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DETERMINATION OF VANADIUM (V) TRACE AMOUNTS IN OIL SLUDGE AFTER PRELIMINARY CONCENTRATION WITH POLYMER SORBENT

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Abstract: *A modified sorbent based on copolymer of maleic anhydride with methacrylic acid was proposed for sorption of vanadium (V) concentration. A polymer chelating sorbent with fragments of para-amino salicylic acid was used in the work. Optimal sorption conditions were determined and the dependence of sorption capacity on the acidity of the solution studied. At pH 5, the degree of sorption attains its maximum. The effect of ionic strength on vanadium sorption was studied. Studies have shown that the ionic strength up to 0.6 mol/l does not affect the sorption, after 0.6 mol/l the increase in the ionic strength at the beginning gradually, and then sharply decreases the sorption. The effect of ionic strength on vanadium sorption was studied to show that the ionic strength up to 0.6 mol/l does not affect the sorption, and after 0.6 mol/l the increase in the ionic strength at the beginning gradually, and then sharply decreases the sorption. All further experiments were carried out in the solutions with an ionic strength of 0.6. It was found that as the concentration of vanadium rises in the solution, the amount of sorbed metal increases, and at a concentration of* $8\cdot10^{-3}$ *mol/l it becomes maximum (pH = 5,* $C_V^{5+} = 8\cdot10^{-3}$ *mol/l,* v_{total} *= 20 ml,* $m_{sorb.}$ *= 0.03 g, SC = 243 mg/g). The isotherm of vanadium (V) sorption with the synthesized sorbent was constructed. Sorption equilibrium is achieved within 1 hour of contact between the solution and the sorbent. Further growth in the sorption time does not change sorbent's characteristics. The sorbent extracts vanadium (V) from solutions with a recovery rate of 93%. The effect of different mineral acids (*$HClO_4$*,* H_2SO_4*,* HNO_3*, HCl) of identical concentrations on vanadium (V) desorption from the sorbent was also studied. The results of the analysis showed that the maximum desorption of vanadium (V) occurs in perchlorate acid. The developed method was applied to determine the trace amounts of vanadium in oil sludge with preliminary concentration.*

Keywords: *vanadium (V), determination, concentration, sorbent, oil sludge.*
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Introduction

Heavy metal ions are among toxic types of water pollutants. Main toxic metals hazardous to human life are Cr, Fe, V, W, Co, Cu, Cd, Hg, As, Pb, etc. Vanadium can exist in the range of oxidation states from +2 to +5 [1]. Vanadium (IV) and vanadium (V) are mainly present in the solution under ambient conditions. The toxicity of vanadium depends on the degree of its oxidation, and vanadium (V) is more toxic than vanadium (IV), and its symptoms of poisoning are sometimes fatal. The concentration of vanadium in water largely depends on geographical location and ranges from 0.2-100 $\mu g\cdot l^{-1}$ in fresh and drinking water; from 0.2-29 $\mu g\cdot l^{-1}$ in seawater.

Wastewater containing heavy metals comes mainly from plating plants, mining, mills, batteries, paper industry and zinc plants for pesticides, stabilizers, thermoplastics, etc. These industries directly or indirectly discharge heavy metals and wastewater into the environment, especially in developing countries. Thus, the purification of industrial wastewater containing soluble heavy metals is necessary to improve the quality of water [2-5]. Therefore, the determination of vanadium (V) in natural waters is required from environmental protection standpoint. There are several analytical methods for the determination of vanadium in various environmental samples, including spectrophotometry [6,7], mass spectrometry [8], atomic absorption spectrometry [9,10]. The direct determination of vanadium in complex matrices is difficult, since it occurs at very low concentrations. To obtain accurate and sensitive results, a suitable pre-concentration step is required to address these problems when analyzing real samples.

Of interest are combined methods that coincide in one technique testing for the presence of metal through forming colored compounds and their concentration on various sorbents. For this purpose, sorption-photometric methods have recently been widely used, especially by means of polymer chelate sorbents [11-21]. In the development of these works, a new method of sorption-spectrophotometric determination of vanadium (V) micro-amounts in oil sludge with preliminary concentration was proposed.

Experimental part

Equipment. The optical density of the solutions was measured on KFK-2 photo-calorimeter. The acidity of the solution was monitored with a glass electrode on PHS-25 ion meter.

Solutions, reagents, and sorbent. We used reagents of chemically pure grade for analysis. A solution of vanadium (V) was prepared by dissolving an exact weighed portion of the ammonium vanadate salt in distilled water [22]. Working solutions were obtained by diluting the original one. The required pH values were maintained with HCl, NaOH solutions and ammonia-acetate buffer solutions. Ionic strength was generated with calculated amounts of KCl. For the photometric determination of vanadium (V), we used 2,3, 4-tri-hydroxy-3'-nitro-4'-sulfo-phenylazobenzidine. A polymer chelating sorbent with fragments of para-amino salicylic acid was used in the work. The sorbent was synthesized as described in [23].

Results and discussion

Effect of pH on sorption. The dependence of sorption capacity on the acidity of the solution was studied. The sorption capacity of the sorbent was explored under static conditions. Sorption of vanadium (V) was carried out of the volume of 20 ml of solution. A vanadium solution is added to 30 mg of the sorbent and left in a buffer medium at pH = 1-8. The mixture is filtered off, then measured. The amount of vanadium remaining in the solution is found on the basis of the dependence curve of the optical density on the concentration and the amount of sorbed vanadium ions is calculated accordingly. At pH 5, the degree of sorption passed through a maximum. All further studies were carried out at pH 5.

Influence of vanadium (V) concentration on the sorption process. To determine the parameters characterizing the sorption capacity, the sorption isotherm of vanadium (V) ions with the obtained sorbent was obtained. The dependence of the sorption capacity on the concentration of vanadium (V) was investigated (Fig. 1).

As the concentration of vanadium in the solution rises, the amount of sorbed metal rises as well, and at a concentration of $8\cdot10^{-3}$ mol/l it riches maximum (pH = 5, $C_V^{5+} = 8\cdot10^{-3}$ mol/l, v_{total} = 20 ml, m_{sorb}. = 0.03 g, SC = 243 mg/g). The increase in the sorption capacity of the sorbent can be explained by the formation of polydentate sorption centers during the matrix processing.

It is known that the ionic strength of a solution significantly affects the flexibility of the solid-phase matrix and the state of functional groups of the analytical reagent. Therefore, the dependence of the analytical signal on the concentration of the KCl solution was investigated in the range of 0.1-1.2 M. The negative effect of increase in the ionic strength of the solution on sorbent properties was revealed due to the screening of coordination-active groups by electrolyte ions. All further experiments were carried out in solutions with an ionic strength of 0.6 M (KCl).

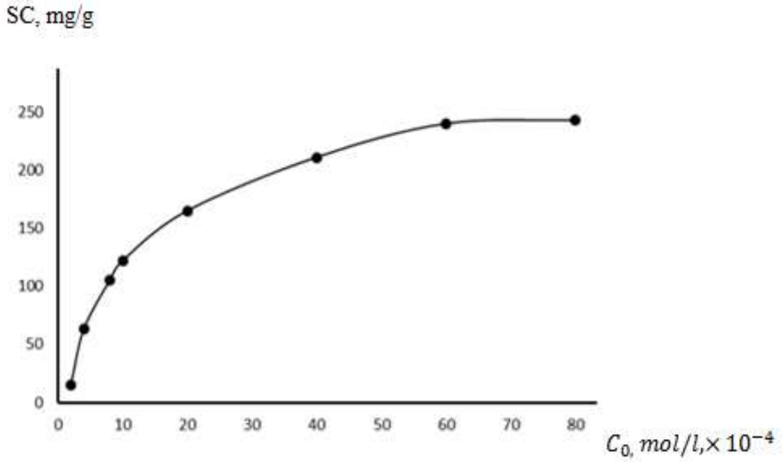

Fig. 1. Sorption isotherm of vanadium (V) with the obtained sorbent: m_{sorb} = 30 mg, V = 20 ml, pH = 5

Sorption equilibrium is achieved within an hour of contact of the solution with the sorbent. A further increase in the sorption time does not change the characteristics of the sorbent.

Desorption study. The effect of different mineral acids ($HClO_4$, H_2SO_4, HNO_3, HCl) with the same concentrations on vanadium (V) desorption from the sorbent was studied. The results of the analysis showed that the maximum desorption of vanadium (V) occurs in perchlorate acid (Table 1).

Table 1. Influence of different acids concentration on the degree of extraction (%) of vanadium (V) (n = 5)

Acid	Concentration, mol/l	Desorption rate, %
HCl	0.5	76
	1.0	80
	1.5	87
	2.0	91
$HClO_4$	0.5	81
	1.0	86
	1.5	93
	2.0	93
HNO_3	0.5	82
	1.0	85
	1.5	90
	2.0	91
H_2SO_4	0.5	86
	1.0	90
	1.5	90
	2.0	91

The developed method was applied to determine the trace amounts of vanadium (V) in oil sludge with preliminary concentration.

Determination of vanadium (V) ions in oil sludge after concentration with a sorbent. 2 g of a sample was evaporated at 105° C in a graphite bowl for 2 days, then burned in a muffle furnace at 550-650°C. The resulting ash was dissolved in a mixture consisting of 8 ml HF +3 ml HCl +1 ml HNO_3. For complete removal of HF from the resulting mass, it is treated 3-4 times with nitric acid at 50-60° C.

Then the resulting precipitate is transferred to a 100 ml flask, dissolved and diluted to the mark with distilled water. In the samples prepared for analysis, the amount of vanadium was determined by the sorption-photometric method.

The solution is transferred to a flask, the pH is adjusted to 5 by adding HNO_3 (conc.), 100 mg of the sorbent is added and left for 1 hour. An hour later, the absorbed vanadium (V) is desorbed by adding 10 ml of 1.5 M $HClO_4$ to the separated sorbent. The concentration of vanadium (V) in the eluate solution is determined according to the previously constructed graduated graph (Table 2). The correctness of the technique was determined by the addition method.

Table 2. Results of samples analysis of oil sludge (n=5, P=0.95).

Sample	Inserted, μg/ml	Found, μg/ml
1	-	0.385±0.04
	5	5.279±0.05
	10	10.402±0.03
2	-	0.377±0.03
	5	5.412±0.02
	10	10.234±0,05

Conclusion

Thus, we can conclude that synthetic sorbents have a high sorption capacity. The sorption properties of sorbents depend on the nature of complexing group included in the composition. Modified chemically, active groups are capable of forming stable chelates and ionic associates with metal ions in the solution. The developed method is more economical, fast and environmentally friendly in comparison with those known in the literature. In addition, it has been found that it is possible to reuse the regenerated sorbent for concentration processes.

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POLİMER SORBENTLƏ İLKİN QATILAŞDIRILMA YOLU İLƏ VANADİUMUN MİKROMİQDARININ NEFT ŞLAMINDA TƏYİNİ

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Vanadiumun(V) sorbsion qatılaşdırılması üçün malein anhidridi-metakril turşusu sopolimeri əsaslı modifikasiya olunmuş sorbent təklif olnub. Tədqiqat işində tərkibində p-aminosalisil turşusunun fraqmentlərini saxlayan polimer xelatəmələgətirici sorbent tətbiq olunmuşdur. Sorbsiyanın optimal şəraiti müəyyən edilmişdir. Sorbsiya tutumunun məhlulun turşuluğundan asılılığı öyrənilib. pH 5-də sorbsiya maksimumdan keçir. Vanadiumun sorbsiyasına ion qüvvəsinin təsiri araşdırılmışdır. Tədqiqatlar göstərdi ki, ion qüvvəsi 0.6 mol/l-ə qədər sorbsiyaya təsir etmir, 0.6 mol/l-dən sonra ion qüvvəsinin artımı sorbsiyanı əvvəl tədricən, sonra isə kəskin azaldır. Bütün növbəti tədqiqatlar ion qüvvəsinin qiyməti 0.6 olan məhlullarda aparılmışdır. Müəyyən olunmuşdur ki, vanadiumun məhlulda qatılığı artdıqca sorbsiya olunmuş metalın miqdarı artır, $8\cdot10^{-3}$ mol/l qatılığında isə maksimal olur (pH=5, $C_V^{5+}=8\cdot10^{-3}$ mol/l, $v_{üm.}$=20 ml, $m_{sorb.}$=0,03 q, ST=243 mq/q).Vanadiumun (V) sintez olunmuş sorbentlə sorbsiya izotermi qurulub. Sorbsiya tarazlığı sorbentin məhlul ilə 1 saat kontaktından sonra yaranır. Sorbsiya müddətinin növbəti artımı sorbentin xarakteristikalarını dəyişmir. Sorbent vanadiumu məhluldan 93% sorbsiya dərəcəsilə ayırır. Eyni zamanda vanadiumun sorbentdən desorbsiyasına eyni qatılıqlı müxtəlif mineral turşuların ($HClO_4$, H_2SO_4, HNO_3, HCl) təsiri öyrənilmişdir. Analizin nəticələri göstərdi ki, vanadiumun(V) maksimal desorbsiyası perxlorat turşusunda baş verir. İşlənmiş metodika ilkin qatılaşdırılma ilə vanadiumun mikromiqdarlarının neft şlamında təyini üçün tətbiq olunub.

Açar sözlər: *vanadium(V), təyini, qatılaşdırma, sorbent, neft şlamı*

ОПРЕДЕЛЕНИЕ МИКРОКОЛИЧЕСТВ ВАНАДИЯ (V) В НЕФТЯНОМ ШЛАМЕ ПОСЛЕ ПРЕДВАРИТЕЛЬНОГО КОНЦЕНТРИРОВАНИЯ ПОЛИМЕРНЫМ СОРБЕНТОМ

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Для сорбционного концентрирования ванадия (V) предложен модифицированный сорбент на основе сополимера малеинового ангидрида с метакриловой кислотой. В работе применен полимерный хелатообразующий сорбент с фрагментами п-аминосалициловой кислоты. Определены оптимальные условия сорбции. Изучена зависимость сорбционной емкости от кислотности раствора. При pH 5 степень сорбции проходит через максимум. Было изучено влияние ионной силы на сорбцию ванадия. Исследования показали, что ионная сила до 0.6 моль/л не влияет на сорбцию, после 0.6 моль/л увеличение ионной силы вначале постепенно, а потом резко уменьшает сорбцию. Все дальнейшие опыты проводили в растворах с ионной силой 0.6. Было установлено, что с увеличением концентрации ванадия в растворе увеличивается количество сорбированного металла и при концентрации $8\cdot10^{-3}$ моль/л оно становится максимальным (pH=5, $C_V^{5+}=8\cdot10^{-3}$ моль/л, $v_{об.}=20$ мл, $m_{сорб.}=0.03$ г, СЕ=243 мг/г). Построена изотерма сорбции ванадия (V) синтезированным сорбентом. Сорбционное равновесие достигается в течение 1 часа контакта раствора с сорбентом. Дальнейшее увеличение времени сорбции не изменяет характеристики сорбента. Степень извлечения ванадия сорбентом из растворов составляет 93%. Также было изучено влияние разных минеральных кислот ($HClO_4$, H_2SO_4, HNO_3, HCl) с одинаковыми концентрациями на десорбцию ванадия (V) из сорбента. Результаты проведенных анализов показали, что максимальная десорбция ванадия (V) происходит в перхлоратной кислоте. Разработанный метод применен для определения микроколичеств ванадия в нефтяном шламе с предварительным концентрированием.

Ключевые слова: *ванадий (V), определение, концентрирование, сорбент, нефтяной шлам.*