

STUDY OF THE SORPTION OF Ni^{2+} , Co^{2+} , AND V^{4+} CATIONS IN A THREE-COMPONENT SYSTEM USING MODIFIED ZEOLITE

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Abstract. *Introduction.* Cobalt, nickel, and vanadium are toxic heavy metals that can concentrate and accumulate in soil, wastewater, groundwater, and even in the human body. One of the effective ways to address these problems is the use of accessible adsorbents capable of purifying various types of water. According to the analysis of literature data, the most suitable sorbents are natural and modified forms of zeolites. *The aim of the study* was to investigate the sorption properties of nickel(II), cobalt(II), and vanadium(IV) ions using the saturation method from aqueous solutions with zeolites modified by guar gum. *Results and discussion.* The sorption efficiency of the modified zeolite in multimetal systems was investigated, and it was established that the obtained sorbent simultaneously absorbs all cations. It was shown that, unlike natural zeolite, a high degree of sorption by the modified zeolite is achieved both for a cation with a fixed concentration and for one with a variable concentration. The degree of uptake of the sorbed cations is determined by the combination of two cations with constant and equal contents and the concentration of the variable cation. In all the studied systems, a high degree of cation sorption (from 75.0 to 99.5%, depending on the process conditions) occurs in the region with a low concentration of the variable cation (0.5–10 mg/L). *Conclusion.* It was revealed that in multimetal systems competitive adsorption of cations occurs. Series of sorption efficiency for the cations were obtained, as well as data on the initiating influence of the variable cation—under conditions of its increased concentration—on the sorption of other ions present in the system. In the system “ $\text{Ni}^{2+} - \text{Co}^{2+} - \text{V}^{4+} - \text{MPC} - \text{H}_2\text{O}$ ” with variable $C(\text{Co}^{2+})$ and saturated solutions, the Co^{2+} cation initiates the sorption efficiency of the modified sorbent toward V^{4+} and Ni^{2+} cations: $\text{RV} (66.6\%) > \text{RCo} (42.4\%) > \text{RNi} (13.4\%)$. With variable $C(\text{Ni}^{2+})$, the Ni^{2+} cation increases the sorption efficiency of V^{4+} and Co^{2+} ions: $\text{RV} (63.6\%) > \text{RCo} (1.8\%) > \text{RNi} (3.8\%)$.

Keywords: modified zeolite, saturation method, sorption, cobalt, nickel, and vanadium cations.

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1. Introduction

At present, under conditions of increasing environmental pollution caused by industrial waste, including drilling waste, the removal of heavy metal ions (Ni^{2+} , Co^{2+} , and V^{4+}) from drilling fluids has become particularly important. Environmental contamination by heavy metals is recognized as one of the major problems of ecology and public health.

Recent studies have shown that sorption purification not only provides competitive removal efficiency compared with traditional chemical methods, but also minimizes the environmental impact of the treatment process. The use of advanced sorbents, often chemically modified, has further improved the removal capacity for heavy metals such as lead, cadmium, and mercury. These advances highlight the potential of sorption methods as a cornerstone of modern drilling fluid treatment systems [1].

The choice of a purification method depends on specific operational and environmental conditions. The integration of sorption processes offers a promising approach to more sustainable and efficient management of drilling fluids contaminated with heavy metals.

Each method for the removal of heavy metals has its own unique advantages and disadvantages, which requires careful selection based on the specific characteristics of wastewater and operational constraints. Chemical treatment methods, including precipitation and oxidation, provide a high degree of purification but often produce hazardous sludge that requires further treatment.

Cobalt, nickel, and vanadium are toxic heavy metals that can concentrate and accumulate in soil, wastewater, groundwater, and even in the human body.

The sorption removal of heavy metals from drilling fluids is based on the interaction of physicochemical mechanisms, including adsorption, absorption, ion exchange, surface complexation, and precipitation. Adsorption, the predominant mechanism, occurs through electrostatic interactions, van der Waals forces, or chemical bonding between metal ions and functional groups on the sorbent surface (e.g., hydroxyl, carboxyl, or amino groups) [2]. Absorption, although less common in solid sorbents, is important for polymeric materials where metals diffuse into the sorbent matrix.

Ion exchange plays a crucial role for aluminosilicate sorbents such as zeolites, where metal cations replace exchangeable ions (e.g., Na^+ , Ca^{2+}) within their porous structures. Surface complexation predominates in oxide-based sorbents (e.g., iron oxides), where metals form coordination bonds with surface hydroxyl groups [3]. Studies of adsorption toward metal cations on zeolites with deposited organic layers have suggested [4,5] that the movement of molecules in the inner sphere is coordinated by the zeolite's own pore system.

In study [6], the adsorption of Cu(II) , Cd(II) , and Pb(II) from aqueous solution onto a methyl methacrylate–Na–Y zeolite composite (MMA–Na–Y zeolite) was analyzed depending on pH, contact time, initial concentration of metal cations, adsorbent dosage, and temperature.

The removal of copper, nickel, cobalt, and iron ions from water resources in the concentration range of 0.5–3.5 mg-eq/dm³ using natural zeolite from the Yagodninskoye deposit in the Kamchatka region was experimentally studied [7]. The results show that natural zeolite can be used as an effective sorbent for the extraction of Cu(II), Ni(II), Co(II), and Fe(II) ions from contaminated water.

The adsorption activity of zeolites from the Kholinskoye deposit toward copper, zinc, and chromium ions was investigated [8], demonstrating the potential of such materials for wastewater treatment from these ions.

One of the effective ways to solve these problems is the use of accessible adsorbents capable of providing the required degree of wastewater purification. These include adsorption technologies based on synthetic, natural, and modified zeolites [9, 10]. According to the analysis of literature data, the application of sorption methods for the treatment of drilling fluids using natural and readily available sorbents capable of reducing the concentration of heavy metals is the most suitable approach. Natural zeolite, significant reserves of which are available in Kazakhstan, largely meets these requirements.

As is known, natural zeolite is characterized by less effective sorption properties compared with synthetic ion-exchange resins. This disadvantage is compensated by the good response of natural zeolite to modification processes. There are various methods for modifying natural aluminosilicates: mechanical, thermal, and chemical modification, which includes acid and alkaline activation, modification with inorganic and organic compounds, and combined activation methods.

Currently, promising modifiers include accessible, inexpensive, natural, and non-toxic organic compounds that possess functional hydroxyl and amino groups active in sorption processes, such as guar gum. This modifier is an inexpensive natural biopolymer with functional hydroxyl and CH₂ groups that participate in the sorption processes of cations.

It should be noted that the scientific literature provides insufficient information on sorption processes for the removal of common pollutants such as Ni(II), Co(II), and V(IV) cations using natural zeolite and its modified polysaccharide forms, especially for environmental purification processes under conditions of their simultaneous presence.

The necessity to improve the sorption characteristics of natural zeolite was experimentally substantiated, since the degree of sorption even in systems containing one metal cation does not exceed 75%, and in multi-metal systems R_{sorb.} of a competing cation is no more than (60–65)%.

The sorption of heavy metals (Ni²⁺, Co²⁺, V⁴⁺) by a guar gum-modified zeolite in single- and multi-metal systems is studied for the first time. The modified zeolite is shown to be an effective sorbent, and sorption efficiency series for cations in multi-metal systems are obtained.

The aim of this study was to investigate the sorption properties of nickel(II), cobalt(II), and vanadium(IV) ions using the saturation method from aqueous solutions with zeolites modified by guar gum.

2. Experimental part

Experiments to determine the sorption characteristics were carried out at room temperature. The preparation of the modified zeolite was performed as follows: natural zeolite was mixed with a guar gum solution at a solid-to-liquid ratio of 1:100 for 10 hours. The precipitate was then separated and dried at 50 °C. The dried samples of the modified zeolite were placed in conical flasks, and model solutions with various concentrations were added. Each test was repeated twice. The margin of error of experimental data is 0.1-1%.

For the preparation of model solutions, the following salts were used: nickel sulfate $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, cobalt sulfate $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, and vanadium sulfate $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$ dissolved in H_2O . To eliminate the influence of impurities, the sorption of divalent and tetravalent cations of nickel, cobalt, and vanadium was studied in the model system “ Ni^{2+} , Co^{2+} , V^{4+} – H_2O – modified zeolite.”

Sorption of nickel(II), cobalt(II), and vanadium(IV) cations was carried out at a constant zeolite-to-solution ratio (solid-to-liquid, 10:100) and equal concentrations of the sorbed cations. The concentrations of nickel, cobalt, and vanadium cations in the solutions were determined using atomic emission spectroscopy.

3. Results and Discussion

The table presents the main sorption characteristics of the resulting sorbent compared to the natural zeolite. The results show that all sorption characteristics of the modified zeolite are higher than those of the PC. For the modified zeolite, SEC cat is 15 times higher, SEC an is 85.6 times higher, TSC is 9.7 times higher, and TPV is 77 times higher than those of the natural zeolite.

Table - Sorption Characteristics of Modified and Natural Zeolites

TPV, g/cm ³	TSC, g/cm ³	SEC _{cat} , mg-eq/g	SEC _{an} , mg-eq/g
Modified zeolite			
1.814	35.44	14.896	42.658
Natural zeolite			
0.0235	3.67	0.997	0.4985

The sorption properties of natural zeolite modified with guar gum were studied in the system “ Ni^{2+} – Co^{2+} – V^{4+} – modified zeolite – H_2O ” under conditions similar to those for sorption of these cations by natural zeolite, where the concentrations of two cations were equal and constant, and the concentration of the third component varied from 0.5 to 500 mg/L.

The sorption curves in all studied systems exhibit a wavelike pattern (Figures 1–3), in contrast to those observed for natural zeolite [12]. Furthermore, the highest degree of sorption by the modified zeolite was observed for all sorbed cations in low-concentration solutions, from 0.5 to 1.0 mg/L for the cation with variable concentration.

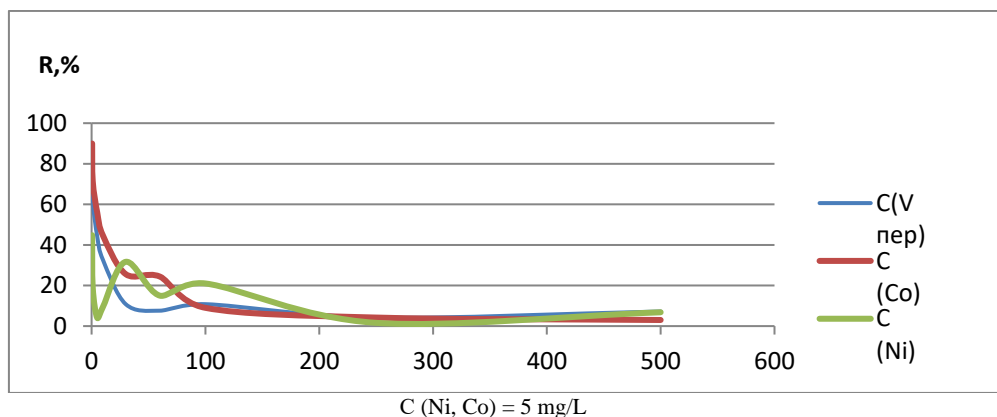


Figure 1 – Influence of vanadium (IV) cation concentration on the extraction efficiency of cations by the modified zeolite in the system “Ni²⁺ – Co²⁺ – V⁴⁺ – modified zeolite – H₂O”

Regardless of the sorption conditions, as the concentration of the variable cation increases, the sorption degree ($R_{sor,b}$) of all sorbed cations decreases. Moreover, unlike natural zeolite, its modified form exhibits high sorption capacity for cations with both constant and variable concentrations, simultaneously absorbing both cations.

In the first scenario, where $C(Ni, Co) = 0.5$ mg/L (constant) and $C(V)$ is the variable factor, the modified zeolite shows preferential sorption toward Co^{2+} ($R_{sor,b} = 90.0\%$) and V^{4+} ($R_{sor,b} = 85.16\%$), while the sorption degree of Ni^{2+} is 44.8% (Figure 1).

The appearance of a weak maximum on the $Co(II)$ sorption curve at $C(V) = 50$ mg/L ($R_{Co} = 25\%$), as well as more pronounced maxima at $C(V) = 30$ and 100 mg/L on the Ni^{2+} sorption curve ($R_{Ni} = 31.7\%$ and 21.0%), is associated with partial desorption processes. From 200 mg/L onward, the dependence of R for Co^{2+} and V^{4+} on the concentration of V^{4+} becomes approximately linear, and $R_{sor,b}$ fluctuates slightly (3.0 – 7.2%).

The sorption degrees of the cations can be ranked as: $R_{Co} > R_V > R_{Ni}$.

In the second scenario, where $C_{Ni} = C_V$ and the concentration of Co^{2+} is variable (Figure 2), the shape of the sorption curves is somewhat simplified compared to the system described above (Figure 1).

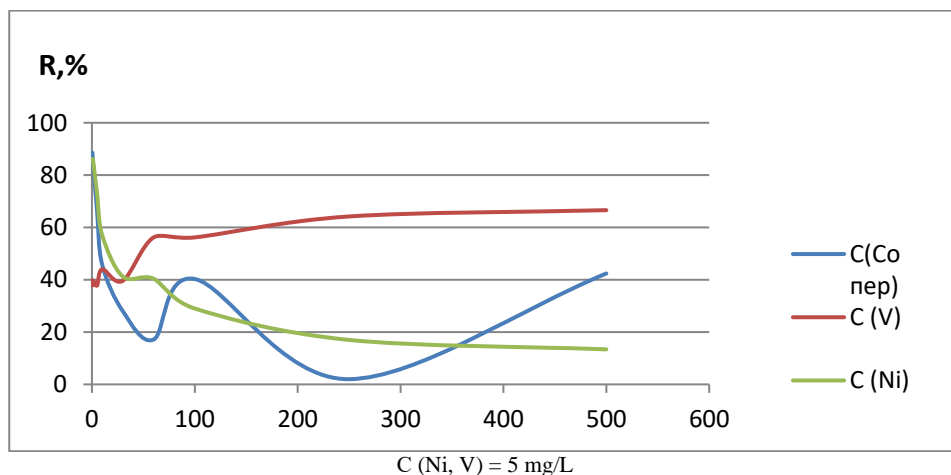


Figure 2 – Influence of cobalt (II) cation concentration on the extraction efficiency of cations by the modified zeolite in the system “ $\text{Ni}^{2+} - \text{Co}^{2+} - \text{V}^{4+} - \text{modified zeolite} - \text{H}_2\text{O}$ ”

In the sorption curves, no maxima are observed for nickel(II) and vanadium(IV) cations, while the cobalt(II) sorption curve exhibits a single pronounced maximum at $C_{\text{Co}} = 100 \text{ mg/L}$. The modified zeolite demonstrates preferential sorption toward Ni^{2+} at constant nickel concentration ($R_{\text{Ni}} = 86.24\%$) and for variable Co^{2+} concentration ($R_{\text{Co}} = 88.6\%$) in the cobalt(II) concentration range of 0.5–1.0 mg/L, while R_{V} ranges from 37.8 to 39.8%.

Starting from $C_{\text{Co}} = 30 \text{ mg/L}$, the sorption degree of vanadium(IV) cations increases, reaching 66.6% at $C_{\text{Co}} = 500 \text{ mg/L}$, which is 26.8–28.8% higher than in the low-concentration range of Co^{2+} . For the Co^{2+} sorption curve (variable), starting from 100 mg/L, R_{sorb} also increases with increasing C_{Co} , reaching 42.4% at 500 mg/L. Meanwhile, the sorption curve of Ni^{2+} decreases, and R_{Ni} drops to 13.4% at 500 mg/L cobalt(II). In this case, cobalt cations initiate the sorption process of vanadium cations, while a decrease in vanadium concentration, in turn, stimulates the sorption of cobalt cations.

The amount of sorbed Co^{2+} at its concentrations of 400 and 500 mg/L is 105 and 212 mg/L, respectively, whereas for natural zeolite under the same conditions it is 99 and 95 mg/L (Figure 1). In this system, at low cobalt concentrations, the sorption ranking is $R_{\text{Co}} > R_{\text{Ni}} > R_{\text{V}}$, whereas in saturated solutions it changes to $R_{\text{V}} > R_{\text{Co}} > R_{\text{Ni}}$.

In the third scenario, according to the data shown in Figure 3, in the system “ $\text{Ni}^{2+} - \text{Co}^{2+} - \text{V}^{4+} - \text{modified zeolite} - \text{H}_2\text{O}$ ” with $C_{\text{Co}} = C_{\text{V}} = \text{const}$ and variable C_{Ni} , the curves are further simplified compared to the previous scenario (Figure 2). As C_{Ni} increases from 0.5 to 30 mg/L, the sorption degree of Co^{2+} and V^{4+} sharply decreases; with further increase in C_{Ni} , its sorption gradually decreases, while Co^{2+} sorption slightly increases and then decreases again at 300 mg/L Ni^{2+} . The V^{4+} sorption curve, in contrast, rises with increasing C_{Ni} .

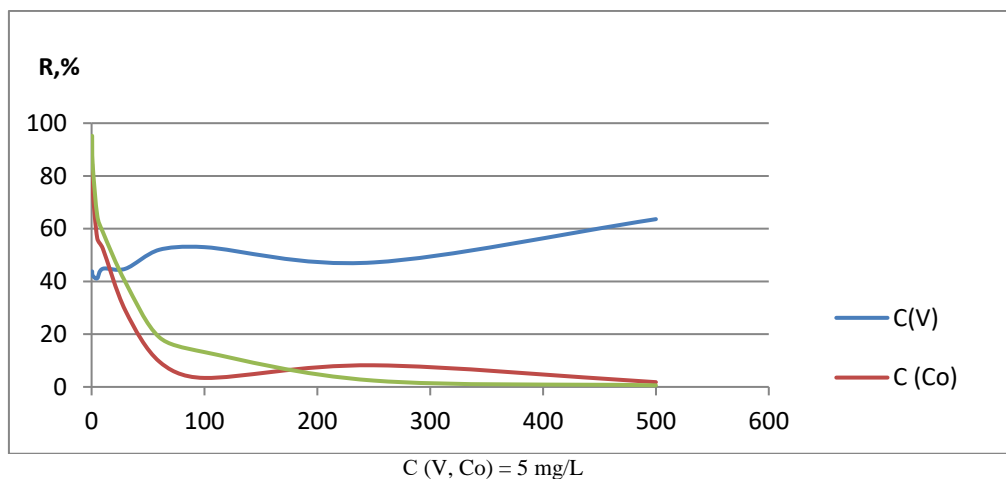


Figure 3 – Influence of nickel (II) cation concentration on the extraction efficiency of cations by the modified zeolite in the system “Ni²⁺ – Co²⁺ – V⁴⁺ – modified zeolite – H₂O”

In the low Ni²⁺ concentration range, the modified zeolite demonstrates preferential sorption for Ni²⁺ ($R_{\text{sorb}} = 95.2\%$) and Co²⁺ ($R_{\text{Co}} = 84.5\%$), while RV under these conditions does not exceed 42.2–43.8%. Starting from 10–30 mg/L Ni²⁺, the sorption degree of vanadium(IV) increases from 44.8% to 63.6%, whereas R_{Co} and R_{Ni} sharply decrease and continue to decline with further increases in C_{Ni} .

Thus, the modified zeolite acts as an effective sorbent for Ni²⁺ and Co²⁺ cations ($R_{\text{Ni}} > R_{\text{Co}} > R_{\text{V}}$) in solutions with low nickel(II) concentrations, while in nickel-saturated solutions it is more effective for V⁴⁺ cations, where $R_{\text{V}} > R_{\text{Co}} > R_{\text{Ni}}$.

4. Conclusion

The sorption efficiency of a modified guar gum zeolite on multiple metal components was studied. It was found that the resulting sorbent consistently controls all cations (Ni²⁺, Co²⁺, V⁴⁺). The degree of cation distribution is determined by the combination of two cations with constant and equal concentrations and the concentration of a variable cation.

In all experimental studies, high cation sorption (75.0–99.5%) was observed, depending on low concentrations of the variable cation (0.5–10 mg/L).

Competitive adsorption of cations was revealed, cation sorption efficiency series were obtained, and data were provided on the onset of the variable cation's existence under conditions of its high concentration on the sorption of other ions present in the system. With variable $C(\text{Ni}^{2+})$, the Ni²⁺ cation increases the efficiency of sorption of V⁴⁺ and Co²⁺ ions: $R_{\text{V}} (63.6\%) > R_{\text{Co}} (1.8\%) > R_{\text{Ni}} (3.8\%)$. The results of the studies using the modified sorbent showed the possibility of using the modified zeolite to purify wastewater from metallurgical production from heavy metal ions, including nickel, cobalt and vanadium.

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МОДИФИКАЦИЯЛАНҒАН ЦЕОЛИТ АРҚЫЛЫ ҮШ КОМПОНЕНТТІ ЖҮЙЕДЕ Ni^{2+} , Co^{2+} , V^{4+} КАТИОНДАРЫНЫҢ СОРБЦИЯСЫН ЗЕРТТЕУ

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Түйіндеме. *Kіріспе.* Кобальт, никель және ванадий - улы ауыр металдар, олар топырақта, ағынды суларда, жер асты суларында және тіпті адам ағзасында шоғырланып, жиналуы мүмкін. Бұл мәселелерді шешудің бір тиімді жолы - әртүрлі су түрлерін тазартуға қабілетті оңай қолжетімді адсорбенттерді пайдалану. Әдеби шолуға сәйкес, ең қолайлы сорбенттер - табиғи және модификацияланған цеолиттер. *Жұмыстың мақсаты* гуар шайырымен түрлендірілген цеолиттермен сулы ерітінділерден қанығу әдісімен никель (II), кобальт (II) және ванадий (IV) иондарының сорбциялық қасиеттерін зерттеу. *Нәтижелер мен пікірталас.* Модификацияланған цеолиттің көпметалды жүйелеріндегі сорбциялық тиімділігі зерттелді және алынған сорбент бір мезгілде барлық катиондарды адсорбциялайтыны анықталды. Табиғи цеолиттен айырмашылығы, модификацияланған цеолиттің жоғары дәрежедегі сорбциясына тұрақты және айнымалы концентрациялы катиондар үшін қолжетімділігі көрсетілген. Адсорбцияланған катиондардың сорбция дәрежесі айнымалы катионның тұрақты және тең мөлшерлі концентрациясы бар екі катионның тіркесімімен анықталады. Зерттелген барлық жүйелерде катион сорбциясының жоғары дәрежесі, процесс жағдайларына байланысты 75.0-ден 99.5%-ға дейін, төмен айнымалы катион концентрациясы аймағында (0.5-10 мг/л) орын алады. *Қорытынды.* Көпметалды жүйелерде катиондардың бәсекеге қабілетті адсорбциясы анықталды және катиондар үшін сорбциялық тиімділік қатарлары, сондай-ақ жоғары концентрациядағы айнымалы катиондар жүйесінде басқа иондардың сорбциясына бастамашылық әсері туралы деректер алынды. Айнымалы $\text{C}(\text{Co}^{2+})$ және қаныққан ерітінділері бар $\text{Ni}^{2+} - \text{Co}^{2+} - \text{V}^{4+}$ -МТЦ- H_2O жүйесінде Co^{2+} катионы модификацияланған сорбенттің тиімділігін V^{4+} және Ni^{2+} катиондарына қарай басымдылық көрсетеді: $R_v (66.6\%) > R_{\text{Co}} (42.4\%) > R_{\text{Ni}} (13.4\%)$. Ni^{2+} катионының $\text{C}(\text{Ni}^{2+})$ айнымалысымен V^{4+} және Co^{2+} иондарының сорбция тиімділігі артады: $R_v (63.6\%) > R_{\text{Co}} (1.8\%) > R_{\text{Ni}} (3.8\%)$.

Түйін сөздер: табиғи цеолит, қанықтыру әдісі, сорбция, кобальт, никель және ванадий катиондары

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ИЗУЧЕНИЕ СОРБЦИИ КАТИОНОВ Ni^{2+} , Co^{2+} , V^{4+} В ТРЕХКОМПОНЕНТНОЙ СИСТЕМЕ МОДИФИЦИРОВАННЫМ ЦЕОЛИТОМ

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Резюме. *Введение.* Кобальт, никель и ванадий — токсичные тяжелые металлы, которые могут концентрироваться и накапливаться в почве, сточных водах, грунтовых водах и даже в организме человека. Одним из эффективных способов решения этих проблем является использование доступных адсорбентов, способных обеспечить очистку различных вод. Согласно анализу литературных данных наиболее подходящими сорбентами являются природные и модифицированные формы цеолитов. *Целью работы* являлось изучение сорбционных свойств ионов никеля(II), кобальта(II) и ванадия (IV) методом насыщения из водных растворов цеолитами,

модифицированными гуаровой камедью. *Результаты и обсуждение.* Исследована сорбционная эффективность модифицированного цеолита в многометалльных системах и установлено, что полученный сорбент одновременно поглощает все катионы. Показано, что в отличие от природного цеолита, высокая степень сорбции модифицированным цеолитом достигаться как для катиона с фиксированной, так и с переменной концентрацией. Степень поглощения сорбируемых катионов определяется комбинацией двух катионов с постоянным и равным содержанием и концентрацией переменного катиона. Во всех исследуемых системах высокая степень сорбции катионов от 75.0 до 99.5 % в зависимости от условий процесса приходится на низкоконцентрированную по переменному катиону область (0.5-10 мг/л). *Заключение.* Выявлено, что в многометалльных системах протекает конкурентная адсорбция катионов и получены ряды сорбционной эффективности катионов, а также данные об иницирующем влиянии переменного катиона в условиях его повышенной концентрации на сорбцию других присутствующих в системе ионов. В системе «Ni²⁺ – Co²⁺ – V⁴⁺ – МПЦ–Н₂О» с переменной C(Co²⁺) и насыщенных растворах катионов Co²⁺ иницируется эффективность модифицированного сорбента к катионам V⁴⁺ и Ni²⁺: R_V (66.6 %) > R_{Co} (42.4 %) > R_{Ni} (13.4 %). При переменной C(Ni²⁺) катион Ni²⁺ повышается эффективность сорбции ионов V⁴⁺ и Co²⁺: R_V (63.6 %) > R_{Co} (1.8 %) > R_{Ni} (3.8 %).

Ключевые слова: модифицированный цеолит, метод насыщения, сорбция, катионы кобальта, никеля и ванадия

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