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CONCENTRATION AND DETERMINATION OF VANADIUM (V) BY SORBENT CONTAINING FRAGMENTS OF N, N' – DIPHENYL – GUANIDINE

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The sorption and complex-forming properties of a modified sorbent based on a copolymer of maleic anhydride with methacrylic acid in regard to vanadium (V) were studied and main parameters of metal sorption determined. Sorbent containing fragments of N, N' – diphenyl – guanidine for the selective extraction of vanadium (V) from solutions were proposed. The sorbent was synthesized according to well-known methods. The optimal conditions for sorption were determined. The sorption was studied under static conditions. In the presented work, a main emphasis was laid on the study into the effect of pH of the medium, time, ionic strength, and metal concentration in a solution on the vanadium sorption. A maximum degree of vanadium extraction by the sorbent was achieved from pH 5 solutions. The influence of the ionic strength of the solution was studied by photometric method. Vanadium (V) was sorbed from solutions containing 0.1-1.4 M KCl. Results of the study showed that a significant decrease in metal sorption was observed in KCl solutions with a concentration of more than 0.6 M. Results of the analysis showed that the sorption equilibrium was achieved in 2 hours. As the concentration of vanadium in the solution increased, its sorption rose as well, and at a concentration of $8 \cdot 10^{-3}$ M it reached maximum: static capacity = 253 mg/g. Also, we researched into possibilities available to determine the conditions for desorption of vanadium (V) with various mineral acids ($HClO_4$, H_2SO_4, HNO_3, HCl) after concentration on the proposed sorbent. Analysis results showed that vanadium (V) was quantitatively desorbed by 2 M HNO_3. Multiple uses of the regenerated sorbent for concentration are possible. The degree of extraction of vanadium (V) under optimal conditions exceeded 95%.

***Keywords**: sorption, modification, vanadium, degree of extraction, desorption*
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Introduction

Analysis of natural and industrial objects aimed at extracting and determining the vanadium is carried out using various physicochemical methods [1-6]. However, the capabilities of the above methods do not always make it possible to determine trace amounts of toxic elements in objects of various compositions. Most of the sorbents used in the course of concentration have certain disadvantages. In some cases, sorption occurs at a high temperature, while no absorption of metal occurs at room temperature [1, 5]. Some of them have a low sorption capacity in relation to vanadium [2, 3, 5, 6]. In some applied concentration methods, the ionic strength is too low (μ = 0.005), after this, the sorption value decreases [4]. Granting this, it is important to develop new, simple, sensitive techniques for their extraction and determination at a level well below the maximum permissible concentration. Recently, sorption methods have been widely used [7-17].

In this work, we propose a new method for the sorption-spectrophotometric determination of micro-amounts of vanadium (V). The proposed technique is based on the preliminary concentration of vanadium (V) from an object using a polymeric chelate sorbent containing fragments of N, N' – diphenyl – guanidine.

Experimental part

Equipment. The acidity of the solution was monitored with a glass electrode on a PHS-25 ion meter. The optical density was measured on a KFK 2 photo-colorimeter (l = 1 cm).

Solutions, reagents, sorbent. Reagents of chemically pure grade were used. A solution of vanadium (V) (10^{-2} M) was prepared by dissolving an exact weighed portion of the ammonium vanadate salt in distilled water according to method 18. Working solutions were obtained by diluting the original. The required pH values were maintained with HCl, NaOH solutions and ammonia-acetate buffer solutions. To maintain a constant ionic strength, a KCl solution was used.

2,3,4 – tri-hydroxy – 3' – nitro – 4' – sulfo-phenylazo benzidine (R) was obtained by azo-coupling of a diazotized amine with pyrogallol in a weakly acidic medium as described in [19].

N, N' – diphenyl – guanidine fragments were used as solid phase. It was synthesized as described in [20]. For use in the analysis, the sorbent granules were ground in an agate mortar and sieved through a sieve (0.14 mm).

Experimental technique. The sorption was studied under static conditions. When studying sorption under static conditions, a solution of vanadium (V) was introduced into a graduated test tube with a ground stopper, and an ammonium acetate buffer solution was added to create the necessary acidity to a volume of 20 ml. Besides, 0.05 g of sorbent was introduced, the tube was closed with a stopper and left for 2 hours; then the solution was decanted. The concentration of vanadium (V) in the eluate was determined photometrically using 2,3,4 – tri-hydroxy – 3' – nitro – 4' – sulfo-phenylazo benzidine. The vanadium (V) concentration was calculated using a calibration graph.

Results and discussion

During the study, the main attention was paid to the study of the effect on the sorption of vanadium (V) of pH, its time, ionic strength, metal concentration in the solution.

Influence of the medium acidity on the sorption process. A maximum degree of vanadium (V) extraction by the sorbent is achieved through solutions with pH 5. The dependence of sorption on time was studied. Results of the study showed that sorption equilibrium was achieved after 2 hours of sorbent's contact with the metal. For all further experiments, the time to establish the sorption equilibrium was 2 hours.

The influence of the ionic strength of the solution was studied by the photometric method. Vanadium (V) was sorbed from solutions containing 0.1-1.4 M KCl. Results of the study showed that a significant decrease in metal sorption was observed from KCl solutions with concentration of more than 0.6 M.

Influence of vanadium (V) concentration. As the vanadium (5) concentration in the solution increases, its sorption increases as well and at a concentration of $8 \cdot 10^{-3}$ M it reaches maximum: static capacity = 253 mg/g.

The possibility of vanadium (V) desorption on the proposed sorbent by different mineral acids after concentration ($HClO_4$, H_2SO_4, HNO_3, HCl) was studied and auxiliary conditions determined. Analysis results showed that vanadium (V) was quantitatively desorbed by 2 M HNO_3. Multiple uses of the regenerated sorbent for concentration are possible.

After determining optimal concentration conditions, the developed method was successfully applied to determine the microquantities of vanadium (V) in the water of the Aqstafa River, Gazakh region of Azerbaijan with preliminary concentration (see Table).

Performing analysis. 30 ml of the filtered analyzed sample was brought to the desired pH value by adding HNO_3 and left for 2 hours in a round-bottom flask with 100 mg of sorbent. The sorbed metal ions were eluted with 5 ml of 2 M HNO_3. In the eluate, the concentration of vanadium (V) was determined photometrically. Results were calculated assuming 100% extraction of vanadium (V).

Table 1. Results of vanadium (V) determination (V) in the Akstafa river, Kazakh region of Azerbaijan (n = 5, P = 0.95)

Found by photometric method, V, mkg/l	Found V, mkg/l (ICP-OES thermo ICAP 7400 DUO)
2.81±0.029	2.88±0.031

Conclusion

The study showed the possibility of using a matrix of maleic anhydride copolymer with methacrylic acid modified with N, N ' – diphenyl guanidine for the sorption-photometric determination of vanadium (V). The sorbent used for the determination of trace amounts of vanadium (V) has higher sorption properties (sorption capacity, analysis time, concentration temperature, influence of ionic strength) in comparison with those known in the literature [1 – 6]. The proposed sorbent can be reused for 7-8 cycles.

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VANDİUMUN (V) TƏRKİBİNDƏ N, N' - DİFENİL -QUANİDİN FRAQMENTİ OLAN SORBENT VASİTƏSİLƏ QATILAŞDIRILMASI VƏ TƏYİNİ

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Malein anhidridinin metakril turşusu ilə sopolimeri əsaslı modifikasiya olunmuş sorbentin vanadiuma (V) görə sorbsiya və kompleksəməlgətirici xassələri öyrənilmiş və metalın əsas sorbsiya parametrləri təyin olunmuşdur. Vanadiumun (V) məhluldan selektiv ayrılması üçün tərkibində N,N'-difenil quanidin fraqmentləri olan sorbent təklif olunub. Sorbsiyanın optimal şəraiti müəyyən olunub. Sorbsiya statik şəraitdə tədqiq olunub. Təqdim olunan işdə vanadiumun sorbsiyasına mühitin pH-ı, zaman, ion qüvvəsi, metalın qatılığının təsirinin öyrənilməsinə xüsusi diqqət ayrılmışdır. Vanadiumun sorbsiyasının maksimal qiyməti pH 5-də müşahidə olunur. Məhlulun ion qüvvəsinin təsiri fotometrik metodla öyrənilmişdir. Vanadiumu (V) 0,1-1,4 M KCl qatılıqlı məhlullardan sorbsiya edirdilər. Tədqiqatın nəticələri göstərdi ki, metalın sorbsiyası KCl-un qatılığı 0,6 M-dan çox olan məhlullarda azalır. Analizin nəticələrinə əsasən müəyyən olundu ki, sorbsiya tarazlığı 2 saatdan sonra yaranır. Məhlulda vanadiumun qatılığının artması ilə onun sorbsiyası artır və $8\cdot10^{-3}$ M qatılığında maksimum olur: statik tutum 253mq/q. Eyni zamanda vanadiumun təklif olunan sorbent üzərində sorbsiyasından sonra müxtəlif mineral turşuları ilə ($HClO_4$, H_2SO_4, HNO_3, HCl) desorbsiya şəraiti və imkanları tədqiq olunmuşdur. Analizin nəticələri göstərdi ki, vanadium (V) 2 M HNO_3 ilə miqdari desorbsiya olunur. Reqenirasiya olunmuş sorbentin qatılaşdırılma üçün dəfələrlə istifadəsi mümkündür. Vanadiumun(V) optimal şəraitdə sorbsiya dərəcəsi 95%-dən yüksəkdir.

Açar sözlər: sorbsiya, modifikasiya, vanadium, ayrılma dərəcəsi, desorbsiya.

КОНЦЕНТРИРОВАНИЕ И ОПРЕДЕЛЕНИЕ ВАНАДИЯ (V) СОРБЕНТОМ, СОДЕРЖАЩИМ ФРАГМЕНТЫ N, N'- ДИФЕНИЛ-ГУАНИДИНА

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Изучены сорбционные и комплексообразующие свойства модифицированного сорбента на основе сополимера малеинового ангидрида с метакриловой кислотой по отношению к ванадию (V) и определены основные параметры сорбции металла. Предложен сорбент, содержащий фрагменты N, N' - дифенил-гуанидина для селективного извлечения ванадия (V) из растворов. Сорбент синтезирован по известной методике. Определены оптимальные условия сорбции. Сорбцию изучали в статических условиях. В представленной работе основное внимание было уделено изучению влияния на сорбцию ванадия pH среды, времени, ионной силы, концентрации металла в растворе. Максимальная степень извлечения ванадия сорбентом достигается из растворов с pH 5. Влияние ионной силы раствора изучено фотометрическим методом. Ванадий (V) сорбировали из растворов, содержащих 0.1-1.4 M KCl. Результаты исследования показали, что значительное уменьшение сорбции металла наблюдалось из растворов KCl с концентрацией более 0.6 M. Результаты анализа показали, что сорбционное равновесие достигается после 2 часов. С увеличением концентрации ванадия в растворе увеличивается его сорбция и при концентрации $8\cdot10^{-3}$ M становится максимальной: статическая емкость 253 мг/г. Была также исследована возможность и определены условия десорбции ванадия (V) разными минеральными кислотами ($HClO_4$, H_2SO_4, HNO_3, HCl) после концентрирования на предлагаемом сорбенте. Результаты анализа показали, что ванадий (V) количественно десорбируется 2 M HNO_3. Возможно многократное использование регенерированного сорбента для концентрирования. Степень извлечения ванадия (V) в оптимальных условиях превышает 95%.

Ключевые слова: сорбция, модификация, ванадий, степень извлечения, десорбция.