Separation Science and Technology
Publication details, including instructions for authors and subscription information:
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To cite this Article Ďurišová, Jana , Jelínek, Luděk , Parschová, Helena and Mištová, Eva(2009) 'Mutual Separation of Vanadium and Tungsten from Aqueous Solution via Electrochemical Reduction and Sorption onto Chelating Resin', Separation Science and Technology, 44: 12, 2750 — 2760

To link to this Article: DOI: 10.1080/01496390903135816

URL: http://dx.doi.org/10.1080/01496390903135816

Separation Science and Technology, 44: 2750–2760, 2009
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ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390903135816

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Mutual Separation of Vanadium and Tungsten from Aqueous Solution via Electrochemical Reduction and Sorption onto Chelating Resin

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Abstract: The possibility of mutual separation of V and W oxoanions from aqueous solution was investigated by elecro-reduction of V(V) to V(IV) in a flow-type electrolyzer combined with column sorption on a selective resin having 1-deoxy-1-(methylamino)-glucitol functional groups. At pH 3, V(V) oxoanion (VO_3^-) was reduced to V(IV) cation, which passed into the effluent, whereas W, existing as WO_4^{2-}, was quantitatively retained by the resin. In this way, complete separation of V and W was achived. By elution with 1 M HCl, the V(IV) in a form of VO^{2+} was eluted. Tunsgten was eluted quantitatively with 1 M NaOH. A co-removal and co-elution of V with W was observed, which is supposed to be due to V(IV)/W heteropolyanion formation during the electro-reduction.

Keywords: Chelating resin, electrolytical reduction, separation, tungsten, vandium

INTRODUCTION

Vanadium is often contained in fossil fuels, and in consequence it comes into wastewaters from assorted branches of power engineering. Due to the similar chemical properties, vanadium may be accompanied by tungsten in ores and fossil fuels. Tungsten is ranked among nontoxic metals, and vanadium has only low toxicity (1). However, both vanadium and tungsten are valuable alloying compounds, therefore their recovery from

Received 9 February 2009; accepted 12 May 2009.

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wastewaters is desirable. In environmental conditions, vanadium and tungsten are present in water in a form of oxoanions. That makes them easily separable from most of other metals by use of ion exchange. Nevertheless, separation of vanadium and tungsten from each other brings some difficulties. Ion exchange chromatography on strongly basic anion exchangers was performed by elution with concentrated hydrofluoric acid (2). Because vanadium(V) can be easily reduced to V(IV) cationic form, reductive vanadium elution from a loaded anion exchanger was developed, originally with a reducing agent (3) and later using electrochemical ion exchange (4).

Besides the ordinary anion exchange resins, selective chelating sorbents can be used with advantage for metallic oxoanion uptake, especially when high concentrations of accompanying anions are present in the treated solution. In this work selective sorbent containing 1-deoxy-1-(methylamino)-glucitol functional groups was used. This sorbent was originally develped for selective sorption of borates (5). It can take up borates even from high excess of common anions (Cl^-, HCO_3^-, SO_4^{2-}) in difficult matrices such as sea water (6). Apart from borates it has been shown to selectively adsorb vanadates and other metal oxoanions (7,8). Sacharide hydroxy groups in the cis positions are able to form diol complexes, which is useful for the selective separation of weak acid oxoanions (9). However, tungstate and vanadate oxoanions exhibited almost identical ability to complex formation with methylamino-glucitol sorbent and therefore their efficient separation was not achieved (8). With respect to different sorption properties of anionic V(V) and cationic V(IV), a study on the sorption of electrochemically generated V(IV) onto 1-deoxy-1-(methylamino)-glucitol sorbent was performed with the aim to find optimal pH for V(IV) sorption (10).

The present work focuses on vanadium and tungsten separation by use of electrochemical reduction combined with sorption onto the methylamino-glucitol sorbent. The combinaton of electrochemical treatment of the solution with subsequent column sorption has been formely tested for the separation of Ce oxidized to Ce (IV) and Eu reduced to Eu (II) from trivalent rare earths (11,12).

EXPERIMENTAL

Reagents and Solution

The test solutions were prepared from NH_4VO_3, Na_2SO_4 (Penta), $Na_2WO_4 \cdot 2H_2O$ (Merck), all of analytical purity. The salts were dissolved in demineralized water. The pH was set up with H_2SO_4.

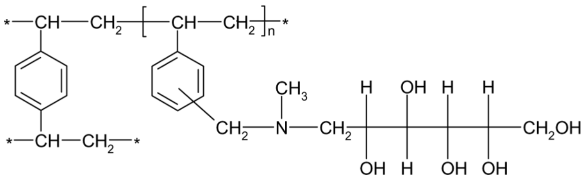


Figure 1. Structure of Purolite D 4123.

The accurate metal concentrations were determined by ICP-OES Optima 2000DV (Perkin-Elmer Instruments, USA). The pH was measured by pH meter InoLab Level 1 (WTW, Germany).

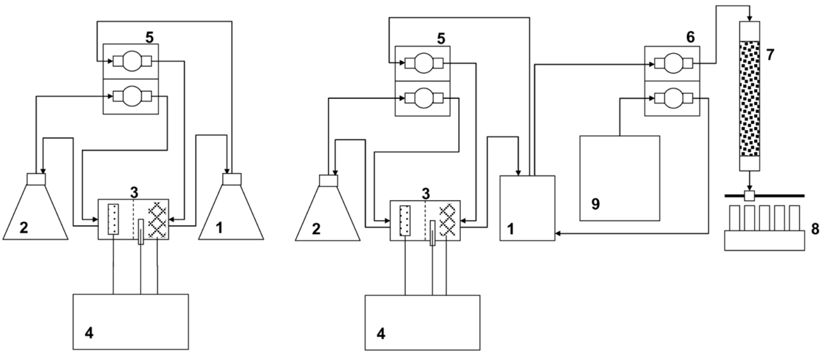
Sorbents. The chelating resin Purolite D 4123 (Purolite International, UK) with 1-deoxy-1-(methylamino)-glucitol functional groups on a styrene-divinylbenzene matrix was used as an experimental sorbent, see Fig. 1. The sorbent was converted into the protonated form by washing with 1 M HCl and rinsed thoroughly with deionized water.

Electrolysis. The reduction of V(V) was carried out in a two compartment flow type electrochemical cell. 1 L of the test solution circulated through a cathode compartment of a volume of 10 mL by a flow rate of 100 mL/min. The solution passed through a 3D carbon felt cathode of a 10 mm thickness. A perforated Pt plate was used as a current feeder for the cathode. The cathodic compartment was separated from the anodic compartment by a Nafion membrane. The anode was a Pt wire. 200 mL of 0.1 M H_2SO_4 was used as an anolyte, and it circulated through the anode compartment of a volume of 10 mL by identical flow rate as the catholyte. The reference Ag/AgCl electrode was situated in the cathode compartment. The experimental setup is shown in Fig. 2a. The reduction proceeded in potentiostatic mode, the potential at the cathode −1.50 V vs. Ag/AgCl was maintained by a potentiostat Solartron 1186 (Sycopel Scientific LTD, UK).

Sorption. The sorption tests were carried out in glass columns of an inner diameter of 10 mm, equipped with a sintered glass support on the bottom. Bed volume was 10 mL.

Breakthrough curves were measured before and after electroreduction. The solution applied on the column contained in all cases V and W of approximate concentration 0.5 mmol/L and a fivefold excess of Na_2SO_4, in terms of molar concentration. After pH adjustment with sulphuric acid resulting SO_4^{2-} concentration was 3.7 mmol/L. Relatively high concentration of salts in solution provides an electric conductivity of the solution. The pH was adjusted to 3 with sulfiric acid.

The specific flow rate through the column was 6 BV/h in all cases.



(a) (b)

Figure 2. Experimental setup: (a) Electro-reduction (b) Continuous electro-reduction and column sorption. 1 catholyte storage; 2 anolyte storage; 3 electrochemical cell; 4 potentiostat; 5 circulating pump; 6 feeding pump; 7 column; 8 fraction collector 9; storage of the new solution.

Desorption. Desorption was carried out in two steps. In the first step, the sorbent was regenerated with 1 M HCl, then it was rinsed by demineralized water, and in the second step it was regenerated with 1 M NaOH. The desorption flow rate was 3 BV/h.

RESULTS AND DISCUSSION

Concurrent Sorption of V(V) and W(VI)

Figure 3 shows the breakthrough curves of V and W without the electrochemical reduction. Tungsten is taken up quantitatively up to 520 BV. Vanadium breaks through at 160 BV and further remains at low concentration of less than 0.1 c/c_0 up until 520 BV, where its concentration increases along with W. Increase of the outlet concentrations is very slow, especially that of vanadium. During the sorption, the sorbent color changed from white to yellow, and from yellow to green gradually from the upper part. The latter change gives an evidence of the reduction of V(V) to V(IV), which was catalyzed by the saccharidic functional groups of the sorbent (13). Formation of mixed-valence oxoanions has probably a positive effect on the complex formation of vanadium with glucitol sorbent.

With 1 M HCl, the mixed-valence anions of vanadium were released, as was seen from the washing out of the sorbent, forming a green eluate. In the HCl fraction 66.7% of total vanadium was eluted. V(V) oxoanion

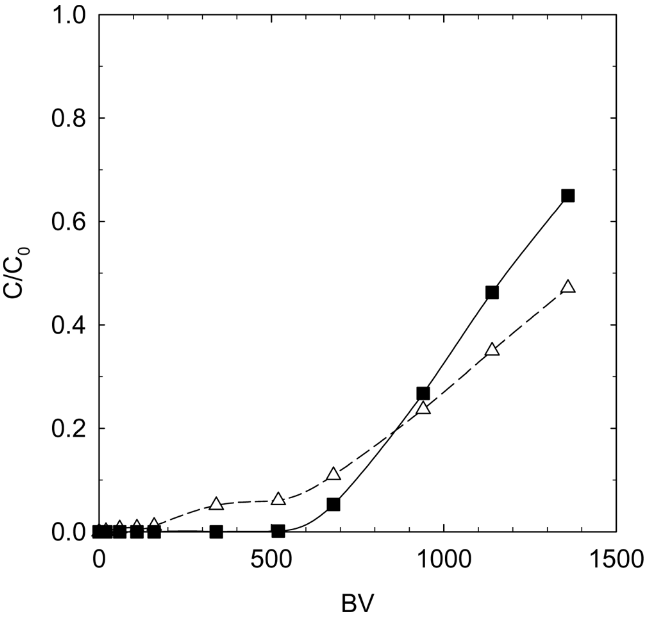


Figure 3. Breakthrough curves of V (Δ) and W (■) on selective sorbent.

was then eluted along with W by 1 M NaOH. The total recovery was 96.6% of vanadium and 100% of tungsten. The course of desorption is plotted in Fig. 4.

Electro-Reduction and Consecutive Sorption

A solution of 2.5 mmol/L of V and W and 12.5 mmol/L of sodium sulphate was treated by electrochemical reduction for 24 hours, afterwards it was dilluted five times by demineralized water of pH 3 and applied to the column.

During the electrolysis, following reactions proceeded on cathode (1) and anode (2):

$$VO_2^+ + 2H^+ + e^- = VO^{2+} + H_2O \qquad E^0 = 1.00\,V \qquad (1)$$

$$H_2O = 1/2O_2 + H^+ + e^- \qquad E^0 = 1.23\,V \qquad (2)$$

$$VO_3^- + 2H^+ = VO_2^+ + H_2O \qquad (3)$$

The redox reaction was accompanied by color change of the solution from yellow to light brown. The breakthrough curves are plotted in Fig. 5. The generated vanadium(IV), which is present in aqueous solution in a form of

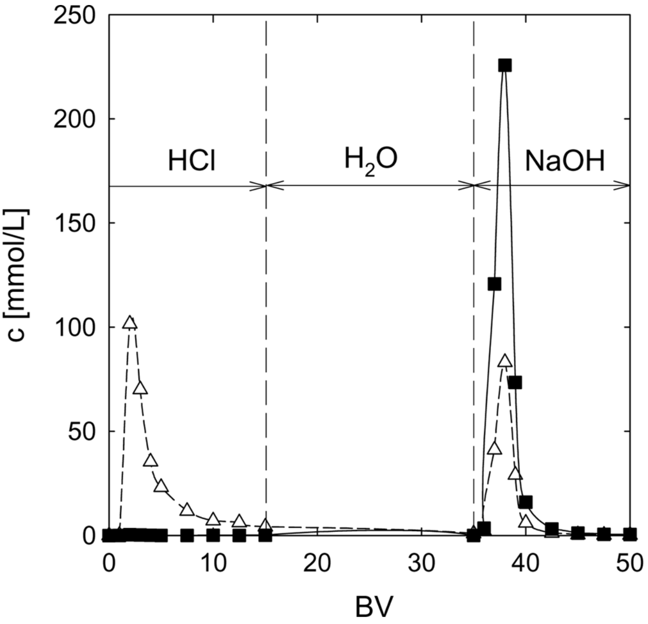


Figure 4. Desorption curve of V (Δ) and W (■).

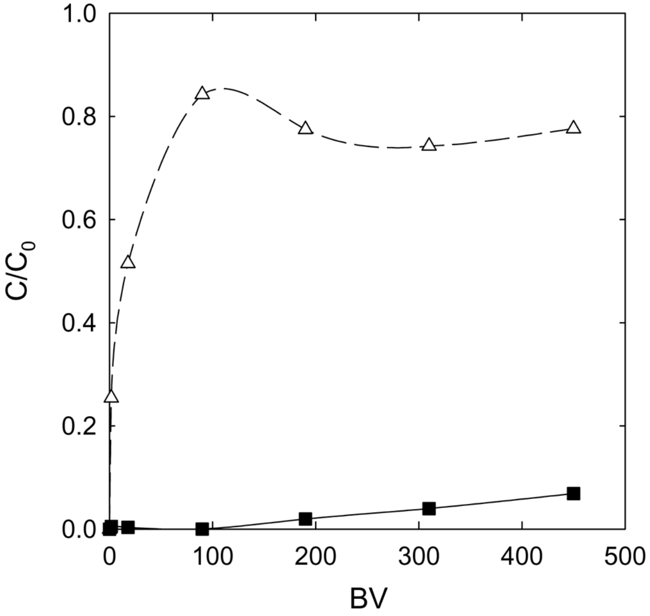


Figure 5. Breakthrough curves V (Δ) and W (■) after electroreduction.

VO^{2+} cation, was not taken up by the sorbent. Vanadium(V) is present in neutral solutions in anionic form while in highly acidic solutions it can form cationic species (3). Tungsten was adsorbed up to 190 BV. Then the W outlet concentration increases very slowly, reflecting a remarkably slow kinetics of the complex formation with the sorbent. The sorbent colour changed from white to light brown during the sorption.

The elution by 1 M HCl gave a blue eluent containing VO^{2+}. However, a remarkable amount of vanadium was still found in the NaOH eluate fraction along with tungsten, as can be seen in Fig. 6. The formation of a heteropolyanion of W and V(IV) was considered, which is in line with the brown color of the reduced solution, compared to blue vanadyl and the colorless tungstate. Another possible reason for the associated elution of V and W could be a back-oxidation (4) of V(IV) by dissolved oxygen in the feed solution after the reduction process was turned off (14). The oxidized form of vanadium(V) would then be taken up by the sorbent.

$$1/2O_2 + 2VO^{2+} + 3H_2O = 2VO_3^- + 6H^+ \tag{4}$$

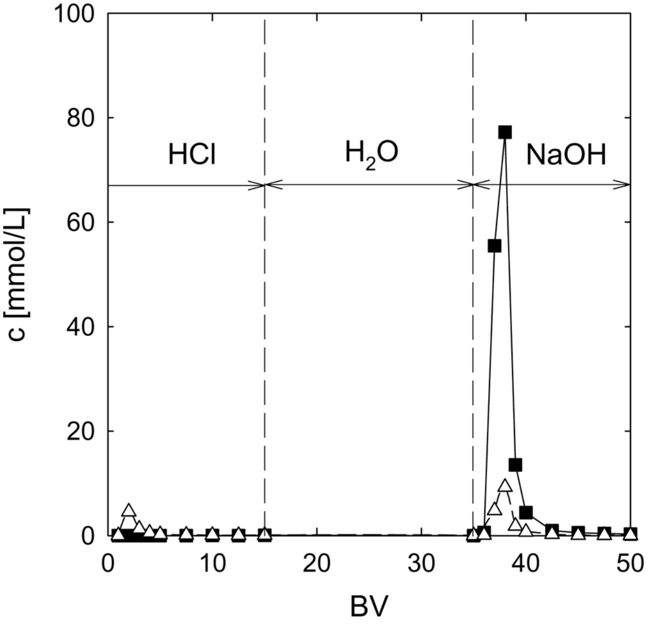


Figure 6. Desorption curve of V (Δ) and W (■) after electroreduction.

Continuous Electro-Reduction and Sorption

A solution of 0.5 mmol/L V and W was reduced for 24 hours, then it was pumped from the storage container to the column and a new solution was fed into the electrolysis circle at the same flow rate, during the continuous reduction process, see Fig. 2b. Using this new experimental setup, the separation of V and W was improved. The sorption is shown in Fig. 7. The vanadium outlet concentration reached the constant maximum value in 20 BV and within first 300 BV the complete separation from W was achieved. The peaks at the sorption curves at BV of 450 and 920 were caused by interception of sorption during weekends. As can be seen, the establishing of equilibrium resulted in the displacement of vanadium out of the sorbent by tungsten.

The results of desorption are plotted in Fig. 8. As in the previous case, vanadium in a form of VO^{2+} was released by 1 M HCl, and all tungsten and a part of vanadium was eluted by 1 M NaOH. Since the back-oxidation of V(IV) was suppressed by continouos electrolysis, the formation of a heteropolyanion of W and V(IV) is plausible. After longer reduction of the experimental solution (for 40 hours), a brown precipitate appeared in the catholyte storage container. Its IR spectrum was similar

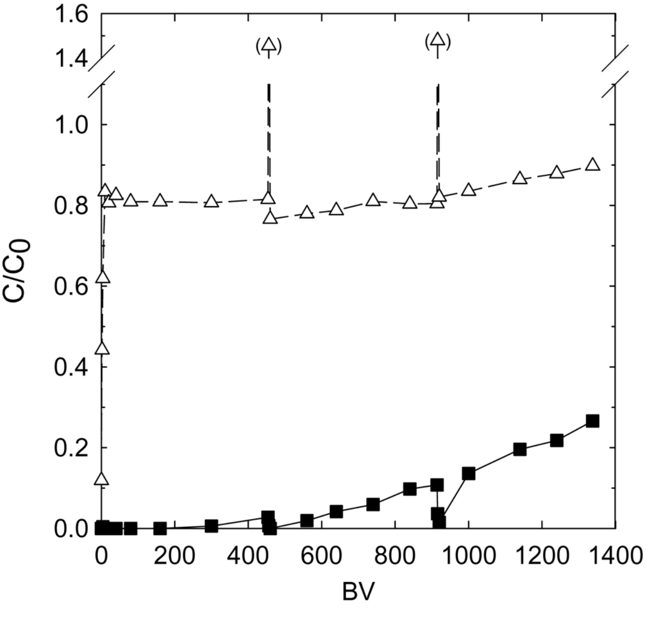


***Figure** 7.* Breakthrough curves V (Δ) and W (■) during continuous electroreduction.

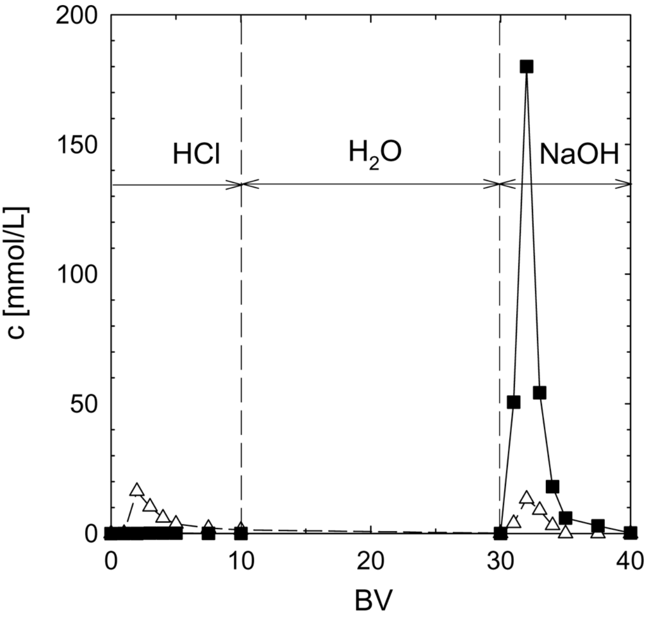


Figure 8. Desorption curves of V (Δ) and W (■) after continuous electroreduction.

to that of $V^{IV}W_5O_{19}^{4-}$ reported by Flynn and Pope (15). They also noted a formation of solid solution of $V^{IV}W_5O_{19}^{4-}$ and $V_2^{V}W_4O_{19}^{4-}$, which may take place in this case during the electro-reduction.

CONCLUSIONS

Electro-reduction/oxidation is one of the possible ways to enhance mutual separation of metal oxoanions. During the electro-reduction in the experimental electrolyzer, vanadate(V) was reduced to vanadyl(IV) cation, which was not taken up by the chelating sorbent having 1-deoxy-1-(methylamino)-glucitol functional groups. Tungsten was strongly bound to the sorbent both before and after electro-reduction. In this manner, complete separation of vanadium from tungsten was achieved.

By elution with 1 M HCl, reduced vanadium was released out of the sorbent. Tungsten was eluted later with 1 M NaOH. However, in the hydroxide fraction was also found a remarkable amount of vanadium. This fact indicates a formation of mixed-compound of V and W during the electro-reduction, that makes the two elements inseparable at given conditions. This finding will be followed to elucidate its mechanism.

The potential of this separation method can be further exploited with respect of tuning the construction and flow rate through of electrolyzer and column to achieve their in-line operation.

ACKNOWLEDGEMENTS

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

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