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Comparison of sorption of electrochemically generated V(IV) and V(V) onto selective sorbent

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ABSTRACT

Reduction of V(V) to V(IV) was performed at carbon felt cathode at a constant potential of - 1500 mV vs. Ag/AgCl. Adsorption of vanadium species onto the sorbent Purolite D 4123 was investigated in the pH range 2.5 to 5. V(V) was efficiently adsorbed throughout pH range studied, whereas V(IV) was barely adsorbed at pHs of 2.5 to 3.5 and it was re-oxidized to V(V) at higher pHs. In column experiments, V(V) was strongly adsorbed . V(IV) broke through the column readily and reached the inlet concentration within 60 BV. Desorption was carried out with combination of 1 M HCl and 1M NaOH, consequently, and the total vanadium recovery was about 100 %.

Keywords: electrochemical reduction, tetravalent vanadium, vanadium oxoanion, glucitol sorbent

INTRODUCTION

Contrary to general believes, vanadium is a metal of rather low toxicity[1]. As a pollutant it is mainly associated with utilization fossil fuels and metallurgy. Vanadium is valuable alloying compound and its recovery from wastewaters is therefore attractive.

In aqueous solution in contact with air, vanadium is present in pentavalent form of V(V) oxoanion. Reduced tetravalent form shows completely different sorption properties because V(IV) is present in aqueous solution in the form of VO^{2+} cation. Sorption properties of anionic V(V) and cationic V(IV) forms are naturally different.

Vanadium sorption onto chelating polymer chitosan was investigated for both V(V) and V(IV). V(V) was well adsorbed onto chitosan up to pH 4.5 which is also the pH of chitosan deprotonation[2]. That indicates the anion exchange mechanism. V(IV)[3] was negligibly adsorbed onto chitosan at pH 3, whereas in the pH range 4 to 6 its adsorption was comparable to that of V(V)[2]. It can probably be ascribed to re-oxidation of V(IV) at higher pHs.

Reduction of V(V) to V(IV) has been used for separation vanadium from molybdenum. Ackermann[4] described ion exchange with selective reductive vanadium elution. An alternative to this process employing electrochemical reduction of V(V) was reported later[5]. Hirai and Komasawa described separation of vanadium from molybdenum by solvent extraction and subsequent reductive stripping primarily using a chemical reducing agent[6] and afterwards using electrochemical reduction[7].

In this work, electrochemical reduction of vanadium aqueous solution and subsequent column adsorption onto a selective sorbent having 1-deoxy-1-(methylamino)-D-glucitol functional group was investigated. This sorbent was previously found capable of V(V) sorption[8].

EXPERIMENTAL

The feed solution contained 100 mg/L (batch experiments) or 50 mg/L (column experiments) of V and 500 mg/L of SO_4^{2-}. pH was set up with hydrochloric acid solution. All reagents used were of analytical purity. Metal concentrations were determined by ICP-OES Optima 2000DV (Perkin-Elmer Instruments, USA). pH was measured by pH meter InoLab Level 1 (WTW, Germany).

Reduction of V(V) was carried out in a laboratory electrolyzer designed at Department of Inorganic Technology, ICT Prague. Cathode and anode compartments were divided with Nafion membrane. The cathode compartment of the volume of 10 mL was equipped with a 3D carbon felt cathode. The cathode thickness was

10 mm and catholyte passed through cathode from the back side. The reference electrode was located between cathode and separation membrane. Perforated Pt plate was used as current feeder for cathode. Pt wire was used as an anode.

As a catholyte, solution of vanadium at pH 3 was used. The volume of catholyte was 1 L, and it was continuously circulated through the cathode compartment with a flow rate of 100 mL/min. As an anolyte, 200 mL of 0.1 M H_2SO_4 was used with identical flow rate as the catholyte. Reduction proceeded in potentiostatic mode, with potential at working electrode -1500 mV vs. Ag/AgCl reference electrode. Potential was controlled by potentiostat Voltalab PGZ 301 (Radiometer Analytical, France). The degree of reduction was monitored visually, according to the color change (from yellow V(V) through green to blue V(IV)).

The sorbent Purolite D-4123 (Purolite International) having 1-deoxy-1-(methylamino)-D-glucitol functional group was used. All the resin volumes are expressed in terms of wet settled resin volume in protonized form. Sorbent was protonized with 1M HCl solution and washed thoroughly with deionized water before use.

Batch experiments were performed by mixing 0.5 mL of the sorbent with 50 mL of solution. pH was adjusted with 1 M HCl or 1 M NaOH, before the addition of the sorbent and during the contact phase. The solutions with sorbent were shaken at 250 rpm for 20 hours. The sorbent was then withdrawn by decantation.

In the column experiments, 10 mL of the sorbent was packed into a glass column of an inner diameter of 10 mm. Sorption and elution proceeded at specific flow rates of 6 and 3 BV/h, respectively.

RESULTS AND DISCUSSION

At given experimental conditions, a reduction of V(V) proceeded at carbon felt cathode (1). Other parasite reactions are taking place at the cathode. The extent of these reactions was not determined in this work.

$$VO_2^+ + 2\,H^+ + e^- \rightarrow VO^{+2} + H_2O \quad E^0 = +1.0\ V \quad (1)$$

At the anode, oxygen was generated (2).

$$H_2O \rightarrow ½\,O_2 + 2H^+ + 2e^- \quad E^0 = -1.23\ V \quad (2)$$

Preliminary batch-wise experiments were done in order to determine optimal sorption pH. The results are shown in Fig.1.

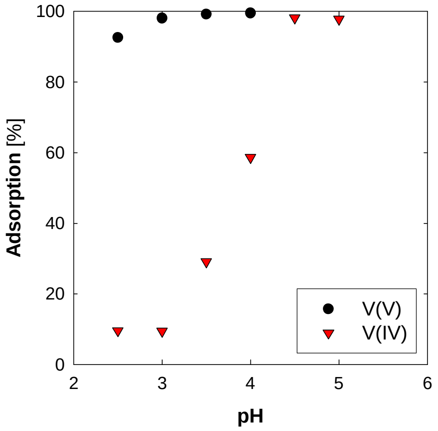

Figure 1 *Effect of pH on the V(IV) and V(V) adsorptivity*

V(IV) prepared by electrochemical reduction of V(V) showed low adsorptivity on the used sorbent at low pHs. Increase of the adsorptivity at higher pH was caused by spontaneous oxidation of V(IV) to V(V), which was deducible out of the color change. Oxidized form of vanadium was well adsorbed onto the sorbent in the pH range from 2.5 to 5.

For column experiments, solutions of either V(V) or V(IV) of about 50 mg/l at pH 3.5 were used. As can be seen in Figure 2, an increase of V(V) outlet concentration was very slow. Photo-catalyzed reduction of vanadium on the loaded ion exchanger accompanied by the color change was observed[9]. Formation of mixed-valence (V/IV) oxoanions had probably positive effect on the vanadium sorption onto the sorbent. The sorption capacity was 0.19 mol/L, calculated with respect to a limit concentration of vanadium in the outlet solution of 0,1 mg/L V(IV). The electrochemically reduced V(IV) broke through the column readily and reached the inlet concentration within 60 BV. The total sorption capacity for V(IV) was 0,013 mol/L.

The course of desorption of V(IV) is shown in Figure 3. It was performed by 1 M HCl. The VO^{2+} cation, captured on the resin, is displaced by the excess of H^+ ions. Consequently, the sorbent was washed with 1 M NaOH in order to wash out a possible residue of vanadium and in the end it was conditioned with 1 M HCl. In between mentioned steps the sorbent was washed with demineralized water.

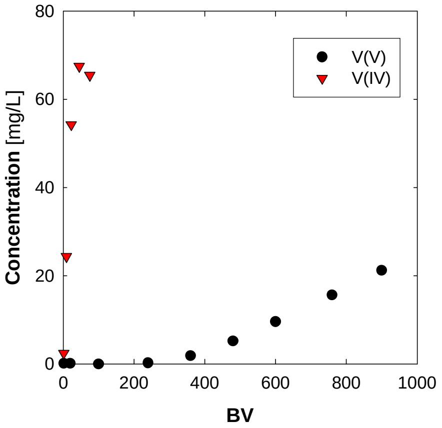

Figure 2 *Comparison of column sorption of V(IV) and V(V)*

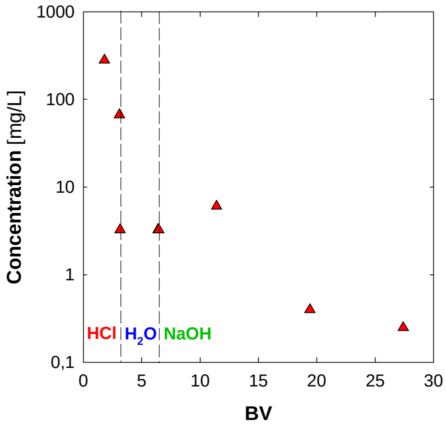

Figure 3 *Desorption course of V(IV)*

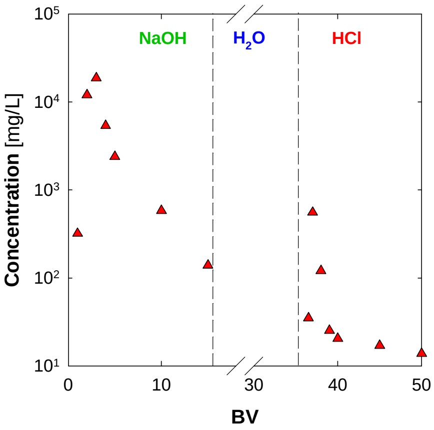

Figure 4 *Desorption course of V(V)*

91.0% of V(IV) was released within 3 BV of 1 M HCl. The rest of vanadium was released out of the resin by 1 M NaOH, resulting in a total vanadium recovery of 100%.

In the case of V(V), the desorption was carried out with 1 M NaOH, followed by conditioning with 1 M HCl. By using hydroxide, the sorbent is transformed to the free base form, and therefore vanadate anion is released out of the resin. The recovery of vanadium in the hydroxide fraction reached 97.7%, and the total recovery after conditioning with HCl was 100%. The course of desorption of V(V) is plotted in Figure 4.

CONCLUSIONS

V(V) is efficiently adsorbed throughout pH range studied, the adsorption reached 98 to 100% in the range of pH 3 to 5. This confirms the fact that in mildly acidic aqueous solution vanadium is present in the form of decavanadate oxoanion. which is highly attracted to the sorbent in protonized form. In contrast to V(V), V(IV) occurs in solutions as VO^{2+} cation. The positive charge most likely prevents vanadium to be retained at the selective sorbent. V(IV) was scarcely adsorbed at pHs of 2.5 to 3.5, the sorption achieved was 9.5 to 29% in batch experiments. At higher pHs a re-oxidation to V(V) was observed. In column experiments, photocatalyzed reduction of V(V) on the loaded sorbent was observed, which resulted in an increase of the sorption capacity. The outlet concentration was lower than 0.1 mg/L up to of 200 BV. V(IV) broke through the column readily and reached the inlet concentration within 60 BV. Desorption was carried out with 1 M HCl and 1M NaOH and the total vanadium recovery was 100%.

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