# REMOVAL OF VANADIUM(V) BY ADSORPTION ONTO ION EXCHANGERS FROM AQUEOUS SOLUTIONS

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## Abstract

Vanadium is considered a strategic metal, and its limited resources and high consumption make its production and recovery of significant importance. The Dowex PSR2's and Dowex PSR3's applicability for vanadium removal from aqueous solutions was examined. The adsorption process optimization was performed for the adsorbent dose (0.01 – 0.1 g) and pH (2 – 10) effects. It was found that the optimum adsorbent dose is equal to 0.1 g and optimum pH = 6. V(V) can be removed with high efficiency (the amount of vanadium adsorbed at time t, $q_t$ = 9.75 mg/g; percentage removal of vanadium, %R = 97.6% - gel Dowex resin or $q_t$ = 9.86 mg/g; %R = 98.6% macroporous Dowex resin).

**Key words:** adsorption, removal, anion exchanger, vanadium

## Introduction

Vanadium was first discovered in 1801 by Andreés Manuel del Rio in lead and vanadium ores, but it was mistaken for a form of chromium (Habashi, 2002). The element was named after the goddess of beauty and fertility Vanadis. It was rediscovered in the 1830s in converter slag by the Swedish chemist Nils Gabriel Seftström and isolated in 1867 by Sir Henry Roscoe, whereas production of pure vanadium (99.7% purity) began after 1925 when two American chemists, J.W. Marden and M.N. Rich reduced vanadium pentoxide ($V_2O_5$) by calcium (Moskalyka et al. 2003; Imtiaz et al. 2015). Vanadium belongs to the fifth group of the periodic table. Vanadium has a high melting point and good corrosion resistance at low temperature. Vanadium usually possesses a steel grey colour with a bluish tinge. It exists in a variety of oxidation states: –1, 0, +2, +3, +4, and +5 (Imtiaz et al. 2015). Vanadium is found in different minerals, as well as phosphate rock, iron ores, crude oils, or meteorites. Among different vanadium minerals carnotite, vanadinite, roscoelite, and patronite play a significant role. Vanadium is soluble in $HNO_3$, $H_2SO_4$ acids but insoluble in HCl, dilute NaOH, and dilute alcohol (Moskalyka et al. 2003). Vanadium forms different types of compounds, e.g. ammonium metavanadate ($NH_4VO_3$), sodium metavanadate ($NaVO_3$), sodium orthovanadate ($Na_3VO_4$), but the most commonly used form of vanadium is vanadium pentaoxide ($V_2O_5$) (Imtiaz et al. 2015). Vanadium applications are found in three main areas. Due to its high resistance to corrosion, vanadium is commonly applied as an additive to stainless steel alloys (Nazarov et al. 2007) and aerospace alloys. In the aerospace industry vanadium is applied with aluminum as well as titanium (this area covers 4.5% of the vanadium market). Another application area is the chemical industry. Vanadium in the form of vanadium pentaoxide is a very important component of catalyst matrices used in the refining and particular sulfuric acid production industries. The third area of vanadium application is the redox battery industry (Baranova et al. 2012; Barceloux et al. 1999). As it was found, the vanadium supply as well as demand increase year by year (Fig. 1). The vanadium demand increase is a results of steel industry development as well as its new applications. Taking into account that the demand is greater than the supply and the very low inventory levels for vanadium, its recovery is of particular importance. Therefore, the purpose of the study was to check Dowex ion exchange resins' applicability for vanadium removal from the model and real solutions. Optimization of the adsorption process was performed and the effect of pH was evaluated.

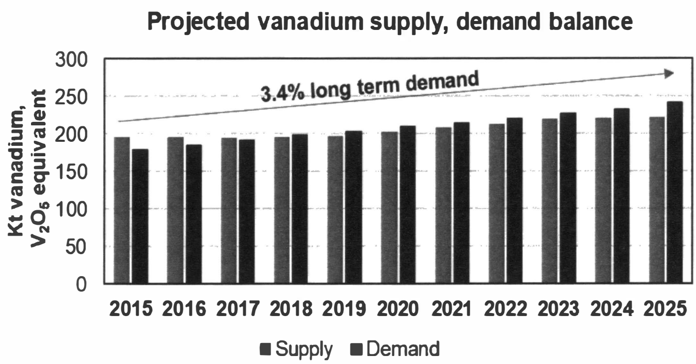


**Figure 1.** Vanadium supply and demand (expectation).

## Materials and Methods

The vanadium(V) stock solution of 1000 mg/L concentration was prepared from sodium metavanadate which was dissolved in distilled water with 5 mL of concentrated ammonia (25%) and 10 mL of concentrated nitric acid(V) (65%). The working V(V) solutions were prepared by dilution and their pH values were adjusted using the $HNO_3$ and NaOH solutions of 1 mol/L concentrations. The properties of ion exchangers applied for V(V) removal are presented in Table 1 and Fig 2.

The studies of vanadium(V) ions removal by the static method were carried out in 100 mL conical flasks tightly sealed with silicone stoppers. Various weights of Dowex ion exchange resin were placed in the flasks: for the effect of pH - 0.1 g, for the effect of weights - 0.01 g, 0.025 g, 0.05 g, 0.075 g, 0.1 g. All samples were weighed with an accuracy of ± 0.0005 g. Then 20 mL of the stock solution, which contained V(V) ions at a concentrations of 50 mg V(V)/L was added to the flasks. The samples were set up in an Elpin+ mechanical shaker, type 357, and its operating parameters were as follows: shaking speed=170 rpm, vibration amplitude A=8, room temperature T=295 K. The flasks were shaken for 4 hours. Then the aqueous phase was separated from the ion exchanger by filtration and the V(V) concentration was determined using Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) (Varian AA240Z spectrometer with a GTA120 graphite cell and a PSD120 automatic dispenser). After that the percentage removal of vanadium was calculated according to the formula (Manohar et al. 2005):

$$\%R = \frac{C_0 - C_t}{C_0} * 100\% \qquad (1)$$

where: $C_0$ is the initial concentration of V(V) ions in the aqueous phase (mg/L), $C_t$ is the concentration of V(V) ions in the aqueous phase after time t (mg/L).

**Table 1.** Physicochemical properties of Dowex ion exchangers (Wołowicz et al. 2020).

| Functional resin | Dowex PSR2 | Dowex PSR3 |
|---|---|---|
| Type | Strongly basic anion exchanger | Strongly basic anion exchanger |
| Matrix | Cross-linked polystyrene | Cross-linked polystyrene |
| Structure | Microporous | Macroporous |
| Functional groups | Quaternary ammonium, type, tri-n-butyl amine | |
| Mean bead size (mm) | 0.3 – 1.2 | 0.3 – 1.2 |
| Total capacity (val/L) | 0.65 | 0.6 |
| Water retention (%) | 40 – 48 | 50 – 65 |

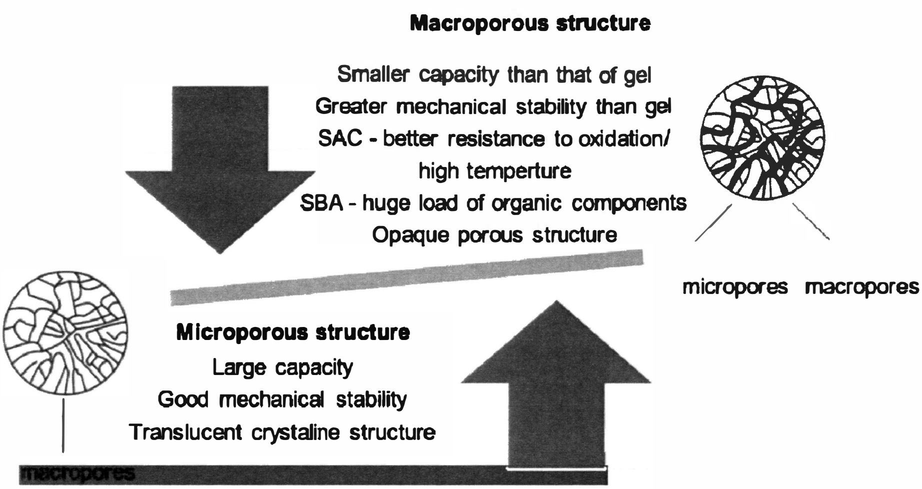


**Figure 2.** Difference between the micro- and macro-porous ion exchange resins (SBA – the strongly basic anion exchange resin, SAC – the strongly acidic cation exchange resin).

## Results

The effect of pH on adsorption of V(V) on Dowex PSR2 and Dowex PSR3 was studied in the pH range from 2 to 10. The results are presented in Figure. 3.

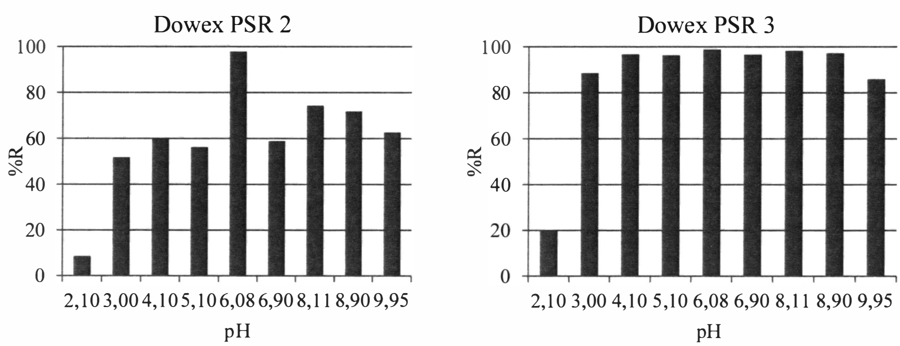


**Figure 3.** Effect of pH on the percentage removal on Dowex PSR2 and Dowex PSR3.

Vanadium can exist in different forms, depending on the solution pH and solution concentration. At least 11 species can be found. At pH 12-14 the tetrahedral orthovanadate ion is the principal species, whereas at lower pH values the monomer $[HVO_4]^{2-}$ and dimer $[V_2O_7]^{4-}$ are formed. As the pH value is reduced, further protonation and condensation to polyvanadates occur. At pH 4-6 $[H_2VO_4]^{-}$ is predominant, while at higher concentrations trimers and tetramers are formed. At pH 2-4 decavanadate predominates (Baes et al. 1976; Bartecki 1996, Peacock et al., 2004, Takaya et al. 1994). The form of vanadium can affect its percentage removal. As it was found, pH = 6 was the optimum for the adsorption of V(V) on Dowex PSR2 as well as PSR3. In the case of microporous Dowex PSR2 the effect of pH is more evident than in the case of macroporous Dowex PSR3. At pH = 6 (initial V(V) concentration 50 mg/L) vanadium exists in anionic forms (Fig. 4) and the ion exchangers belong to the anion exchange resin type therefore, the uptake is large and %R is equal to 97.6% for the Dowex PSR2 and %R = 98.6% for Dowex PSR3 resins. A slightly greater or much greater adsorption was observed for macroporous Dowex PSR3.

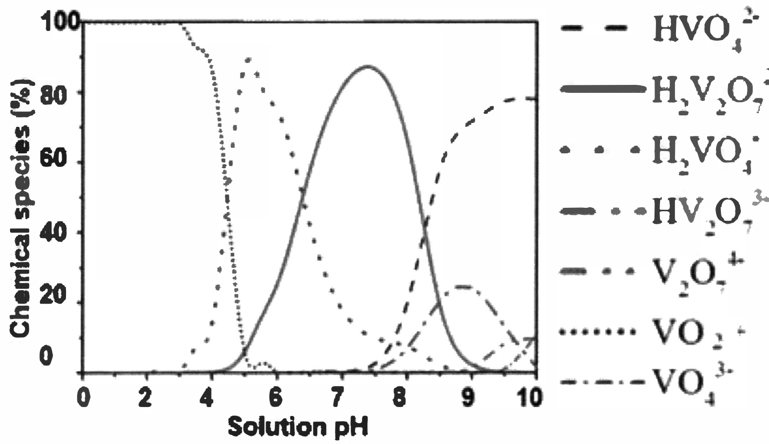


**Figure 4.** Forms of vanadium in aqueous solution calculated using Visual MINEQL ver. 3.0 at the initial concentration 50 mg/L.

As is reported in literature, pH is an important parameter affecting the adsorption efficiency of V(V) ions. The elimination efficiency of vanadium ions at the initial concentration $C_0$ = 40 mg/L on the composite adsorbent ranged from 46.1% (pH=7) to 72.1% (pH=3.5). The removal of vanadium ions decreased with the pH increasing above 3.5. The optimum pH was 3-3.5 (Mojiri, 2017), while when using the porous ceramic containing amino groups ($C_0$ = 50 mg V(V)/L) the optimum pH was 4-4.5 (99.8% of ions was removed). Additionally, a decrease in %R was observed with the increasing pH (He et al. 2018). The optimum pH for vanadium adsorption on Fe(III)/Cr(III) hydroxide treated with hydrochloric acid was 4.0 (Prathap et al. 2010).

The adsorption optimization was also achieved by changing the adsorbent dose from 0.01 g to 0.1 g. The experimental conditions were as follows: adsorbent mass = 0.1±0.0005 g, initial concentration $C_0$ = 50 mg V(V)/L, volume of added solution, V = 20 mL, pH = 6, agitation speed = 170 rpm, amplitude, A = 8, temperature, T = 295 K, t = 4 h. It was found that the increase in the adsorbent dose increased the removal of V(V) (Fig. 5). With the increase in the ion exchanger resin dose, larger numbers of active sites in the adsorbent surface are accessible for V(V) adsorption, which results in greater adsorption (Jana et al. 2015).

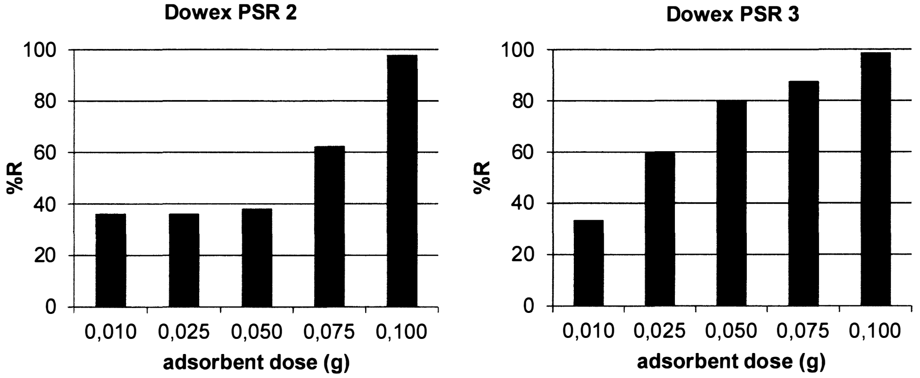


**Figure 5.** Effect of adsorbent dose on the V(V) adsorption on Dowex PSR2 and Dowex PSR3.

## Conclusions

Studies of optimization of adsorption of V(V) on the Dowex ion exchange resins prove that the best adsorption uptake was obtained at pH=6 and adsorbent dose 0.1 g. Moreover, the studies show a high percentage removal of V(V) from aqueous solutions. Further studies to prove the ion exchange resins' applicability for V(V) removal from real wastewaters are in progress.

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