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SORPTION OF VANADIUM (V) IONS BY CHEMICALLY MODIFIED CHELATING ADSORBENT BASED ON MALEIC ANHYDRIDE STYRENE COPOLYMER AND ITS APPLICATION TO INDUSTRIAL WATER SAMPLES

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Abstract. A new chelating polymeric sorbent has been synthesized on the basis of styrene maleic anhydride copolymer by the chemically modification with hydrazide of maloney acid. The synthesized sorbent and its complex with metal has been investigated by IR spectroscopy and its sorption characteristics toward vanadium (V) ions have been studied. Synthesized sorbent has been applied for investigation of pre-concentration of V (V) ions in liquid phase. The optimal sorption conditions such as effect of pH, ionic strength, effect of initial metal ion concentration and time to reaching chemical equilibrium on sorption have been established. The synthesized sorbent was selective to vanadium ions within better response time of 120 min. In static state adsorption was found to be pH dependent with maximum removal efficiency at 4. The removal efficiency of vanadium (V) increased by increasing of initial vanadium (V) concentration. The maximum adsorption capacity of vanadium (V) onto this adsorbent has been established and found to be 183.6 mg$\cdot$g^{-1}. The proposed method has been successfully applied to the determination of micro amount of vanadium in industrial water samples. Also desorption of vanadium ions with mineral acids of the different concentrations has been studied. Results of desorption have been represented in this work.

1. Introduction

Vanadium - a very spread and heavy transition metal and is among the 20 most abundant elements in the Earth's crust: the content in the crust is 0.0015% (mass) (Larsson *et al.,* 2014). The world's vanadium production volume has been growing steadily. Vanadium compounds have been widely used in the chemical industry, as catalysts in organic synthesis, in the manufacture of polymeric materials. In the chemical industry vanadium has been used for production of rechargeable batteries and as a catalyst for the production of sulfuric acid, acetic acid, and many others. The use of vanadium in steels continues to be very significant to this day. One of the main sources of contamination of natural waters vanadium is also oil and products of its processing. Increasing concentrations of toxicant-metals such as vanadium in the surface waters of lakes may result from acid rain. Vanadium pollution can cause potential harmful effects on ecological systems, and lead to animal poisoning and human disease (Yanguo *et al.,* 2006).

In recent years, increasingly there are various materials on the impact of heavy metals on human health. Soluble form of vanadium compound is a part of the water and

sewage also in the waste and intermediate products of some industrial productions which represent a serious environmental hazard for human͵s life. Vanadium is a toxic element and its determination is advisably from analytic and ecologic point of view. Compounds of vanadium-vanadates are generally very soluble and its compounds, eventually, fall into water. This is because their determination in water represented a big interest for many years. It is known that with increasing degree of valence vanadium toxicity increases when finding it in the form of an anion and a cation. The workplace exposure limit for vanadium pentoxide is according to the Health and Safety Executive (HSE) 0.05 mg·m^{-3}/8h (Cooper, 2007). Elevated concentrations of vanadium are harmful to human health.

Determination of vanadium carried out by using of atomic absorption spectroscopy, ion chromatography and flow injection method (López-García *et al.,* 2009; Huang *et al.,* 2002; Wuilloud *et al.,* 2000). Preconcentration and separation of inorganic ions occupy a leading position in the chemical analysis. The ions of toxic elements, such as vanadium (V)-are the common component of waste water. To separate these ions synthetic polymeric sorbents had been widely used for many years. Spectrophotometric methods are quite fast, sensitive and objective; this is their advantage over many chemical methods. Well known that spectrophotometric methods of analysis are characterized by high accuracy and are not inferior in accuracy to classical methods of analysis and used in the checking in analytical methods and reference materials.

Polymeric chelating sorbents have been widely used in industry to recover the heavy metals (Barakat, 2011). Therefore, there is a need to find new sorbents differing high selectivity for metal ions. For this experiment, have been used synthetic sorbents, as is well known, exchange capacity of synthetic sorbents is substantially higher than that of the inorganic. There are many novels in literature about sorption determination of vanadium (Pyrzyńska & Wierzbicki, 2005; Filik *et al.,* 2004; Dogan & Köklü, 2006; Yadamari *et al*., 2014; Mthombeni *et al.,* 2015; Luo *et al.,* 2017; Chaudhari, 2007). The authors used both synthetic (Pyrzyńska & Wierzbicki, 2005; Filik *et al.,* 2004; Dogan & Köklü, 2006; Yadamari *et al.,* 2014; Mthombeni *et al.,* 2015) and natural (Luo *et al.,* 2017; Chaudhari, 2007; Cutter & Nunn, 1979) adsorbents. The proposed method of sorption concentration of vanadium from solutions allows analyzing of small sample volumes. In general, solving the problems of concentration and separation of heavy elements in last years has been carried out by using sorption process. The method is particularly effective in determining them in complex materials. Besides the use of sorption concentrating process has its advantages, such as low cost equipment, high absorption capacity of adsorbents. The separation and pre-concentration process is also necessary for improving the sensitivity of the analytical detection method and for providing low detection limits. Therefore, pre-concentration and separation of heavy metals by synthetic sorbents followed by the instrumental determination used as one of the main step in determining the elements.

The aim of this work is grafting to the polymer matrix chelating functional groups, synthesis of new sorbent and studying its adsorption properties. The styrene maleic anhydride copolymer has been used as a polymer matrix for pre-concentration of vanadium (V) ions. Copolymer of hydrazide of maloney acid has been chosen as sorbent due to its reasonable cost and ease of regeneration.

2.   Experimental part

Apparatus

Optical density of solutions was measured on spectrophotometer «Lambda 40» (Perkin Elmer) and photocolorimeter KFK-2 in a ditch with thickness of a layer ℓ =1см. pH value of solutions was checked up by the ionomer I-130 with a glass electrode. The solutions were mixing using thermomixer ORBITAL SHAKER TS-1. The sorbent was dried on evaporator Zymark TurboVap LV. Identification of sorbent has been carried out by IR spectroscopy on LUMOS FTIR microscope, and its thermal stability has been investigated by thermo gravimetric analysis on Derivatograph – Simultaneous Thermal Analyzer (STA) 6000.

Reagents

All using reagents were of analytical grade. For the preparation of the metal solution of V (V) has been used it chemically pure salt NH_4VO_3. The vanadium solution was prepared by the following procedure. Certain amounts of ammonium metavanadate was placed in a heat-resistant glass, and then add water and H_2SO_4 in a 1:1 ratio. Then the resulting mixture is heated in an oven at a temperature of 60-70 until it evaporates. After the end of the evaporation and cooling process, the contents of the glass are poured into a flask and diluted to the mark with distilled water. It was identified ion equilibrium concentration of V (V) in a solution by photometric method - using a 10^{-3} M solution of the reagent 2, 2', 3, 4-tetrahydroxy-3'-sulfo-5'-nitrobenzene.

For photometric and sorption studies have been used 10^{-3} and 10^{-2} M metal solutions accordingly. To create the desired value of the solution ionic strength of chemically pure KCl solution was used. Ammonia-acetate buffer solutions (pH 3-11) were used to create the desired value system pH. KOH solution used in desorption process was prepared from a chemically pure potassium hydroxide by dilution to a stock with distilled water.

The synthesis of the sorbent was performed by known method (Cutter & Nunn, 1979). Schematic representation of polycondensation process is the following:
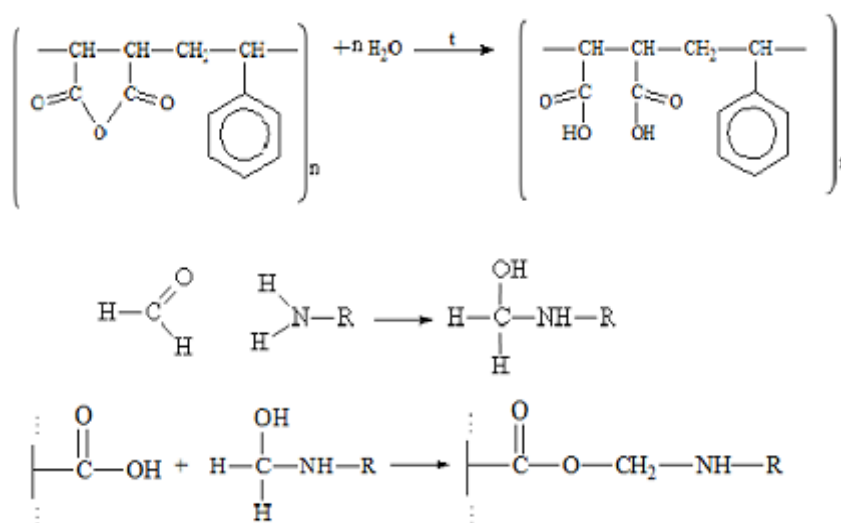

Figure 1. Amine fragment crosslinked styrene maleic anhydride

3. Results and discussions

Thermogravimetric analysis

The detailed data of TG curve are shown in Fig. 2 and 3. The thermogram shows that the decay temperature of the sorbent with the sorbed vanadium ion higher than the decay temperature of the sorbent.

In the TG curve observed a certain flexure. At the same time the exo and endo effects in DTA by temperature different from each other.
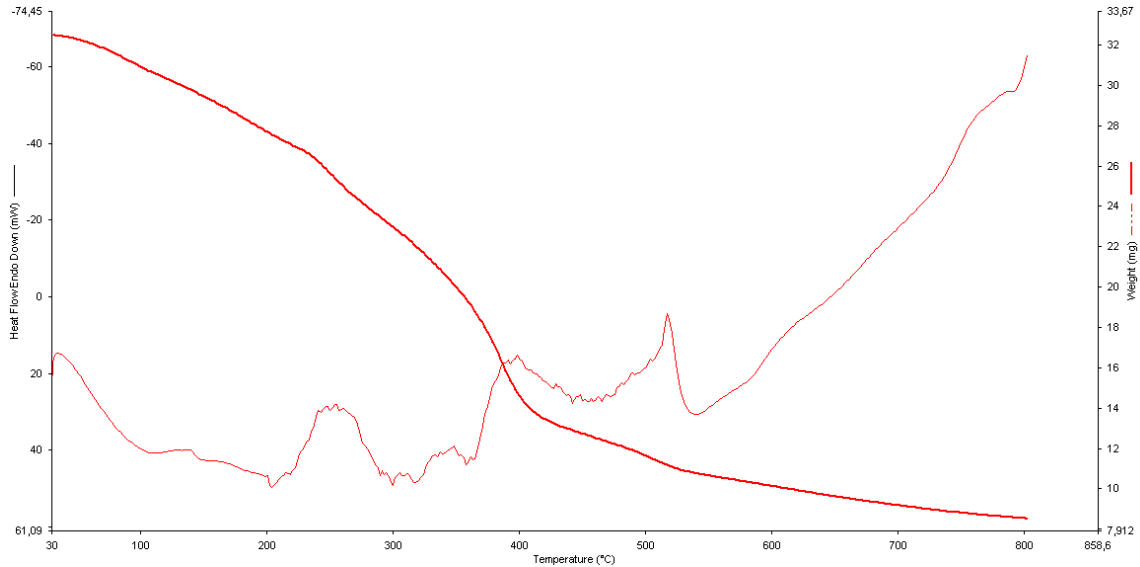
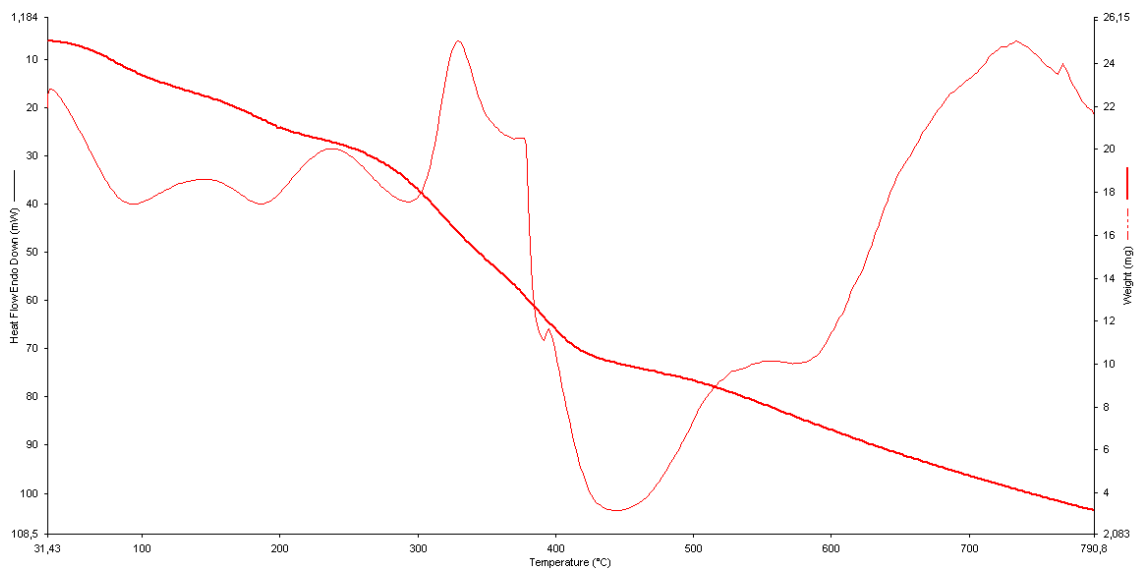

Figure 2. TG curve before sorption process

Figure 3. TG curve after sorption process

Infrared spectroscopy

Certain shifts are shown in the spectra. The IR spectra of the samples were recorded on an infrared Fourier microscope LUMOS (BRUKER Germany) in a wave frequency range of 600-4000 cm^{-1}.
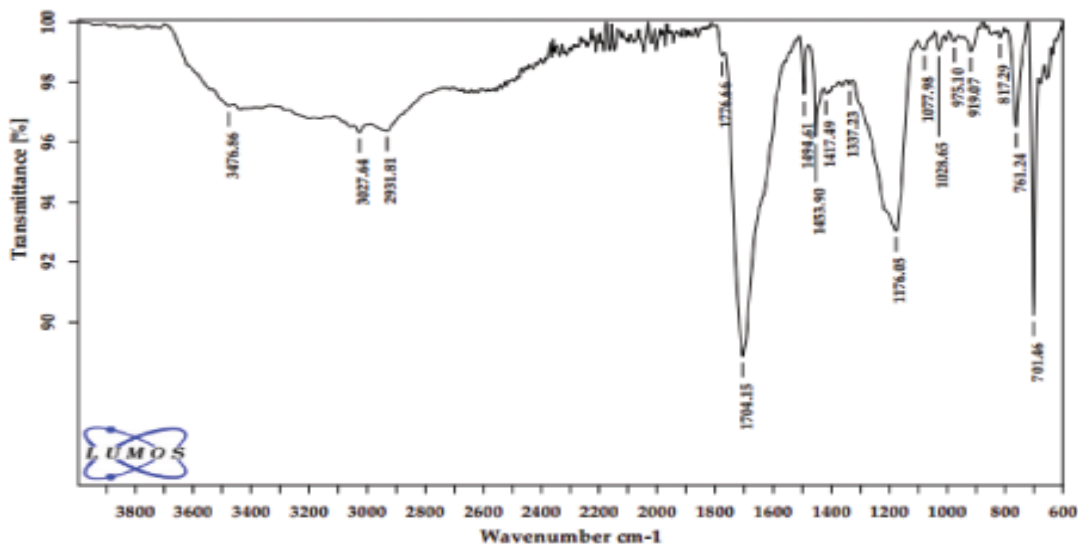

Figure 4. IR spectra of the sorbent before sorption process

The following absorption bands are observed on the IR spect rum (Fig.5) of the sorbent: deformation (701, 761, 1494 cm^{-1}) and valence (3027 cm^{-1}) vibrations of the C-H bond of the substituted benzene ring; deformation (1453 cm^{-1}) and valence (2931 cm^{-1}) vibrations of the CH bond of the CH and CH$_2$ group; valence (1704 cm^{-1}) vibrations of the C = O group of the acid; valence (1176 cm^{-1}) vibrations of the C-O bond of the acid; valence (1776 cm^{-1}) vibrations of the C = O ester group; valence (1028, 1077 cm^{-1}) vibrations of the C-O bond of the ester; valence (1337 cm^{-1}) oscillations of the Sar-N bond.
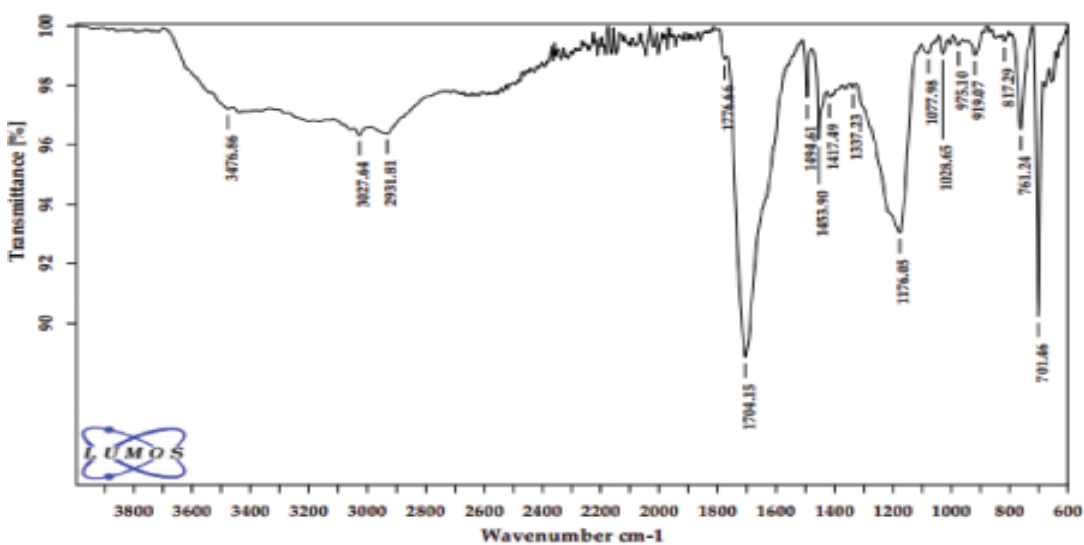

Figure 5. IR spectra of the chelate after sorption process

The following absorption bands are observed on the IR spectrum (fig.6) of the chelate: deformation (701 761, 1494 cm^{-1}) and valence (3029 cm^{-1}) vibrations of the C-H bond of the substituted benzene ring; deformation (1453 cm^{-1}) and valence (2936 cm^{-1}) vibrations of the CH bond of the CH and CH$_2$ group; valence (1702 cm^{-1}) vibrations of the C = O group of the acid; valence (1176 cm^{-1}) vibrations of the C-O bond of the acid; valence (1776 cm^{-1}) vibrations of the C = O ester group; valence (1029, 1079 cm^{-1}) vibrations of the C-O bond of the ester.

There are no absorption bands characteristics of nitrogen-containing bonds in the spectrum. Comparison of the IR spectra of the sorbent and the chelate allows us to conclude that the metal atoms coordinated by the -NH$_2$ group.

Determination of the static sorption capacity of sorbent
To determine the dependence of the sorption process from the ionic strength and static sorption capacity of sorbent have been taken 8 clean flasks, to each of which add 30 mg of sorbent, weighted on an analytical scale, 2 ml 10^{-2} M solution of a metal, a certain number of optimal pH and 2M KCl. The summary amount of pH and 2M KCl should be 18 ml. Solutions were mixing by using thermomixer ORBITAL SHAKER TS-1.

In 25 ml flask add the appropriate amount of metal and the optimal amount of reagent of 2,2,3,4-tetrahydroxy-3-sulpho-5-nitroazobenzene (1.5 ml) and diluted with optimal photometric pH=4 up to the mark. The background is the optimal amount of reagent diluted to the mark with optimal photometric pH = 4. Photometric determination is carried out in a cell with thickness of 1 cm at a wavelength of 490 nm.

Effect of pH on the retention of V (V)
One of the main characteristics of synthetic sorbents is the dependence of sorption of metal ions from the medium acidity. Sorption investigation of vanadium has been carried out from buffer solutions in the range of pH from 3 to 8.0. To determine the optimal range of pH values sorption equilibrium solution pH effect has been studied on the distribution of vanadium ions in the aqueous system - sorbent. The equilibrium pH was measured and the vanadium (V) concentration determined spectrophotometrically by using the 2, 2', 3, 4-tetrahydroxy-3'-sulpho-5'-nitroazobenzene at 490 nm. The maximal sorption capacity observed at pH 4. The obtained data were used to calculate the sorption capacity in mg g^{-1}. With decreasing the acidity of the solution at pH = 3 ÷ 6 sorption of ions increases, reaches a maximum at a pH 4 and then decreases. At pH 4 the surface of the sorbent is fully saturated with vanadium(V) ions. Then at acidity of environment pH=5-8 the concentration of metal ions decreases on the surface of the sorbent.

Adsorption Balance Time
The complete sorption equilibrium or time to reaching adsorption balance has been established. The experiment has been performed under static conditions at an optimum pH value, a constant ionic strength and at various time intervals. From the liquid phase has been taken aliquot to determine the metal ion concentration in solution. The total volume of the liquid phase was constant. Experience has been shown that the time at which the full sorption equilibrium established is 2 hours.

Effect of Preconcentration Factor on V (V) Adsorption

For practical study sorption process according static sorption has been conducted experience at different concentrations of the metal ion at a constant value of optimal pH and ionic strength without changing the total volume of the liquid phase. On the basis of the results get in any metal ion concentrations observed maximum sorption capacity of the sorbent. Experience shows that the maximum adsorption capacity observed in the value of concentration $60 \cdot 10^{-3}$ mol L^{-1}.

The Saturation Capacity of Adsorption

The saturation capacity Q was calculated by the following equation:

$$Q = \frac{(C_0 - C)m}{V}$$

where, Q -is adsorption capacity of the sorbent, V-is the volume of solution (L), C_0 - is the initial concentration of vanadium (V) ion (mg L^{-1}), C - the concentration of vanadium ion after adsorption process (mg L^{-1}) and m-the mass of the sorbent (mg).
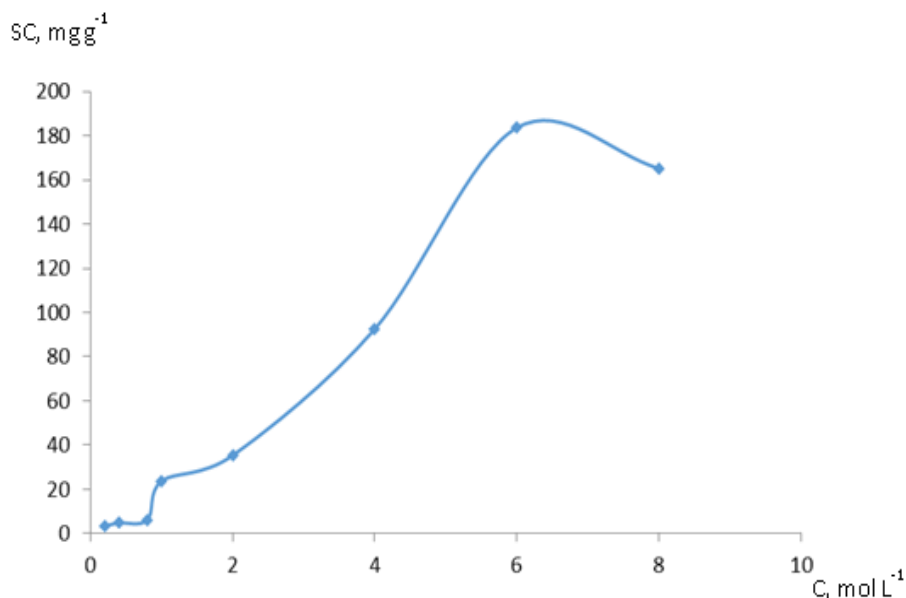

Figure 6. The effect of initial concentration of vanadium ions on vanadium adsorption by hydrazide of maloney acid $C_{V(V)} = 1 \cdot 10^{-2}$ mol L^{-1}, contact time = 120 min., pH=4

The quantities of sorption capacity of sorbent for vanadium ions constitute $3.6 \cdot 10^{-3}$ mol·g^{-1}, which corresponds to a degree of extraction 90%. These results indicate a good equilibrium and kinetic properties of the sorbent.

Table 1. Removal efficiency percentage of V(V) ions by the chelating sorbent

C_{Me}, 10^{-3}, mol L^{-1}	0.2	0.4	0.8	1.0	2.0	4.0	6.0	8.0
Sorp. cap., mg g^{-1}	3.4	4.76	6.12	23.8	35.36	92.48	183.6	165.24
R, %	50	35	22.5	70	52	68	90	60.75

Effect of ionic strength

It has also been studied the influence of ionic strength to the sorption process. Ionic strength of solution has a significant impact to the selectivity of ion exchange and

experimentally has been established that it observes at 0.6. The desired ionic strength achieved by adding to the buffer solution calculated amounts of KCl.

Desorption process

In order to extract the absorbed solutes of metal by adsorbent has been used desorption process. This process has been carried out by using mineral acids: HCl, HNO_3, H_2SO_4, CH_3COOH with different (0.5; 1.0; 1.5; 2.0 mol L^{-1}) concentration. HNO_3. Experiments show that solutions of 1 mol L^{-1} HNO_3 possess the best desorbing ability to the vanadium ion. The most desorption relative error of the experiments was calculated on the basis of equilibrium in which each point represents the mean of three parallel experiments. It was also found that the adsorption capacity of the adsorbent was not significantly changed after regeneration.

Effects of coexistent ions

The effect of coexistent ions on the vanadium(V) adsorption by hydrazide of maloney acid have been studied. The presence of coexistent ions in wastewater might affect the adsorption behavior of hydrazide of Maloney acid. The results show that no influences were observed from ions of Na^+, K^+, Ca^{2+}, Mg^{2+}, Zn^{2+}, Fe^{3+}, Al^{3+}, i.e. they did not interfere to the adsorption process. Pd^{2+} ion is slightly interfering to the sorption process, but UO_2^{2+} prevents to proceeding the process.

Sample analysis

Vanadium is one of the environmentally hazardous heavy metals in water. The extraction of vanadium in the waste water of Sumgayit Technological Park (a complex of factories) of Azerbaijan Republic was studied and compared with the results of extraction of vanadium from real water sample.

To a portion of the water sample, add 2-3 ml of dilute (1:1) H_2SO_4. The solution is filtered; the excess acid is neutralized with 0.1 M KOH to a pH of 4. 0.03 g of maloney acid hydrazide sorbent is introduced into the solution and the optimum pH for the sorption have been established. The mixture is stirred with a magnetic stirrer for 100-120 minutes at the room temperature. Then the sorbent is filtered through filter paper, washed 2-3 times with distilled water with a total volume of 20 ml. The elements are desorbed by washing the sorbent on the filter with 20ml of a solution of 1 M HNO_3. The results of analysis were checked up by addition method. The results of the work are presented in Table 2.

Table 2. Determination of V(V) in real water and waste water samples

Aliquots	Found (μg L^{-1})	Added (μg L^{-1})
Real water sample	2.48 ± 0.07	2.52 ± 0.09
Waste water sample[1]	29.8 ± 0.15	29.5 ± 0.13
Waste water sample[2]	32.5±0.17	31.7±0.11

The comparative study of sorption of vanadium with different sorbents known in literature is shown in following table:

Table 3. Comparative study of maximum adsorption capacity for V(V) onto different adsorbents

Sorbent	pH	Sorption capacity	Contact time	References
Hydrazide of maloney acid	5	183.6 mg·g^{-1}	2 h	Present work
Pine sawdust	5	130 mg·g^{-1}	24 h	Leiviskä *et al.* 2015
Chitosan derivates	3	148.15 and 171.82 mg·g^{-1}	9 and 8 h	Mujeeb *et al.*, 2014
Metal sludge	7.6	24.8 mg·g^{-1}	2 h	Bhatnagar *et al.*, 2008
ZnCl$_2$ activated carbon	4-9	24.9 mg·g^{-1}	40 min	Namasivayam & Sangeetha, 2006

4. Conclusion

According to the results, studied the optimal sorption conditions, dependence sorption process from the pH of the solution, the initial concentration of the metal, the effect of ionic strength, determined time required to achieve complete sorption equilibrium and at the final stage of the process was carried out desorption of vanadium by using of mineral acids with different concentration. The experiments carried out by static method. In assessing the effectiveness of sorbents are important value of sorption capacity and the time to reach equilibrium sorption. According to the results, physic-chemical and analytical properties of the complexion sorbents depend both to the nature of the functional-analytical group of sorbent so and metal. Based on these results it can be concluded that chelating polymeric sorbent have sufficiently high sorption capacity to the vanadium ions and that the resulting sorbent can be used to concentrate the ions V (V) in natural and industrial facilities.

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