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СОРБЦИОННАЯ СПОСОБНОСТЬ МОДИФИЦИРОВАННЫХ МЕЗОПОРИСТЫХ МАТЕРИАЛОВ ПО ОТНОШЕНИЮ К ИОНАМ ВАНАДИЯ

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С целью изучения сорбционных свойств модифицированных мезопористых кремнеземных сорбентов по отношению к ионам ванадия(V) синтезированы реагенты со структурой пор МСМ-41, модифицированные N',N'-диметилгидразидами трет-карбоновых кислот Versatic фракции С10. Установлено, что прививка функциональных групп на поверхность МСМ-41 активизирует его в отношении сорбции ионов ванадия (V). Максимальная сорбционная емкость (ЕМ = 2,8 ммоль/м^2) наблюдается в сернокислой среде (рН=3,5 - 4) при 40 мин контакте сорбента с раствором. Увеличение концентрации привитых групп приводит к значительному росту сорбционной емкости модифицированного силикатного материала. Построена изотерма адсорбции, ее параметры проанализированы с помощью моделей Ленгмюра и Фрейндлиха. Опираясь на значения коэффициентов корреляции, можно заключить, что адсорбционные процессы ионов ванадия (V) в большей степени подчиняются уравнению Фрейндлиха. Механизм сорбции определен установлением лимитирующей стадии адсорбции с использованием графоаналитического метода анализа зависимости степени завершенности процесса адсорбции (F) от времени (τ). Показано, что процесс сорбции протекает во внутридиффузионном режиме и описывается моделью псевдо-второго порядка, т.е. интенсивность протекания сорбционного процесса зависит не только от концентрации извлекаемых ионов, но и от концентрации активных центров на поверхности адсорбата, которая напрямую связана с количеством привитых групп. С повышением температуры извлечение металла увеличивается. В координатах модели Дубинина-Радушкевича выполнен расчет значения свободной энергии адсорбции. Ее высокое значение (32,62 кДж/моль) и рост сорбционной ёмкости при увеличении температуры процесса указывают на образование химических связей между привитыми на мезопористый кремнезем МСМ-41 N',N'-диметилгидразидными группами и ионами ванадия.

Ключевые слова: мезопористый кремнезем, модифицирование, диметилгидразид, сорбция, кислоты Versatic, ванадий, метод пропитки

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SORPTION ABILITY OF MODIFIED MESOPOROUS MATERIALS TOWARDS VANADIUM IONS

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With the purpose of studying the sorption properties of mesoporous silica sorbents towards vanadium(V) ions, MCM-41pore-structured reagents modified with N′,N′-dimethylhydrazides of Versatic C10 tert-carboxylic acids have been synthesized. Functional groups grafted onto the surface of a MCM-41 structured reagent have been ascertained to activate it towards the sorption of vanadium (V) ions. Maximal sorption capacity (EM = 2.8 mmol/m^2) is observed in a sulfuric medium (pH 3.5-4.0) after a 40-min contact with solution. With increasing concentration of grafted groups, the sorption capacity of a modified silica material grows markedly. An adsorption isotherm has been plotted, with its parameters analyzed using the Langmuir-Freundlich model. With the correlation coefficients' values as a basis, one can conclude that the vanadium(V) adsorption processes are to a greater extent subject to the Freundlich equation. The sorption mechanism has been determined by establishing a limiting adsorption stage, using a graph-analytic method to analyze the completeness degree of the adsorption process (F) with time (τ). The sorption process has been evinced to proceed in an inter-diffusive regime and to be described by a pseudo-second order model, i.e. the intensity of the sorption process is dependent not only on the concentration of ions being extracted, but on that of active centers on the adsorbate surface, which is directly attributed to the number of the groups grafted. With increasing temperature, the extraction of a metal enhances. In the Dubinin-Radushkevich model coordinates, a value of adsorption free energy has been calculated. Its value (32.62 kJ/mol) and the enhancement of sorption capacity, with increasing temperature, indicate the formation of chemical bonds between N′,N′-dimethylhydrazide groups grafted onto the MCM-41 mesoporous silica, and vanadium ions.

Key words: mesoporous silica, modification, dimethylhydrazide, sorption, Versatic acids, vanadium, impregnation method

INTRODUCTION

Iron and titanium-vanadium ores containing vanadium as an impurity have been basic commercial sources to extract vanadium. Apart from natural resources, a great deal of vanadium has been amassed as technogenic raw materials (tailing dumps of the works recycling vanadium dross, exhausted catalysts of sulfuric productions, waste solutions of metallurgical works, etc.) [1].

To extract vanadium from technological solutions and industrial sewage, the sorption materials of different types have been offered, including: active coals [2], inorganic sorbents, strongly-basic anionites, cellulose-based fiber anionites [3-7], ion-exchange resins [8], natural materials – kaolinite and montmorillonite [9], silicon dioxide [10], "humic acid-silica" system [11]. The use of sorption materials extracting vanadium via different routes is foreordained by different forms (cationic, anionic, and polymerized) of its presence in solutions.

Earlier [12, 13], we had explored the sorption of tungsten (VI) and molybdenum (VI) by means of highly-ordered silicates of MCM-41 type modified with dimethylhydrazide groups. Owing to an appreciable surface area and the ordered structure of mesopores, these materials are characterized by a high adsorption capacity. The accessibility of mesopores for volumetric organic molecules to penetrate, a hardstructured inorganic matrix, and a possibility for organic monolayers of a modifier to be grafted enable highly-selective sorbents to be produced.

This work is aimed at studying the sorption capacities of mesoporous silica sorbents modified with dimethylhydrazide groups towards vanadium(V) ions.

EXPERIMENTAL METHODS

A silica basis for MCM-41structured sorbents was obtained by template hydrothermal synthesis at 100 °C for 48 h [14]. Tetraethoxysilane (TEOS) was used as a source of silica, cetyltrimethylammonium bromide (CTAB) was used as a structure-forming agent, with the synthesis components taken at the ratios TEOS 1 : CTAB 0.2 : NH_3 3.5 : H_2O 100. Versatic tert-carboxylic acid N',N'-dimethylhydrazides – $CH_3R_1R_2CC(O)OH$, where R_1 and R_2 are alkyl radicals with the number of carbon atoms totaling 10, – were prepared by acylation of 1,1-dimethylhydrazine with Versatic acid chloroanhydride in hexane.

The surface of mesoporous silicas was functionalized by the post-synthetic modification method as follows: a weighed portion of MCM-41 was put into a round-bottom flask and, with a calculated quantity of DMH and ethyl alcohol added, refluxed for 4 h, whereupon the sample was filtered, dried out at 80 °C until removal of ethanol.

The structural pore organization of the silica basis was corroborated by X-ray phase analysis with use of a XRD-7000 diffractometer (Shimadzu, Japan) using CuK_α-radiation ($\lambda_{av.}$ = 1.54184 Å); the structure of functionalized silica sorbents – by FTIR spectroscopy using a Vertex 80V spectrometer (Bruker, Germany) [12].

A standard stock solution of $NaVO_3$ salt was prepared from a preparation of chemical pure grade (2.5 mg of vanadium (V) per 1 ml of solution). Solutions with lesser contents of vanadium (V) were prepared from the stock solution successively diluted. Exploring the sorption properties of the reagents involved the following steps: (a) hydrochloric (or sulfuric) acids, or ammonia, were added to 100 ml of a solution containing only vanadium (V) ions to attain a needful pH value; (b) the mixture produced was stirred with 0.200 g of modified silica (MCM-41 + DMH), with establishing sorption equilibrium taking 40 min; (c) next, the solution was filtered to separate the sorbent; (d) the residual content of V(V) in the filtrate was determined titrometrically with Moore salt of analytical pure grade, the milligram concentrations of V(V) – photometrically with potassium permanganate.

To construct adsorption isotherm, solutions containing 3.06 to 10.188 g/l concentrations of vanadium (V) were used. Adsorption was carried out at 20 °C for 40 min. The value of static metal sorption capacity (E^M) and the degree of extraction (E) were calculated as described in [12].

To determine the limiting stage of the adsorption process, the graph-analytic method for analyzing the completeness degree of the adsorption process (F) with time (τ) was employed. The completeness degree of the F process was calculated as per the formula:

$$F = \frac{At}{Amax} \tag{1}$$

Herein, A_{max} stands for limiting adsorption value, A_t – for current adsorption value.

For external diffusive processes, the kinetic equation has the form as below:

$$\ln(1 - F) = y \cdot t \tag{2}$$

where *y* is the constant under given conditions of the process; t – duration of adsorption [17].

The quantity of adsorbate in a diffusion-controlled process can be expressed by the following equation:

$$A_t = k_d \cdot t^{\frac{1}{2}} \tag{3}$$

where A_t is a quantity of adsorbate per one unit of adsorbate area, mol/m^2; k_d is the rate constant of internal diffusion, mol/m^2·min$^{0.5}$; t – time, min.

RESULTS AND DISCUSSION

In accord with the textural-structural characteristics of the sorbents explored earlier [12], a carrier sample is a mesoporous material with developed specific surface area (up to 952 m^2/g), with grafted groups firmly enough linked to the surface of the carrier. Modifying markedly (to 239 m^2/g) curtails the surface area. However, taking into account a high content of functional groups (13-22 mmol/g) capable of forming complex compounds with non-ferrous/rare metal ions, the materials produced can exhibit themselves as efficient sorbents for concentrating elements from aqueous solutions.

Sorption properties of MCM-41 + DMH

The starting MCM-41 at pH 1-10 was found to practically not sorb vanadium (V) ions ($E^M = 1 \cdot 10^{-2}$ mmol/m^2). However, when modified with DMH groups, it drastically changes its sorption properties (E^M = 2.8 mmol/m^2).

Modified silica appears to be a polyampholyte and, depending on the pH value of a medium, can behave as either a polyacid or a polybase (4):

$$RCONHNH^+(CH_3)_2 \rightleftharpoons$$
$$RCONHN(CH_3)_2 \rightleftharpoons RC(O^-)NN(CH_3)_2 \tag{4}$$

Protolytic equilibriums can be characterized by following constants: pK = 3.13±0.02; pKa = 14.20±0.02 [19].

Vanadium is featured by a great variety of its valence form changing as dependent on pH values and vanadium ions' concentration in solutions [20, 21].

In diluted solutions, such monomer species as VO_2^+, HVO_3, VO_3^-, HVO_4^{2-}, VO_4^{3-} are in equilibrium and predominate at pH 0-3, 3.5-8, 8.0-12.0 и 12-14, respectively:

$$VO_2^+ \overset{+OH^-}{\rightleftharpoons} HVO_3 \overset{-H^+}{\rightleftharpoons} VO_3^- \overset{+OH^-}{\rightleftharpoons} HVO_4^{2-} \overset{-H^+}{\rightleftharpoons} VO_4^{3-}.$$

At concentrations of vanadium over $1 \cdot 10^4$ mmol/m^2 and pH 0-3, the VO_2^+ species remain predominant. With decreasing acidity (pH > 3), these species react with OH^- ions to form vanadium polyions. For example, $V_3O_9^{3-}$ and $V_4O_{12}^{4-}$ ions are present in a solution at pH 5.0-8.0, and $H_2V_2O_7^{2-}$ ions – at pH 10-12. These ions, when condensed, give rise to more complicated polyions [22, 23].

As follows from the data in Table 1, the maximal capacity of vanadium (V) ions is observed in the interval pH 3.5-4, apparently, at the expense of linking the anion forms of VO_3^- and $HV_{10}O_{28}^+$ [1] into a complex with protonated [18] grafted DMH groups. The composition of an electrically neutral complex being formed with DMH at pH 3-4 during the extraction process, was earlier found as corresponding to formula $(C_{12}H_{26}N_2O)_5 \cdot HVO_3$ [24].

Table 1

Extraction of vanadium (V) ions by the MCM-41 + DMH sorbent in sulfuric and hydrochloric solutions. Conditions: m_{sorb} = 0.200 g, V_{flask} = 100 ml, $C_{V(V)initial}$ = 0.026 mol/l

Таблица 1. **Извлечение ионов V(V) сорбентом MCM-41+ДМГД в серно- и солянокислых растворах; $m_{сорб}$ = 0,200 г, $V_{колб}$ = 100 мл; $C_{V(V)}^{исх.}$= 0,026 моль/л**

	E^M, mmol/m^2	
C_{H+}, mol/l	H_2SO_4	HCl
3	0.5	0.5
2	0.2	0.2
1	0.1	0.15
pH		
1.6	0.5	0.4
2	1.0	-
3	2.0	0.5
3.8	2.8	0.15
4.5	2.7	-
5.0	2.5	0.1
6.8	1.2	-
10.5	0.5	-
12.8	1.23	-
14.0	2.0	-

At pH < 3, vanadium is present basically as the VO_2^+ cation form being inacceptable to interaction with the DMH form protonated at these pH values [1]. In the interval pH 4-10, the sorption capacity decreases. This phenomenon is, apparently, attributed to the instability of a "sorbent-metal" complex being formed under these conditions.

The nature of an acid markedly affects the extraction of vanadium (V) ions (Table 1). In hydrochloric medium, vanadium (V) ions are extracted to a lesser degree as compared with that in sulfuric one. Such regularity is due to a possible redox reaction with participation of vanadium (V) ions in the presence of Cl^- ions. Therefore, sulfuric acid was used in all the subsequent experiments.

The sorption of vanadium (V) as affected by the modifier's concentration was investigated as well. With the mass ratio of "matrix solvent : modifier" increasing from 1: 0.1to 1: 0.2 at pH 3, the sorption capacity markedly grows in acidic media from 0.6 mmol/m^2 to 2.8 mmol/m^2, respectively.

The adsorption isotherm of vanadium (V) ions by the MCM-41 + DMH sorbent (Fig. 1) resembles the Langmuir dependence; however, the complete saturation of the surface, being to a greater extent typical of microporous sorbents, is not observed.

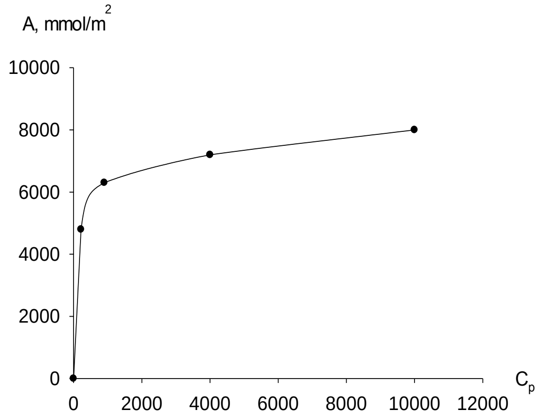


Fig. 1. The adsorption isotherm of vanadium (V) ions by the MCM-41 + DMH sorbent at pH 3.5

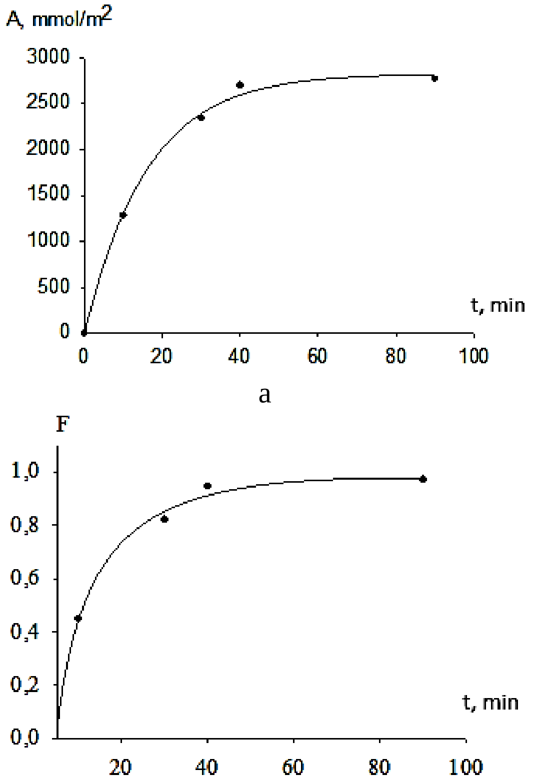
Рис. 1. Изотерма адсорбции V(V) сорбентом MCM-41+ДМГД; pH = 3,5

The smooth growth of adsorption, with increasing concentration of the substance being absorbed, is explained by intrapore diffusion. The dependence of that kind can be described in the coordinates of both the Langmuir and Freundlich equations, for which correlation coefficients (r^2) equaling respectively 0.848 and 0.976, were obtained from the adsorption isotherm graphically processed. With these values as a basis, the conclusion can be drawn that the adsorption processes of vanadium (V) ions are to a greater extent subject to the Freundlich equation which takes into account the adsorbate-adsorbate interactions occurring on the energetically non-uniform surface of modified sorbent.

Kinetics and sorption mechanism of vanadium (V) ions

The mechanism describing interaction between substance and adsorbent was determined by ascertaining the limiting stage of the sorption process, the steps of which are: (a) external diffusion of absorbed substance to adsorbent, (b) internal diffusion of adsorptive inside pores to active centers of adsorbent, and (c) condensation of absorbed substance on internal surface of pores as a result of physical adsorption, or chemisorption.

The findings are graphically interpreted in Fig. 2, whence it follows that the complete sorption period of vanadium takes 40 minutes (Fig. 2a). The curve mirroring the completeness degree of the adsorption process (F) with time (t) in the coordinates of external (ln(1-F) – t) and internal (F – $t^{1/2}$) diffusive kinetics and expressed numerically is presented in Table 2.



a

b

Fig. 2. Kinetic adsorption curve of vanadium (V) by MCM-41 + DMH sorbent (a); dependence of the degree of completion of the process on time (b)

Рис. 2. Кинетическая кривая адсорбции V(V) сорбентом МСМ-41+ДМГД (a); (a) и зависимость степени завершенности процесса от времени (b)

Table 2

Processing results in coordinates of external and internal diffusive kinetics

***Таблица 2.* Обработка результатов в координатах внешне- и внутридиффузионной кинетики**

Kinetics coordinates	Correlation coefficients of starting (r_1^2) and completive (r_2^2) steps of the process	
	r_1^2	r_2^2
External diffusive kinetics (ln(1-F) – t)	0.974	0.999
Internal diffusive kinetics (F – $t^{1/2}$)	1	1

The fairly expressed linear kinetic dependence in the coordinates F – $t^{1/2}$ permits the conclusion that the adsorption of vanadium (V) ions is to a larger extent limited by internal diffusive processes [17].

To determine the order of the quasi-chemical interaction reaction between modified MCM and vanadium ions, the findings obtained were processed using the kinetic models of pseudo-first and pseudo-second orders.

In the systems under consideration, the pseudo-first order kinetics is described using the Lagergren equation [25]:

$$\lg(C_\tau - C_e) = \lg C_e - k_1 \cdot \tau \qquad (5)$$

Herein, C_τ – current concentration of adsorptive, mmol; C_e – equilibrium concentration of adsorptive, mmol; τ – duration of adsorption, min; k_1 – rate constant, min^{-1}.

The pseudo-second order kinetics is described using the classical equation, in its integral form as below:

$$\frac{1}{C\tau} = \frac{1}{k_2 \cdot C_e^2} + \frac{\tau}{C_e}, \qquad (6)$$

Herein, k_2 – rate constant, $(mmol\cdot min)^{-1}$; C_τ – current concentration of adsorptive, mmol; C_e – equilibrium concentration of adsorptive, mmol.

Proceeding from kinetic dependences lg(C_t-C_e) with *t* and the values of correlation coefficients (r^2 = 0.983 in the starting step, and r^2 = 0.974 in the completive step of the adsorption process), the adsorption process of vanadium (V) is with a high degree of probability described by the pseudo-second order model, i.e. with rectilinear dependence (t/C_e with *t*, min), the correlation coefficient r^2 = 1. This permits the conclusion that the intensity of the adsorption process would depend not only on the concentration of the ions being extracted, but on the active centers' concentration on the surface of adsorbate as directly linked to the number of the groups grafted.

The adsorption of vanadium (V) as affected by temperature

Generally, with rising temperature, the degree of metal extraction increases (Fig. 3), being, arguably, attributed to the chemical adsorption of vanadium (V) on DMH-modified sorbent.

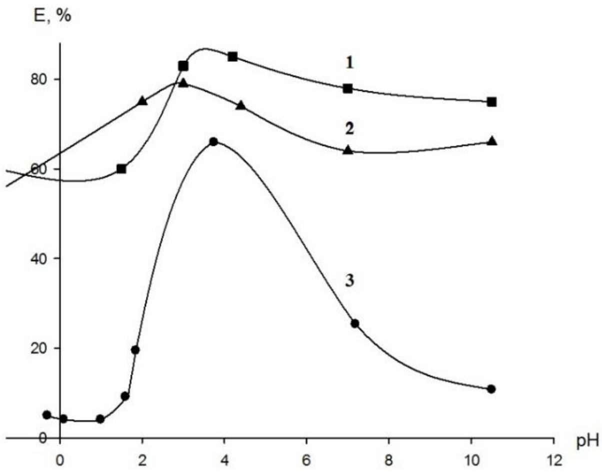


Fig. 3. Ther influence of temperature and pH on degree of V (V) ions' extraction by MCM-41 + DMH sorbent. 1 - 90 °C, 2 - 60 °C, 3 - 20 °C. Conditions: m_{sorb} = 0.200 g, V_{flask} = 100 ml, $C_{V(V)initial}$ = 0.026 mol/l
Рис. 3. Влияние температуры и рН на степень излечения ионов V(V) сорбентом МСМ-41+ДМГД:1 - 90 °C, 2 - 60 °C, 3 - 20 °C; $m_{сорб}$ = 0,200 г, $V_{колб}$ = 100 мл, ; $C_{V(V)}^{исх.}$= 0,026 моль·л$^{-1}$

To corroborate this assumption, the dependences lnE (E^M, mmol/m^2) with (lnε)^2 were sectioned at pH 3.5, whereupon the results were processed in the coordinates of the Dubinin-Radushkevich model [27]:

$$\ln E = \ln E_\infty - \left(\frac{R\cdot T}{E}\right)^2 \cdot \left(\ln\frac{C_s}{C_e}\right)^2 \qquad (7)$$

From the dependence produced, the free energy of adsorption was calculated (Table 2). Its value, equaling 32.62 kJ/mol, corroborates the extraction of vanadium (V) by DMH-modified MCM-41 to be accompanied by forming a chemical bond between ions being extracted and groups grafted.

CONCLUSIONS

In this work, modifying the surface of MCM-41 by means of Versatic acid dimethylhydrazide groups has been experimentally ascertained to activate the surface of mesoporous silicate material towards vanadium (V) ions. Maximal extraction is observed at room temperature in sulfuric medium (pH 3-4) for 40-min contact of adsorbent with solution.

The adsorption isotherms obtained are with a high degree of correlation described using the Freundlich models, thereby indicating the surface non-uniformity of the sorbent synthesized. The adsorption process has been evinced to proceed in internal diffusive regime and is described by the pseudo-second order model, i.e. increasing concentration of the groups grafted onto the MCM surface markedly increases its adsorption capacity.

The value of activation energy and the growth of adsorption capacity, with rising temperature, indicate forming chemical bonds between ions being extracted and groups grafted.

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