was also performed (8). The removal of Cr(VI) by cone biomass of *Pinus sylvestris* (9) and fungus *Rhizopus nigricans* (10) was studied. Chitosan (11–13) and cellulose (14) were used for the sorption of As(III), As(V), Ge(IV), Sb(III), B(III), W(VI). V(V), and Mo(VI).

Ascophyllum nodosum (15) is brown seaweed. It is used for the extraction of alginic acid, a polysaccharide used in the food industry and biotechnology. Seaweed contains a heterogeneous mixture (16) of different polysaccharides such as alginic acid (20–25%), mannitol (5–10%), cellulose, chitosan and others. These polysaccharides contain –OH groups in different configurations, and some of them can form poly-ol-complexes with metal anions (W, Mo, V, Ge, Sb, As). This process is one of the methods for removing these anions from contaminated water.

The hydroxycompounds (17–20) can form two kinds of the coordination diol- or polyol-complexes with metal-oxoanions: *mono-nuclear complexes* (Ge, B, As) and/or *bi(or poly)-nuclear complexes* (V, W, Mo). The complexation reactions between oxoanions and diol-compounds (diol-ligands) are pH-sensitive. The optimum pH-range (Table 1) for particular oxoanions to form diol (polyol) complexes was determined.

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 diol-ligands with appropriate steric configuration of –OH groups as a selective sorbent. Such possibility was studied in this work. As the biomass particles are not mechanically stable enough for the column operation, it is necessary to improve their properties. Polyacrylonitrile (PAN) was used as the binding polymer for the preparation of the mechanically stable beads. This polymer was already successfully used for the production of the composite biosorbents (11,21,23).

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

Received 10 December 2009; accepted 7 April 2010.

Address correspondence to Eva Mištová, Department of Power Engineering, Technická 5, 166 28 Prague, Czech Republic. E-mail: mistovae@vscht.cz

TABLE 1
Optimal pH to form complexes (20)

	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

(i.e., 1 bead volume – BV) of the sorbent with the specific flow rate s of 3 or 6 $BV \cdot h^{-1}$. 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, and $Na_2MoO_4 \cdot 2H_2O$ of analytical purity were used. The solutions were freshly prepared before the use, the initial concentration of metal was 0.5 or $1.0\,mg \cdot L^{-1}$, and the concentration of the accompanying anions (Cl^-, SO_4^{2-}) was 100 or $500\,mg \cdot L^{-1}$. The experimental pH values ranged from 3.5 to 5.5. All sorbents were regenerated with $0.1\,mol \cdot L^{-1}$ NaOH solution. Before every sorption run the sorbent was conditioned by $0.5\,mol \cdot L^{-1}$ HCl solution, to keep all –OH groups and also carboxylic groups in the protonated form. The sorbent was washed with demineralized water before starting the sorption.

For the sorption run the limiting breakthrough concentration was $0.1\,mg \cdot L^{-1}$ of metal. The sorption breakthrough capacities q of the sorbent were calculated according to the following Eq. (1):

$$q = \frac{V \cdot c_0}{V_0} \quad [mg \cdot L^{-1}] \tag{1}$$

V... volume at the breakthrough point [mL]
c_0... metal concentration in the feed solution [$mg \cdot L^{-1}$]
V_0... volume of the sorbent in column [mL]

Sorbents Preparation

For the preparation of the modified biosorbents, waste material after alginic acid extraction from *Ascophyllum nodosum* seaweeds supplied by ISP Alginates UK Ltd. (23) was used in March 2001. This raw material was used directly without further pretreatment for the preparation of the composite sorbent DS-2 or after esterification and amidation of the raw material DS-3.

Sorbent DS-2

The granulation process was as follows: the original grain size of waste biomass (dealginated seaweed *Ascophyllum nodosum*) was <0.16 mm, therefore the biomass was carefully grinded in the mortar before its granulation. Composite sorbents were prepared according to the one modification of the general procedure (22,24). Fibrous polyacrylonitrile (PAN) was dissolved in dimethylsulfoxide and powdered biomass was gradually added to the PAN solution and suspension was carefully mixed. The homogeneous suspension was then dispersed into a 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. According to the procedure used, granulated beads contain 80 wt.% in dry product. From the total volume of the granulation product and weight of the added biomass to the process it was calculated that 1 mL of the swollen sorbent contained about 0.1 g of the biomass.

To improve the mechanical properties granulation was the only chemical modification carried out. Thus, the sorbent contained –OH, $–COO^-$, and the original amino groups.

Sorbent DS-3

The esterification process (25) was as follows: dry waste material of the seaweed matrix (dealginated seaweed *Ascophyllum nodosum*, which contains 1.64% of nitrogen) with methanol and H_2SO_4 (98%, p.a.) under a reflux condenser was boiled for five hours. After esterification 30 wt% NH_3 solution was added to the dry matrix and reacted 4 days at the temperature of about 5°C. These processes were important for the elimination of the negative effect of the carboxylic group, especially amidation is important at alkaline medium (after the amidation process the product contains 3,15% of nitrogen). This material was granulated by the same method as the biosorbent DS-2.

By chemical modification the carboxylic groups were partially eliminated and amino groups were introduced to the sorbent. They can function as anion-exchange sites. The sorbent contains –OH, residual $–COO^-$, and the original and added amino groups. Granulation improves the mechanical properties of the sorbent DS-3.

RESULTS AND DISCUSSION

Tungstate Sorption

First, the effect of the flow rate was studied. The result signalled that the kinetic of the sorption was rather fast. In the case of the sorbent DS-2 the difference between the sorption capacity, when $c(W) = 0.5\,mg \cdot L^{-1}$; $c(Cl^-, SO_4^{2-}) = 100\,mg \cdot L^{-1}$; at $pH = 5.5$ and at the specific flow rates 3 $BV \cdot h^{-1}$ and 6 $BV \cdot h^{-1}$ was minimal (Table 2).

The hypothesis was that tungsten's coordination complexes are more stable in the acidic pH range of pH. This is obtained in the case of sorbent DS-3 when the sorption capacity (Table 2) of W(VI) anion at the pH of 3.5,

TABLE 2
The comparison of breakthrough capacities for W-oxoanions

c(Me) [mg · L^{-1}]	c(Cl$^-$) [mg · L^{-1}]	c(SO$_4^{2-}$) [mg · L^{-1}]	pH	s [BV · h^{-1}]	Sorption capacity [mg · L^{-1}]	
					DS-2	DS-3
0.5	100	100	5.5	3	178.6	–
0.5	100	100	5.5	6	178.2	–
1	100	100	3.5	6	80.3	340.0
1	100	100	5.5	6	226.0	228.0
1	500	500	5.5	6	110.0	158.4
1	500	500	3.5	6	136.0	187.9

$c(W) = 1\,mg \cdot L^{-1}$, $c(Cl^-, SO_4^{2-}) = 100\,mg \cdot L^{-1}$ $s = 6\,BV \cdot h^{-1}$, was $340\,mg \cdot L^{-1}$ and at the pH of 5.5 the capacity decreased to $228\,mg \cdot L^{-1}$. In the case of sorbent DS-2 it was contrariwise at the pH of 3.5 only $80.3\,mg \cdot L^{-1}$ and at the pH of 5.5 the breakthrough capacity decreased to $226\,mg \cdot L^{-1}$ (Fig. 1). At the acidic pH range where W is present in the form of isopolyanions (26) $W_{12}O_{41}^{10-}$ or $H_2W_{12}O_{40}^{6-}$, and the sorbent DS-2 probably contains many different ballast substances (as ectoplasm, etc.) which obstructs the formation chelates of these big polyolcomplexes with saccharide –OH groups and so simple WO_4^{2-} anion (pH = 5.5–6) is better for separation from the water solution.

Increased concentration of accompanying anions (as competitor's anions) had a negative effect on the sorption capacity. When the concentration of sulfates and chlorides in the feed solution was increased from $100\,mg \cdot L^{-1}$ to $500\,mg \cdot L^{-1}$ at pH = 5.5 the sorption capacity of DS-2 and DS-3 decreased from $226\,mg \cdot L^{-1}$ to $110\,mg \cdot L^{-1}$ and from $228\,mg \cdot L^{-1}$ only to $158.4\,mg \cdot L^{-1}$, respectively (Table 2). At pH = 3.5 (optimal pH for sorption W(VI) by DS-3) the sorption capacity of DS-3 decreased by 45% (from $340\,mg \cdot L^{-1}$ to $189.7\,mg \cdot L^{-1}$).

The recovery of W(VI) oxoanion provided good yields for both sorbents. In Fig. 2 the recovery curves of W and Mo from DS-2 are shown. W and Mo were completely stripped within 10 BV of $0.1\,mol \cdot L^{-1}$ NaOH regeneration solution. This high desorption efficiency enables the effective reuse of the sorbents.

Molybdenate Sorption

When the specific flow rate was $3\,BV \cdot h^{-1}$, the sorption capacity of the sorbent DS-2 was $248\,mg \cdot L^{-1}$. Capacity decreased to $158\,mg \cdot L^{-1}$ with increased specific flow rate $s = 6\,BV \cdot h^{-1}$ (Table 3). In this case, results signalized that the kinetic of the sorption was not optimal and in the following experiments the specific flow rate $3\,BV \cdot h^{-1}$ was used. The difference in the case of DS-3 was minor and the capacity was higher when $s = 6\,BV \cdot h^{-1}$ was used.

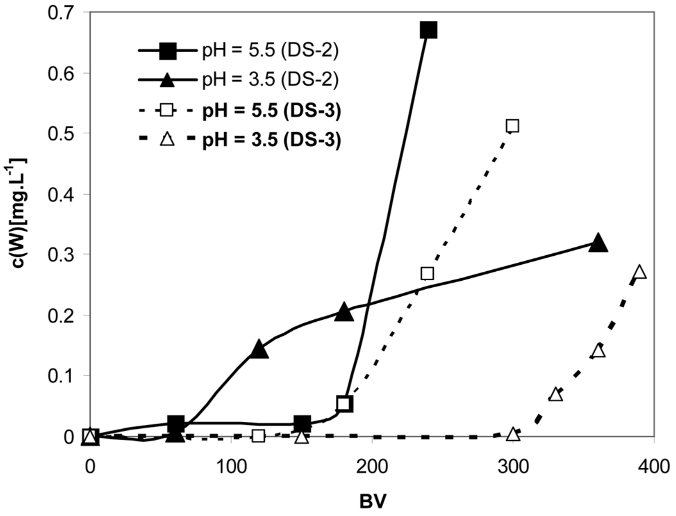

FIG. 1. Sorption of W(VI) – Effect of pH, $c(W) = 1\,mg \cdot L^{-1}$, $c(Cl^-, SO_4^{2-}) = 100\,mg \cdot L^{-1}$, $s = 6\,BV \cdot h^{-1}$.

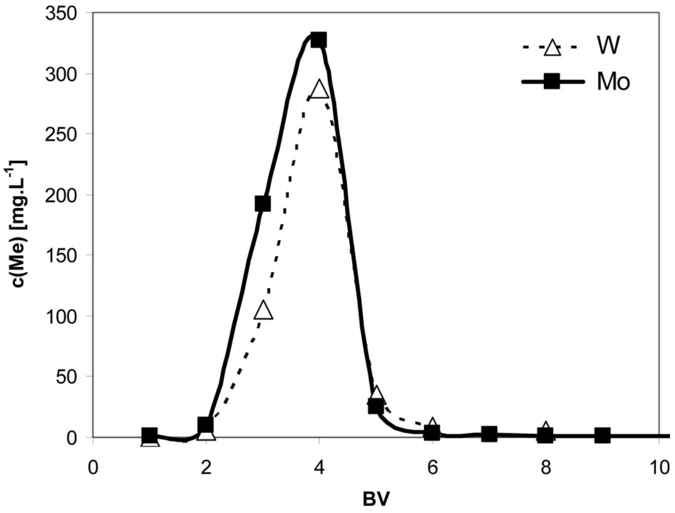

FIG. 2. Regeneration curves of W(VI) and Mo(VI) by regeneration of DS-2 by solution NaOH ($c = 0.1\,mol \cdot L^{-1}$).

TABLE 3
The comparison of breakthrough capacities for Mo-oxoanions

c(Me) $[mg \cdot L^{-1}]$	$c(Cl^-)$ $[mg \cdot L^{-1}]$	$c(SO_4^{2-})$ $[mg \cdot L^{-1}]$	pH	s $[BV \cdot h^{-1}]$	Sorption capacity $[mg \cdot L^{-1}]$ DS-2	Sorption capacity $[mg \cdot L^{-1}]$ DS-3
0.5	100	100	3.5	3	248.0	–
0.5	100	100	3.5	6	158.0	–
0.5	100	100	5.5	3	73.5	–
0.5	500	500	3.5	3	193.0	–
1	100	100	3.5	6	–	390.0
1	100	100	5.5	6	–	76.9
1	100	100	3.5	3	244.5	323.1
1	500	500	3.5	6	–	286.5

Thus, this specific flow rate was used in the following sorption cycles.

Because the chelate of Mo-oxoanion is less stable than the W-chelate (26) and Mo(VI) is much more sensitive to the pH change (e.g. (13,14,27)), the influence of pH (Fig. 3) on the Mo(VI) sorption was different from the case of tungstate sorption. However, in compliance with this theory, the sorption capacities were higher at pH = 3.5 for both sorbents. At the concentration of Mo(VI) in the feed solution $0.5 \, mg \cdot L^{-1}$, the concentration of the accompanying anions (Cl^-, SO_4^{2-}) $100 \, mg \cdot L^{-1}$ and s = 3 $BV \cdot h^{-1}$, the breakthrough capacity of the sorbent DS-2 was $248 \, mg \cdot L^{-1}$ at pH of 3.5, and at the pH of 5.5 the capacity decreased down to $73.5 \, mg \cdot L^{-1}$ i.e., by 70%. The breakthrough capacities for DS-3 (s = 6 $BV \cdot h^{-1}$; c(Mo) = $1 \, mg \cdot L^{-1}$) were $390 \, mg \cdot L^{-1}$ and $76.9 \, mg \cdot L^{-1}$ i.e., decreased by 80%.

The effect of the concentration of the accompanying anions was negative. The differences of the sorption capacities of molybdate oxoanion at concentrations of sulfates and chlorides $100 \, mg \cdot L^{-1}$ and $500 \, mg \cdot L^{-1}$ were similar for both sorbents, about 25% (Fig. 4). The sorption capacity in the presence of $500 \, mg \cdot L^{-1}$ of the accompanying anions was $193 \, mg \cdot L^{-1}$ in the case of the sorbent DS-2 (c(Mo) = $0.5 \, mg \cdot L^{-1}$ and s = 3 $BV \cdot h^{-1}$) and $286.5 \, mg \cdot L^{-1}$ in the case of the sorbent DS-3 (c(Mo) = $1 \, mg \cdot L^{-1}$ and s = 6 $BV \cdot h^{-1}$).

The recovery of molybdate oxoanion was similar to the recovery of W(VI) (Fig. 2). Mo(VI) was completely stripped from both sorbents within 10 BV of the regeneration solution of $0.1 \, mol \cdot L^{-1}$ NaOH.

Vanadate Sorption

The influence of pH (Table 4) on the sorption was similar to the cases of molybdate sorption and the optimal pH

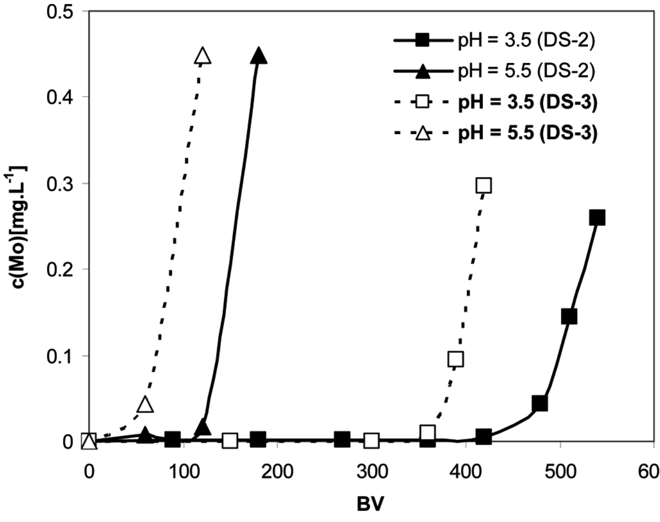

FIG. 3. Sorption of Mo(VI) – Effect of pH DS-2: c(Mo) = $0.5 \, mg \cdot L^{-1}$, c(Cl^-, SO_4^{2-}) = $100 \, mg \cdot L^{-1}$, s = 6 $BV \cdot h^{-1}$ · DS-3: c(Mo) = $1 \, mg \cdot L^{-1}$, c(Cl^-, SO_4^{2-}) = $100 \, mg \cdot L^{-1}$, s = 6 $BV \cdot h^{-1}$.

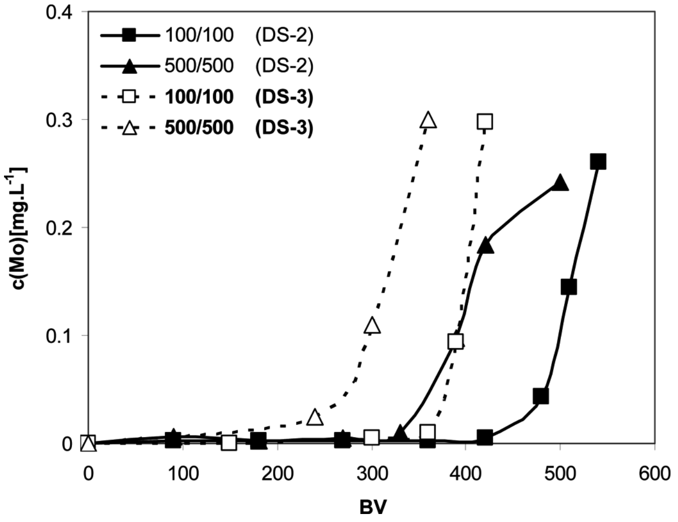

FIG. 4. Sorption of Mo(VI) – Effect of accompanying anions, DS-2: c(Mo) = $0.5 \, mg \cdot L^{-1}$, pH = 3.5, s = 6 $BV \cdot h^{-1}$. DS-3: c(Mo) = $1 \, mg \cdot L^{-1}$, pH = 3.5, s = 6 $BV \cdot h^{-1}$.

TABLE 4
The comparison of breakthrough capacities for V-oxoanions

c(Me) [mg · L^{-1}]	c(Cl$^-$) [mg · L^{-1}]	c(SO_4^{2-}) [mg · L^{-1}]	pH	s [BV · h^{-1}]	Sorption capacity [mg · L^{-1}] DS-2	DS-3
0.5	100	100	3.5	3	278.9	–
0.5	100	100	3.5	6	267.7	265.1
0.5	100	100	5.5	6	120.9	95.9
0.5	500	500	3.5	6	137.8	172.5
0.5	500	500	5.5	6	75.0	70.1

value for the sorption of V oxoanions was pH = 3.5. At the concentration of V(V) in the feed solution 0.5 mg · L^{-1} and the concentration of the accompanying anions (Cl$^-$, SO_4^{2-}) 100 mg · L^{-1}, the breakthrough capacity of the sorbent DS-2 was 267.7 mg · L^{-1} at pH of 3.5, at pH of 5.5 the capacity was 120.9 mg · L^{-1} (about 55% difference), in the case of DS-3 capacities were 265.1 mg · L^{-1} and 95.9 mg · L^{-1}, respectively (about 64%).

The effect of the concentration of the accompanying anions was negative and similar as in the case of the sorption of W(VI) or Mo(VI). When the concentration of the accompanying anions (Cl$^-$, SO_4^{2-}) was 500 mg · L^{-1} the sorption capacity at pH = 3.5 was 137.8 mg · L^{-1} and at pH = 5.5 only 75 mg · L^{-1} for the sorbent DS-2, and 172.5 mg · L^{-1} and 70.1 mg · L^{-1} for the sorbent DS-3, respectively (Fig. 5).

The recovery of the vanadate oxoanion provided good yields, as in the cases of W and Mo. Vanadate was completely stripped within 10 BV of the regeneration solution of 0.1 mol · L^{-1} NaOH, for both sorbents.

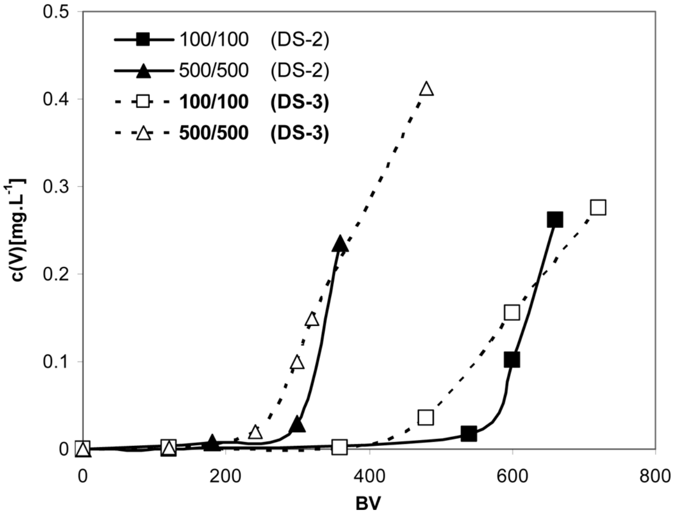

FIG. 5. Sorption of V(V) – Effect of accompanying anions, c(V) = 0.5 mg · L^{-1}, pH = 3.5, s = 6 BV · h^{-1}.

CONCLUSIONS

The composite biosorbents of modified brown seaweed *Ascophyllun nodosum* with polyacrylonitrile, DS-2, and DS-3 are suitable for separating tungstate, molybdate, and vanadate oxoanions from water.

For the sorption of all studied oxoanions the specific flow rate 6 BV · h^{-1} was used, same as in the case of biosorbents NS-1 and DS-1 (27), only in the case of Mo(VI) sorption on the DS-2 sorbent, the flow rate of 3 BV · h^{-1} must be used, when the kinetic of the sorption of the Mo(VI) oxoanion was not fast.

The optimal pH for the sorption of molybdenate and vanadate oxoanion according to the theory was 3.5. For the sorption of W(VI) this applies to using of sorbents DS-3 and DS-1 (27), but in the case of the sorbent NS-1 and DS-2 the optimal pH was 5.5.

Selectivity of the sorbent was not as good as the special chelating ion-exchanger resin, because the effect of the concentration of the accompanying anions was negative in all the cases.

Sorbent DS-3 contained more amino groups, which can behave after being conditioned with hydrochloric acid as anion-exchanger; this was the reason of its high capacities than for sorbent DS-2.

When we compare the breakthrough capacities of composite sorbents—DS-2 and DS-3 with sorbent DS-1 (dealginated seaweed crosslinked with epichlorhydrin and following esterification and without granulation) (27), with regard to the mass of the active matrix, the composite sorbents have lower sorption capacities. The difference is about 30% in the case of Mo(VI) and V(V), and for the sorption of W(VI) it is more than 70%. Part of the difference can be eliminated by the preparation of the composite sorbent with a more active matrix. When we compare the chemical and mechanical stability of the composite matrix of the biosorbents, the studied sorbents showed better properties than the sorbent DS-1. Therefore, these sorbents are more suitable for the column separation.

This work presents other successful steps in the utilization of natural materials as selective sorbents for dynamic column processing in water treatment.

ACKNOWLEDGEMENTS

This work was carried out with the financial support of the Research proposal (MSM 6046137304) from the Ministry of Education, Youth and Sports of the Czech Republic.

REFERENCES

1. Volesky, B. (2003) *Sorption and Biosorption*, 1st Ed., BV Sorbex, Inc., Montreal, Canada.
2. Loukidou, M.X.; Matis, K.A.; Zouboulis, A.I.; Kyriakidou, M. (2003) Removal of As(V) from wastewaters by chemically modified fungal biomass. *Water Res.*, 37 (18): 4544.
3. Murugeasan, G.S.; Sathishkumar, M.; Swaminathan, K. (2006) Arsenic removal from grounwater by pretreated waste tea fungal biomass. *Bioresource Technol.*, 97 (3): 483.
4. Seki, H.; Suzuki, A.; Maruyama, H. (2005) Biosorption of chromium(VI) and arsenic(V) onto methyladed yeast biomass. *J. Colloid and Interface Science*, 281 (2): 261.
5. Tsui, M.T.K.; Cheung, K.C.; Tam, N.F.Y.; Wong, M.H. (2006) A comperative study on metal sorption by bdown seaweed. *Chemosphere*, 65 (1): 51.
6. Xie, J.Z.; Chang, H.L.; Kilbane, J.J. (1996) Removal and recovery of metal ions from wastewater using biosorbents and chemically modified biosorbents. *Bioresource Technol.*, 57 (2): 127.
7. Peréz-Corona, T.; Madrid, Y.; Cámara, C. (1997) Evaluation of selektive uptake of selenium (Se(IV) and Se(VI)) and antimony (Sb(III) and Sb(V)) species by baker's yeast cells (*Saccharomyces cerevisiae*). *Anal. Chim. Acta*, 345 (1–3): 249.
8. Nasir, K.; Shujaat, A.; Aqidat, T.; Jamil, A. (2000) Potential of rice husks for antimony removal. *Applied Radiation and Isotopes*, 52 (1): 31.
9. Ucun, H.; Bayhan, Y.K.; Kaya, Y.; Cakici, A.; Algur, O.F. (2002) Biosorption of chromium(VI) from aqueous solution by cone biomass of *Pinus sylvestris*. *Bioresource Technol.*, 85 (2): 155.
10. Bai, R.S.; Abraham, T.E. (2002) Studies on enhancement of Cr(VI) biosorption by chemically modified biomass of *Rhizopus nigricans*. *Water Res.*, 36 (5): 1224.
11. Matějka, Z.; Parschová, H.; Jelínek, L.; Mištová, E.; Houserová, P.; Ruszová, P.; Šebesta, F. (2003) Selective removal of As, Sb, Se and Be from water streams; screening of uptake mechanisms and sorbent-types. *J. Ion. Exch.*, 14: 237.
12. Matějka, Z.; Ruszová, P.; Parschová, H.; Jelínek, L.; Kawamura, Y. (2002) Selective uptake of (Mo, V, W, As)-o.xoanions by crosslinked chitosan; beats vs. fibres. *Advances in Chitin Science*, 6: 213, NTNU Trondheim 2002.
13. Matějka, Z.; Parschová, H.; Ruszová, P.; Jelínek, L.; Houserová, P.; Mištová, E.; Beneš, M.; Hrubý, M. (2001) Selective uptake and separation of oxoanions of molybdenum, vanadium, tungsten, and germanium by synthetic sorbents having polyol moieties and polysaccharide-based biosorbents, Fundamental and Applications of Anion Separation, 222nd ACS National Meeting, Chicago, IL, United States, August 26–30, 2001.
14. Mištová, E.; Parschová, H.; Matějka, Z. (2007) Selective sorption of metal oxoanions from dilute solution by bead cellulose sorbent. *Sep. Sci. Technol.*, 42 (6): 1231.
15. http://seaweed.ucg.ie/descriptions/Ascnod.html (1.11.2004)
16. http://www.brandonproducts.com/plantcare/technical/ascophylum.htm (1.11.2004)
17. Mikešova, M.; Bartušek, M. (1979) Complexes of germanic acid with mannitol, sorbitol, maltol, and chromotropic and kojic acids. *Coll. Czech. Chem. Commun.*, 44 (11): 3256.
18. Mikešova, M.; Bartušek, M. (1978) Reaction of molybdate and tungstate with oxalate, mannitol, and sorbitol. *Coll. Czech. Chem. Commun.*, 43 (7): 1867.
19. Mikan, A.; Bartušek, M. (1980) The reactions of oligoalcohols with arsenic, arsenous, boric and germanic acids. *Coll. Czech. Chem. Commun.*, 45 (10): 2642.
20. Bartušek, M.; Šustáček, V. (1983) Chelates of vanadium(V) with organic hydroxy compounds in aqueous solutions. *Coll. Czech. Chem. Commun.*, 48 (10): 2785.
21. Zouboulis, A.I.; Matis, K.A.; Loukidou, M.; Šebesta, F. (2003) Metal biosorption by PAN-immobilized fungal biomass in simulated wastewaters. *Colloids Surf., A Physicochem. Eng. Aspects*, 212 (2–3): 185.
22. Vítor, V.J.P.; Šebesta, F.; Botelho, C.M.S.; Boaventura, R.A.R. (2005) Equilibrium and kinetic modelling of Pb^{2+} biosorption by granulated agar extraction algal waste. *Process Biochemistry*, 40 (10): 3276.
23. http://www.ispcorp.com (23.11.2004)
24. Šebesta, F. (1999) Preparation of granular forms of powdered materials for their application in column packed beds. In: *Natural microporous materials in environmental technology*. P. Misaelides et al. (eds.), Kluwer Academic Publishers, pp. 473–484.
25. Hirozawa, A. Alginic acid esterification, Japan Patent JP 04023801, 1992.
26. Angus, H.J.F.; Weigel, H. (1964) Complexes between polyhydroxy compounds and inorganic oxy-acids. IV. Dimolybdate and ditungstate ions as complexing agents, and paper electrophoresis of maltodextrinols and isomaltodextrinols in molybdate and tungstate solutions. *Journal of the Chemical Society*. 10: 4000.
27. Mištová, E.; Parschová, H.; Jelínek, L.; Matějka, Z.; Plichta, Z.; Beneš, M. (2008) Selective sorption of metal oxoanions from dilute solution by chemicaly modified brown seaweed *Ascophyllum Nodosum*. *Sep. Sci. Technol.*, 43 (11–12): 3168.