

## Preconcentration and Determination of Vanadium (V) in Environmental Samples by Using Chemically Modified Styrene Maleic Anhydride

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**Abstract:** *The new adsorbents were synthesized by polycondensation of styrene maleic anhydride with some amines. A rapid, sensitive and selective method is described for preconcentration and determination of vanadium(V) by using this polymers. The synthesized sorbents was selective to vanadium(V) within a better response time of 60 and 120 min. In this work the ability of adsorbent was examined and affecting factors such as; optimal pH of solution, sorption capacity, ion strength, concentration of vanadium(V) and desorption. The method was selective in presence of some foreign ions. The maximum capacity of vanadium(V) onto the sorbent 267,6 mg/g. The developed adsorbents was successfully applied for the determination of vanadium(V) in environmental samples.*

**Keywords:** *Vanadium(V), polymer sorbents, preconcentration, environmental samples, styrene maleic anhydride*

### 1. INTRODUCTION

Heavy metals are one of the metal ions toxic types of water pollutants. The major toxic metal ions hazardous to human's life are Cr, Fe, V, W, Co, Cu, Cd, Hg, As, Pb etc. The average aqua regia-soluble vanadium concentration is 38 mg V kg<sup>-1</sup> [1]. The most important anthropogenic sources of vanadium are associated with the burning of fossil fuels and its main field of application is in the steel industry, in alloys. These are precipitated on the soil drained by rain and groundwater and directly adsorbed by plants, animals and humans. Vanadium can exist in a range of oxidation states, from +2 to +5 [2]. In solution, under environmental conditions, mainly vanadium(IV) and vanadium(V) are present. The toxicity of vanadium is dependent on its oxidation state, with vanadium(V) being more toxic than vanadium(IV) and its poisoning symptoms are sometimes fatal.

Vanadium content in food is directly dependent upon the concentrations present in soil. Concentration of vanadium in water is largely dependent on geographical location and ranges from 0.2 to >100 µg·L<sup>-1</sup> in fresh and drinking water, from 0.2 to 29 µg·L<sup>-1</sup> in sea water.

Wastewater containing heavy metals originated mainly from metal plating facilities, mining operations, tanneries, batteries, paper industries and pesticides galvanizing plants, stabilizers, thermoplastics, etc. These industries discharge heavy metals and wastewater directly or indirectly into the environment especially in developing countries. Thus, treatment of industrial wastewater containing soluble heavy metals has become essential in order to increase the quality of water [3, 4]. Therefore, the determination of vanadium(V) in environmental samples is necessary in terms of environmental protection. Several analytical techniques have been reported for the determination of vanadium, which include spectrophotometry [5, 6], mass spectrometry [7], atomic absorption spectrometry [8, 9] in various environmental samples. In direct determination of vanadium in complex matrices is difficult as they occur at very low concentrations. In order to obtain accurate and sensitive results, a suitable preconcentration step is required to treat these problems during the analysis of real samples.

The use of chemically modified styrene maleic anhydride as synthetic sorbents to treat low concentration of heavy metals from environmental samples has grown, because it has high adsorptive capacity.

Therefore, in this work, we synthesized and characterized new cation exchanger based on styrene maleic anhydride and amines (p-sulfanilic acid (aminobenzenesulphonic acid), thiouracil,

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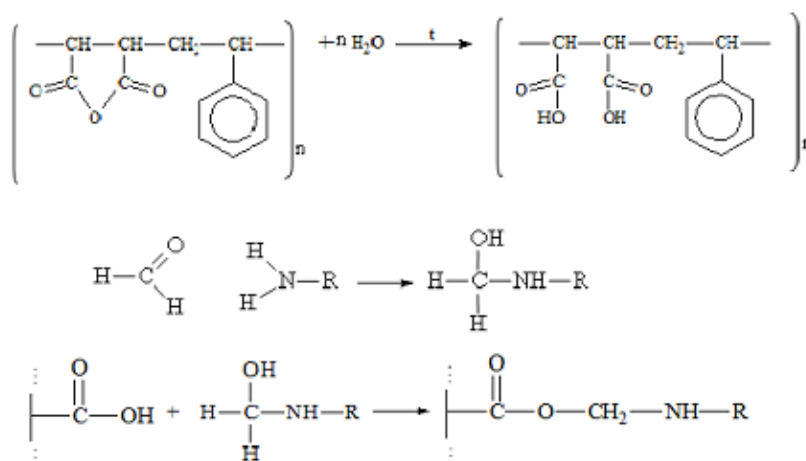
4-Aminosalicylic acid) a rapid sensitive and selective method is described for preconcentrative determination of vanadium(V) using these modified sorbents.

### 2. EXPERIMENTAL

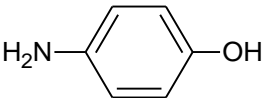
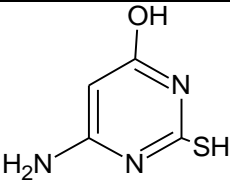
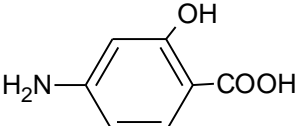
#### 2.1. Chemicals and Reagents

All the reagents used in this work were of analytical grade and standard solutions of vanadium(V) were prepared by dissolving appropriate amounts of ammonium metavanadate in double distilled water. The buffer solutions were prepared with hydrochloric acid (pH 1-2) and acetic acid/ammonia by adjusting the pH to 3-7. All used sorbents were synthesized by polycondensation of styrene maleic anhydride and p-sulfanilic acid (S<sub>1</sub>) (aminobenzene sulphonic acid), 6-amino 2-thiouracil (S<sub>2</sub>), 4-Aminosalicylic acid (S<sub>3</sub>) (table 1).

**Synthesis of sorbents and reagent.** Styrene maleic anhydride (SMA) is a synthetic polymer that is built-up of styrene and maleic anhydride monomers. SMA was synthesized by known method [11]. The sorbents was synthesized by adding suitable amine and formaldehyde onto gotten copolymer. Reaction was performed on sand bath with continuously mixing. The reaction was performed in water medium, therefore copolymer's anhydride groups were hydrolyzed. The synthesis reactions are shown below.



**Table1.** Amine fragments crosslinked styrene maleic anhydride

| Transcription  | Fragment  | Duration of reaction, hour |
|----------------|---|----------------------------|
| S <sub>1</sub> |  | 8-9                        |
| S <sub>2</sub> |  | 4-5                        |
| S <sub>3</sub> |  | 9-10                       |

S1: In IR spectras 3675-3050 cm<sup>-1</sup>, 3419-3200 cm<sup>-1</sup>, 1771-1717 cm<sup>-1</sup>, 1558-1540 cm<sup>-1</sup>, 1623-1540 cm<sup>-1</sup> are due to the presence of hydroxyl group (-OH), amine (-NH), carbonyl (-C=O), (-C=N), (-C-C-) stretching vibrations respectively.

S3: In IR spectras 3600-3100 cm<sup>-1</sup>, 3400-3200 cm<sup>-1</sup>, 1750-1715 cm<sup>-1</sup>, 1620-1520 cm<sup>-1</sup>, 1623-1540 cm<sup>-1</sup> are due to the presence of hydroxyl group (-OH), amine (-NH), carbonyl (-C=O), (-C=N), (-C-C-) stretching vibrations respectively.

For photometric determination of vanadium(V) was used azocompound (bisazo derivate of pyrogallol) – bis-(2,3,4-threehydroxyphenylazo)benzidin (R). This reagent was synthesized by known method [5].

## 2.2. Apparatus

For spectrophotometric determination of vanadium(V) as a complex measurements were performed in spectrophotometer Lamda 40 (Perkin Elmer). IR spectrometer SPECORD used for the analysis of functional groups in the synthesized sorbents.

## 2.3. Procedures

A measure of 2 ml  $10^{-2}$  M of an aqueous solution of V(V) was add to a beaker and adjusted to a desirable pH value by 18 ml (pH 3-6). The 30mg adsorbent was add onto the solution vibrated for 60 min at room temperature, and filtered. Then from filtrate of V(V) was taken 1 ml, add to flask of 25 ml and onto vanadium solution add 2,5 ml  $10^{-3}$  M reagent solution. This mixture was diluted with pH 4. Residual V(V) was detected by spectrophotometer at a wavelength of 447 nm.

## 2.4. Preparing of Real Water and Wastewater Samples

The developed methods were used for preconcentrative determination of vanadium(V) in real water and wastewater samples. The wastewater samples were taken from different oilfield from Baku (Azerbaijan). Dissolved and particulate matter in the water samples were commonly separated by filtration through a cellulose membrane filter. Considering that at higher pH vanadium(V) undergoes reduction to vanadium(IV) filtered aliquots (20 ml) were acidified by 1ml HCl. Then samples were immediately analyzed.

## 3. RESULTS AND DISCUSSION

### 3.1. Experimental Optimum Conditions. Effect of pH.

In the first to determine the effect of pH on removal efficiency of vanadium(V) by this sorbents were carried out this work at pH 3-6. Considering that, in strong acid medium the adsorbents were swelling and they couldn't adsorb metal ions and also after pH 5 oxocation of vanadium(V) turns to  $HVO_3$  and then to oxyanion of V(V) consequently we didn't used to work at pH higher 6 [2].

It was found that vanadium binding to adsorbent was pH dependent and the maximum sorption of vanadium (V) to adsorbent was found having an initial pH 4. Figure 1 also shows the dependence of removal efficiency on pH of sorption system.

### 3.2. Effect of Contact Time on V(V) Adsorption

For the adsorption of  $1020 \mu\text{g}$  V(V) at pH 4.0 the removal efficiency reached a maximum value when the adsorption time was 60 min with  $S_1$  and 120 min with  $S_2$ ,  $S_3$ .

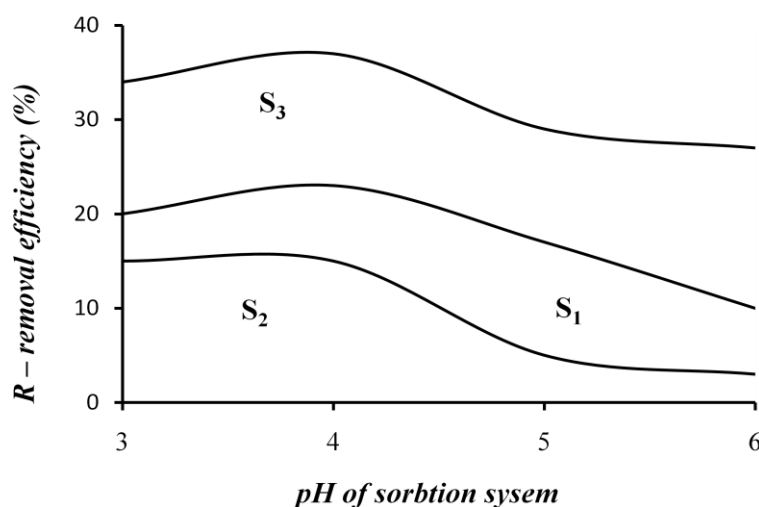


Figure 1. V(V) removal efficiency% versus the various pH from 3 to 6

**3.3. Adsorption Capacity of Sorbents and Removal Efficiency(%) of Vanadium(V)**

The V(V) adsorption was particularly dependent on the initial concentration in solution. The different concentrations of V(V) solutions ranging from 1.0 to 8.0 mM·L<sup>-1</sup> were performed with fixed contact time and dosage (30 mg) of sorbents. Their concentrations were determined after adsorption for 1 (S<sub>1</sub>) and 2 h (S<sub>2</sub>, S<sub>3</sub>) by sorbents at pH 4 by spectrophotometric method. At low concentration, V(V) ions were adsorbed at specific sites on adsorbent, while saturated with increasing the concentration. The adsorption capacities were calculated as

$$Q = V(C_0 - C) / m \tag{1}$$

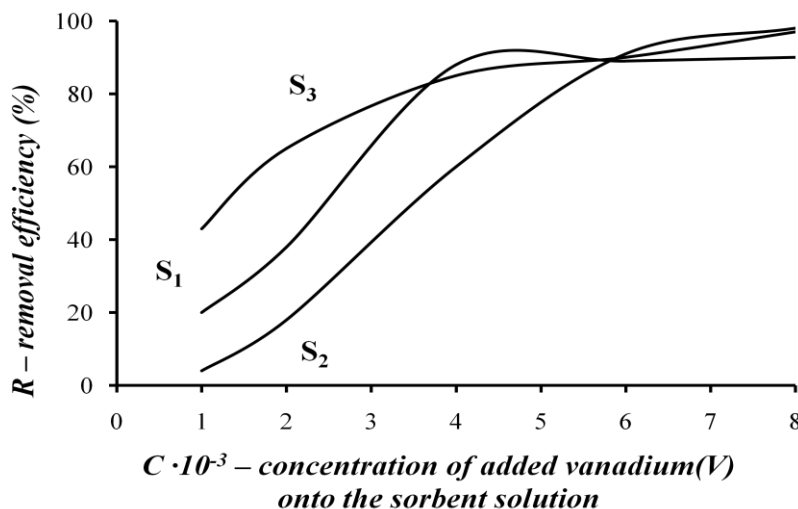
where Q is adsorption capacities of sorbents (mg V/g sorbent), V is the volume of solution (mL), C<sub>0</sub> – initial concentration of V(V) and C – concentration of V(V) after adsorption (mg/L), and m is weight of sorbents (g). In table 2 were introduced adsorption capacities of sorbents. It is evident from the table 2 that adsorption capacity of S<sub>2</sub> and S<sub>3</sub> close to each other and difference between adsorption capacities of all sorbents is little. The maximum adsorption capacity of V(V) ions on the suggested polymer adsorbents, which was higher than other adsorbents reported in the literature, which were listed in Table 3.

**Table2.** Parameters of adsorption of V(V) onto sorbents based styrene maleic anhydride.

| Sorbent        | Opt. pH | Exp. Duration (min) | Opt. Concen. (mM/L) | Ion strength (KCl) | Adsorption capacity (mg/g) | Optimal desorption condition |
|----------------|---------|---------------------|---------------------|--------------------|----------------------------|------------------------------|
| S <sub>1</sub> | 4       | 60                  | 8.0                 | 0,6                | 241,4                      | 0,5 M HCl                    |
| S <sub>2</sub> | 4       | 120                 | 8.0                 | 0,6                | 267,6                      | 1,0 M HClO <sub>4</sub>      |
| S <sub>3</sub> | 4       | 120                 | 8.0                 | 0,8                | 265,2                      | 1,0 M HClO <sub>4</sub>      |

Adsorbent size particle = 0,14 mm

Adsorbent dosage = 30 mg



**Figure 2.** V(V) removal efficiency % versus the various vanadium(V) concentration. from 1.0 · 10<sup>-3</sup> to 8.0 · 10<sup>-3</sup> M/L

The percent of vanadium (V) removal, R%,

$$R\% = C_0 - C_e / C_0 \cdot 100\% \tag{2}$$

where C<sub>0</sub> and C<sub>e</sub> are the initial and the residual vanadium concentrations (mg/L). The effect of initial V(V) ions concentration on V(V) uptake was studied in a range from 1.0 to 8.0 mM·L<sup>-1</sup>. The percentage removal of vanadium(V) increased with increasing initial vanadium concentration (Figure 2) and showed that maximum values reach on 8.0 mM·L<sup>-1</sup> concentration of vanadium(V) for all adsorption process (table 2).

**3.4. Effects of Co-Existent Ions**

The presence of co-ions in wastewater might affect the adsorption behaviors of sorbents S<sub>1-3</sub> for V(V) ions. By keeping the initial concentration of V(V) (30 mg·L<sup>-1</sup>) and the dosage of the adsorbent (30

mg), the adsorption capacity of adsorbents were investigated in the presence of co-ions. The results indicated that no influences were observed from  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ , but V(V) slightly affected by the presence  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ .

**Table3.** Maximum adsorption capacity for V(V) onto different adsorbents.

| No | Adsorbent  | Maximum adsorption capacity [mg/g] | References   |
|----|--|------------------------------------|--------------|
| 1  | S <sub>1</sub>   | 241,4                              | Present work |
|    | S <sub>2</sub>   | 267,6                              |              |
|    | S <sub>3</sub>   | 265,2                              |              |
| 2  | Cross-linked chitosan functionalized with threonine moiety   | 46.92                              | [12]         |
| 3  | Amine-modified poly(glycidyl methacrylate)-grafted cellulose | 197.8                              | [13]         |
| 4  | Chitosan-Zr(IV) composite                                    | 208                                | [14]         |
| 5  | Crosslinked chitosan   | 6.27                               | [15]         |
| 6  | TiO <sub>2</sub> based adsorbent/FeOOH based adsorbents      | 45.66/111.1                        | [16]         |

### 3.5. Desorption and Regeneration

In order to reduce operation cost and make the process economical, the reusability of polymers based on styrene maleic anhydride is an important aspect to evaluate its potential for practical application. Desorption of V(V) from metal adsorbed adsorbent was carried out in a batch mode by using different acids with different concentrations (0.5, 1.0, 1.5, 2.0 mol·L<sup>-1</sup> HCl, H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>COOH, HNO<sub>3</sub>, HClO<sub>4</sub>). The greatest affect on desorption of V(V) ions 1.0 mol·L<sup>-1</sup> HClO<sub>4</sub> (S<sub>2</sub>, S<sub>3</sub>) and 0.5 mol·L<sup>-1</sup> HCl (S<sub>1</sub>) solution and the desorption efficiency shown in table 4. Besides, it was also found that the adsorption capacity was not significantly changed after regeneration and we can use these adsorbents in later experiments.

**Table4.** Desorption parameters of V(V)

| Adsorbent      | Acid and its concentration                | Removal efficiency (%) of V(V) |
|----------------|---|--------------------------------|
| S <sub>1</sub> | 0.5 mol·L <sup>-1</sup> HCl               | 99.5 %                         |
| S <sub>2</sub> | 1.0 mol·L <sup>-1</sup> HClO <sub>4</sub> | 97.3 %                         |
| S <sub>3</sub> | 1.0 mol·L <sup>-1</sup> HClO <sub>4</sub> | 99.0 %                         |

### 3.6. Analysis of the Samples

The developed method for preconcentration and determination of vanadium(V) were tested on the water samples – real water and wastewater samples. The experiments carried out by static method. For checking the obtained results used the standard addition method. All results are shown in table 5.

**Table5.** Determination of V(V) in real water and waste water samples

| Aliquots                 | Found (μg·L <sup>-1</sup> ) | Added (μg·L <sup>-1</sup> ) |
|--------------------------|-----------------------------|-----------------------------|
| Real water               | 2.31 ± 0,09                 | 2.34 ± 0,08                 |
| Waste water <sup>1</sup> | 38.8 ± 0,12                 | 38.1 ± 0,11                 |
| Waste water <sup>2</sup> | 35.9 ± 0,09                 | 36.3 ± 0,07                 |

## 4. CONCLUSION

The present study showed that the polymers based on styrene maleic anhydride can be easily synthesized by polycondensation method, and could be employed as a synthetic sorbent for the removal of vanadium(V) ions from aqueous solution. The adsorption was dependent on the solution of pH and contact time. The maximum adsorption occurred at pH 4.0. The kinetic batch experiment syndicated that more than 99% of the V(V) was absorbed onto the adsorbents within 60 and 120 min. Regeneration of adsorbents based on styrene maleic anhydride was achieved by using 1.0 mol·L<sup>-1</sup> HClO<sub>4</sub> with efficiency of greater than 99%. These results suggested that adsorbents based on styrene maleic anhydride may have potential applications for the removal of V(V) from wastewater.

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