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SORPTION OF HEAVY METAL CATIONS FROM A WATER-SALT SYSTEMBY NATURAL MONTMORILLONITE

Abstract. The sorption properties of natural montmorillonite from the Tagan deposit with respect to heavy metal cations were researched on the model system "Mn^{2+}–Co^{2+}–Ni^{2+}–V^{4+}–H_2O–montmorillonite". The influence of temperature, duration of the process and concentration of solutions, as well as the norm of the sorbent on the degree of sorption of cations is considered. The optimal conditions for the sorption process (25ºC, 30 min, Т:Ж = 1,5:100) have been determined, at which the degree of solution purification is up to 86.36% cations of Co^{2+}, 85.59% of Ni^{2+}, 82.64% of Mn^{2+} and 52.29% of V^{4+}. The nature of the sorption curves is determined by the nature of the sorbed cation. According to the absorption efficiency of natural montmorillonite, ions are arranged in the following order: $Ni^{2+} \geq Co^{2+} > Mn^{2+} > V^{4+}$. The results of the conducted studies indicate the possibility of effective use of bentonite clays of the Tagan field in the purification of wastewater from heavy metal cations.

Keywords: sorption, natural montmorillonite, heavy metals, sorption, cations.

Introduction. At present, enterprises specializing in the extraction and processing of oil are the largest industrial sources of wastewater pollution with highly toxic substances, among which the most dangerous are compounds of heavy metals. The composition of polluted industrial wastewater contains Co, Mn, Ni, V, Cr, Pb and other metals, even small amounts of which can lead to adverse consequences for human health and the environment. Heavy metals are able to concentrate in organisms to quantities that are hundreds and thousands of times higher than their content in the natural environment. It should be noted that the joint presence of several elements enhances their toxic effect several times. It should be noted that the joint presence of several elements enhances their toxic effect several times [1].

Existing methods and means are not always effective in processes of purification of oil containing water. The most effective, allowing to achieve the maximum degree of purification are adsorption methods [2] using cheap natural sorbents with ion exchange and sorption properties [3]. Clays (bentonites) with a highly developed inner surface, high swelling and chemical resistance meet these requirements [4,5]. Bentonites exhibit sorption properties due to a highly branched surface with active adsorption centers [6,7].

Due to the high ability of montmorillonite to adsorb various organic and inorganic compounds, bentonite clays with a high content of montmorillonite are often used. Montmorillonite (MMT) refers to sorbents with micropore sizes changing during adsorption and with an expanding unit cell; the parameter from the crystal cell of the mineral can increase by 3–10 Å [8].

The large reserves of bentonites explored in Kazakhstan make it possible to classify the republic as a producer country, such as the USA, China, and Russia. The main bases of bentonites in the southeastern region of the republic are the deposits of the Primonrak and Kyngrak groups. The mineral montmorillonite, which is widespread in the East Kazakhstan region, purifies water by absorbing heavy metals from it[9].

EXPERIMENTAL PART

As a sorbent, we used montmorillonite-containing bentonite from the Tagan deposit, located in the Zaisan depression (Eastern Kazakhstan). The content of montmorillonite in bentonite horizons reaches 90-92%. The chemical composition of the clay is shown in table 1.

Table 1 – The chemical composition of montmorillonite

Composition, %								
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	K_2O	Na_2O	TiO_2
69.2	23.40	3.05	1.78	1.55	0.47	0.08	0.04	0.37

The sorption capacity of natural montmorillonite with respect to the V^{4+}, Co^{2+}, $Ni^{2+}$and Mn^{2+}cations was studied under stirring conditions in a thermostatically controlled reactor, which was evaluated by the change in their content in the solution, i.e. by the difference between the initial and residual concentration of cations (after the completion of the process). The degree of sorption (extraction) is the ratio of the difference between the initial concentration and the concentration of cations V (IV), Co (II), Ni (II), and Mn (II) attained to a fixed point in time to their initial content. The initial and final concentrations of vanadium, cobalt, nickel and manganese ions in solutions were determined on an AA-7000 atomic absorption spectrophotometer, «ShimadzuCorporation», Japan, № A30664901456.

The study of the process of sorption of the studied cations by natural montmorillonite was carried out in a multimetal aqueous solution.

The specified concentration of V^{4+}, Co^{2+}, Ni^{2+}, and Mn^{2+} cations was created by introducing into the aqueous solution the calculated amount of the corresponding sulfates $VOSO_4{\cdot}3H_2O$, $CoSO_4{\cdot}7H_2O$, $NiSO_4{\cdot}7H_2O$, $MnSO_4{\cdot}5H_2O$ of chemically pure grade.

RESULTS AND DISCUSSION

According to the information available in the scientific literature, it can be assumed that natural montmorillonite will exhibit a sorption capacity for cations of divalent and tetravalent metals (V^{4+}, Co^{2+}, Ni^{2+}, Mn^{2+}) present in oily waters. In this regard, studies of the sorption capacity of natural montmorillonite with respect to the indicated cations were carried out, depending on a number of main process factors in a multicomponent system «Ni^{2+}– Co^{2+}–Mn^{2+}–V^{4+}–H_2O».

Preliminary studies have shown that the pH of the solution has no significant effect on the sorption capacity of natural montmorillonite in relation to the studied cations.

The degree of purification of various media significantly depends on the fractional composition of natural aluminosilicate. To determine the main properties of natural montmorillonite as a sorbent of heavy metals in wastewater treatment, the influence of the size of its granules on the efficiency of sorption of Ni^{2+}, Co^{2+}, Mn^{2+}, V^{4+} cations was studied. The study of the sorption capacity of montmorillonite of different dispersion with respect to the indicated cations was carried out at a constant temperature (25°C), S: L = 1.5:100 and the concentration of Ni^{2+}, Co^{2+}, Mn^{2+}, V^{4+} ions equal to 100 mg/l in the time interval from 5 to 60 min process. So granular (7 mm) montmorillonite and dispersed powder MMT with a grain size of 0.2 mm were used.

The data obtained show that the degree of purification of metal-containing systems significantly depends on the size of the sorbent granules (figure 1). With an increase in the degree of dispersion of montmorillonite grains, the degree of sorption of cations, regardless of their nature, increases. Sorption of the studied cations on the coarse phase (7 mm) is on average 10-20% higher than on the fine phase. The contact time of the sorbent with the solution also affects the degree of purification of the metal-containing solution. However, the nature of the sorption curves is determined by the nature of the cation and the duration of the process.

Figure 1a shows that, regardless of the granule size, the degree of sorption of Ni^{2+} cations slightly increases with increasing time.

Sorption curves of Co (II), Mn (II) and V (IV) cations are characterized by the presence of a maximum or a minimum (figure 1 b, c, d). The degree of sorption of cobalt (II) by the studied sorbents increases up to 30 min, and over the specified time decreases, which is probably due to the desorption of cobalt cations from montmorillonite into the solution (figure 1b). At the same time, desorption is less pronounced when using a granular sorbent (0.7 mm). The optimal time for the sorption of Co^{2+} cations by dispersed and granular MMT is 30 min.

The sorption curve of Mn^{2+} (II) ions for both sorbents has a weakly pronounced minimum at 30 min (Figure 1c). It should be noted that with an increase in time from 30 to (40-60) min, the degree of sorption of manganese (II) cations increases insignificantly.

As for the sorption of V^{4+} cations, for dispersed (0.2 mm) and granular (0.7 mm) montmorillonite at 15 min of the process, the degree of their sorption is

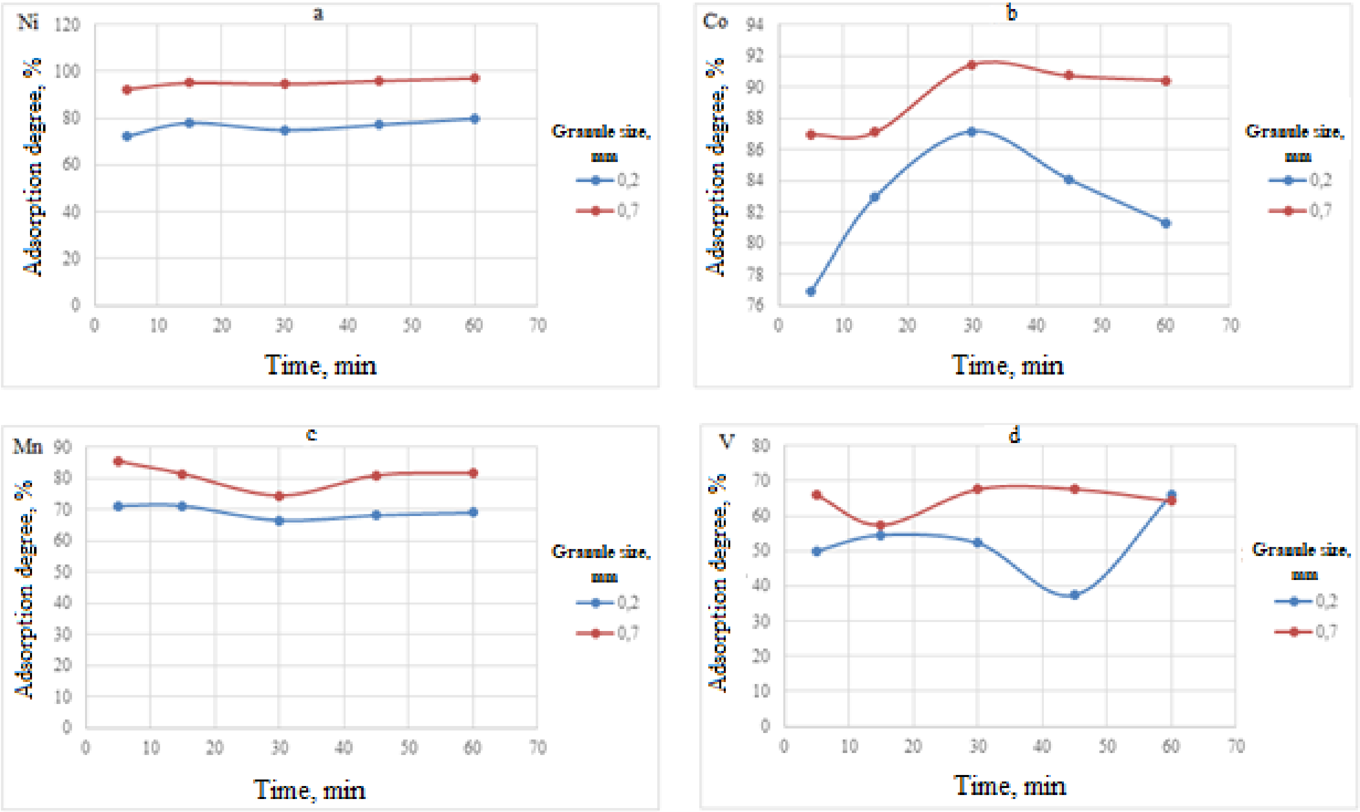

Figure 1 – Influence of the size of granules of montmorillonite on its sorption capacity in relation to cations of nickel (a), cobalt (b), manganese (c) and vanadium (d)

practically the same and amounts to (56.0-58.0)% (figure 1 c). Moreover, the sorption curve for coarse-grained montmorillonite has the opposite character of the sorption curve of the powdered sorbent. Thus, coarse-grained montmorillonite sorbs 15% more in the first 5 minutes of the process compared to the dispersed sample. With an increase in time from 5 to 15 min, the degree of vanadium sorption by granular MMT decreases by 8%, and in dispersed ones increases by 5%. In the system under study, the opposite processes occur: when coarse-grained MMT is used, desorption of sorbed cations from MMT into the solution takes place, while dispersed MMT is accompanied by sorption of ions. With an increase in the time from 15 to 30 min, the degree of sorption by granular MMT already increases to 68.0%, and, on the contrary, decreases to 52.0% with the hyperglymed. In this case, coarse-grained MMT adsorbs ions, while dispersed MMT is characterized by desorption of ions, which occurs most intensively in the interval of 20-30 min. At 60 min, the degree of sorption of V^{4+} cations becomes practically the same for both types of MMT(64,0 -66,0)%. Based on the data, it follows that in the sorption of vanadium, coarse-grained MMT is also more effective at 30 min of the process. Thus, in the sorption purification of wastewater from heavy metals, it is advisable to use montmorillonite with a granule size of 0.7 mm for 30 min.

The degree of purification of metal-containing aqueous medium significantly depends on time, temperature, concentration of sorbed cations and the rate of montmorillonite (S:L ratio).The study of the effect of temperature, time and consumption of montmorillonite was studied at a constant concentration of heavy metal cations equal to 200 mg/l (figure 2 a, b, c).

The analysis of the obtained results showed that the sorption curves depending on the factors under study for all cations are of the same type and are represented by almost rectilinear straight lines. However, the course of the ion sorption curves is determined by the process parameter. With the duration of the process, the sorption curves of cations have a weakly pronounced tendency to increase (figure 2 a), while with increasing temperature they slightly decrease (figure 2 b). With an increase in temperature, the degree of sorption of cations slightly decreases, which is due to a slight desorption of cations from the sorbent into the solution (figure 2b). Moreover, this tendency is most pronounced for the sorption of V (IV) cations, the degree of sorption of which decreases by 24% at 90°C. That is, an increase in temperature initiates the process of desorption of cations, but most of vanadium (IV) ions.

The most significant effect on the sorption of all cations is exerted by the S:L ratio (MMT norm). It follows from the results obtained that an increase in the load of the sorbent has a direct proportional effect on the residual content of all cations in the solution (figure 2 c). Thus, the best degree of its purification is achieved at the highest consumption of 1.5 g of MMT per 100 g of metal-containing solution and amounts to 82.64% Mn^{2+}, 85.59% Ni^{2+}, 86.36% Co^{2+} and 52.29% V^{4+}.

Based on the data, it follows that the duration and temperature of the process do not have a significant effect on the sorption capacity of MMT. The process of purification of a metal-containing solution in the presence of all studied cations is largely determined by the sorbent norm.

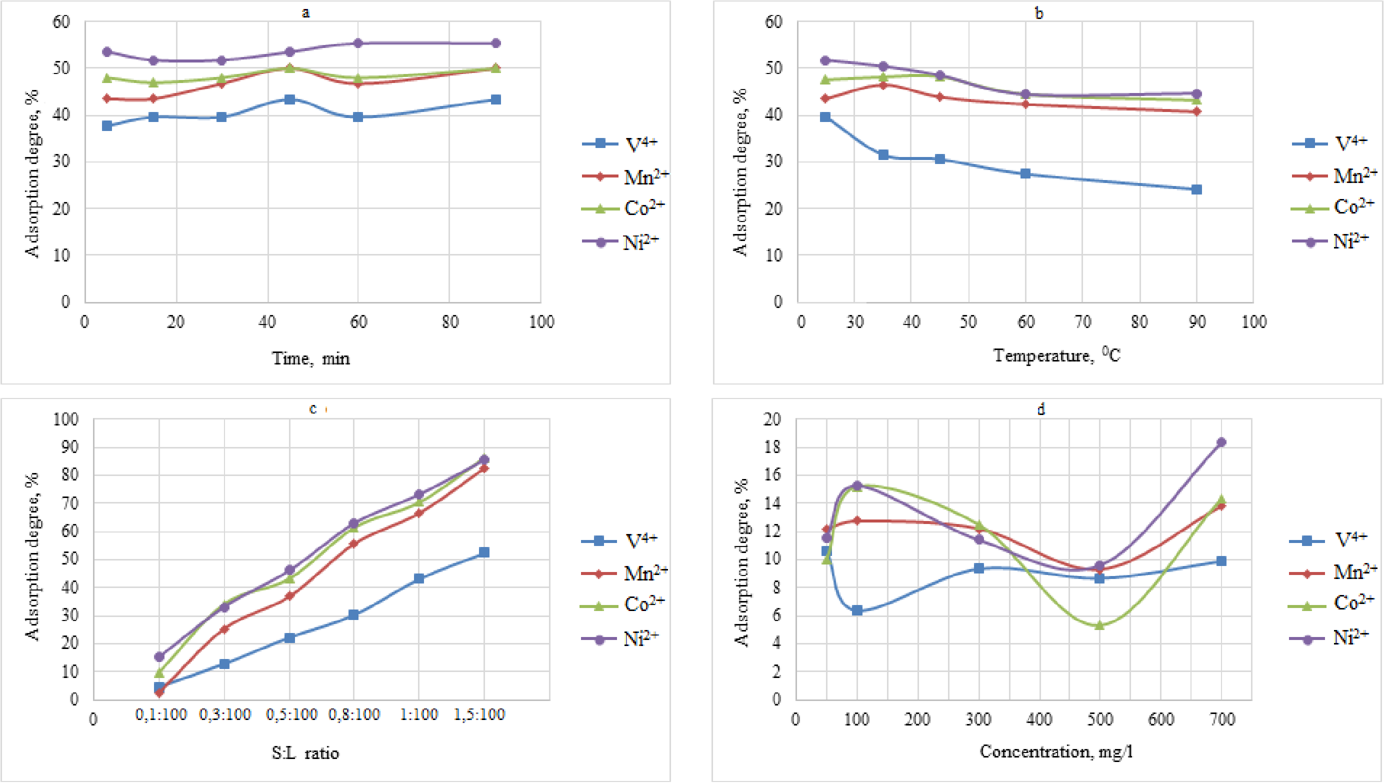

Figure 2 – Influence of various factors on the degree of sorption of Mn^{2+}, Co^{2+}, Ni^{2+}, V^{4+}cations in their joint presence

The influence of the concentration of the sorbed cations was investigated at a constant temperature of 25°C and the ratio S:L = 1.5:100 for 30 min. The sorption curves depending on the concentration of the sorbed cations have an abrupt (extreme) character (figure 2d). So the curves of sorption of cations Co^{2+} and Ni^{2+} have an identical character, on which max and min are prescribed at their concentration of 100 mg/l and 500 mg/l, respectively. When the content of cations is up to 50 mg/l, the process of their sorption occurs, from 50 to 500 mg/l – desorption, and in a more concentrated solution (500 mg/l) - sorption again.The process of sorption of Mn^{2+} and V^{4+} cations proceeds according to a different type, their sorption curves are characterized by the presence of one min at a concentration of 100 mg/l for V^{4+} ions and 500 mg/l for Mn^{2+}cations. At the indicated concentrations of tetravalent vanadium and divalent manganese, sorbed cations are released from MMT into the solution (desorption), which is apparently due to the tendency of the system to an equilibrium state.

The behavior of the sorbed cations in solution is possibly related to the size of their ions. The ionic radii of the Co^{2+} and Ni^{2+} ions are 0.78 and 0.74 Å, respecttively, and the closeness of the size of their ionic radii determines practically the same character of the sorption curves. The Mn^{2+} cation has a larger radius size (0.91 Å) compared to the two previous ions and in the range of their concentrations from 50 to 300 mg/l the degree of solution purification remains almost constant, desorption is recorded only in a concentrated solution at 500 mg/l. In quantitative terms, Co^{2+} and Ni^{2+} ions are sorbed more than Mn^{2+} cations, which affects the effect of ion size on the sorption capacity of MMT. However, the sorption of V^{4+} ions does not fit into this pattern. Having a small ionic radius (0.61 Å) in comparison with other cations, instead of the expected high degree of solution purification, MMT exhibits the lowest sorption capacity with respect to tetravalent vanadium. It is possible that the vanadyl cation VO^{2+} is sorbed from the solution, the ionic size of which is larger than not only the V^{4+} ion, but also the Co^{2+}, Ni^{2+}, and Mn^{2+} ions. As a result, first of all, montmorillonite adsorbs smaller ions (Ni^{2+}, Co^{2+}, Mn^{2+}), and vanadyl ion is sorbed on the remaining free sorption centers. It is this that can explain the lower degree of purification of the solution from vanadium for all studied factors in comparison with others. The degree of purification from vanadium (IV) is 34.0% less than the degree of purification from cobalt (II), 33.3% less than that of nickel (II) and 30.0% from manganese (II).

Graphic processing of the results obtained showed that, regardless of the factors affecting the sorption of cations, the sequence of sorbed cations in the system. According to the efficiency of absorption of Mn^{2+}, Co^{2+}, Ni^{2+}, V^{4+} ions by natural montmorillonite in their joint presence, they are arranged in the following order: $Ni^{2+} \geq Co^{2+} > Mn^{2+} > V^{4+}$.

The results of the conducted studies indicate the possibility of effective use of bentonite clays of the Tagan field in the purification of wastewater from heavy metal cations.

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Резюме

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СУЛЫ-ТҰЗДЫ ЖҮЙЕДЕН ТАБИҒИ МОНТМОРИЛЛОНИТ АРҚЫЛЫ АУЫР МЕТАЛЛ КАТИОНДАРЫН СОРБЦИЯЛАУ

«Mn^{2+} – Co^{2+} – Ni^{2+} – V^{4+} – H_2O – монтмориллонит» моделді жүйесіндегі ауыр металл катиондарына қатысты Таған кен орнының табиғи монтмориллонитінің сорбциялық қасиеттері зерттелді. Температураның, процесс ұзақтығы мен ерітінді концентрациясының, сондай-ақ сорбент мөлшерінің катиондардың сорбциялану дәрежесіне әсері қарастырылды. Сорбция процесінің оңтайлы жағдайлары (25°С, 30 мин, Т:Ж = 1,5:100) анықталды, осы жағдайларда ерітіндіні Co^{2+} катионынан тазарту дәрежесі 86,36 %, Ni^{2+}- 85,59 %, Mn^{2+} - 82,64 % және V^{4+} - 52,29 % құрайды. Сорбция қисықтарының сипаты сорбцияланатын катионның табиғатына байланысты. Табиғи монтмориллонитпен сорбциялану тиімділігі бойынша иондар келесі ретпен орналасады: $Ni^{2+} \geq Co^{2+} > Mn^{2+} > V^{4+}$. Жүргізілген зерттеу нәтижелері Таған кен орнының бентонитті саздарын ағын суларды ауыр металл катиондарынан тазартуда тиімді қолдану мүмкін екенін дәлелдейді.

Түйін сөздер: сорбция, табиғи монтмориллонит, ауыр металдар, сорбция, катиондар.

Резюме

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СОРБЦИЯ КАТИОНОВ ТЯЖЕЛЫХ МЕТАЛЛОВ ИЗ ВОДНО-СОЛЕВОЙ СИСТЕМЫ ПРИРОДНЫМ МОНТМОРИЛЛОНИТОМ

Исследованы сорбционные свойства природного монтмориллонита Таганского месторождения по отношению к катионам тяжелых металлов на модельной системе «$Mn^{2+} – Co^{2+} – Ni^{2+} – V^{4+} – H_2O$ – монтмориллонит». Рассмотрено влияние температуры, продолжительности процесса и концентрации растворов, а также нормы сорбента на степень сорбции катионов. Определены оптимальные условия процесса сорбции (25ºС, 30 мин, Т:Ж = 1,5:100), при которых степень очистки раствора составляет до 86,36 % от Co^{2+}, 85,59 % от Ni^{2+}, 82,64 % от Mn^{2+} и 52,29 % от V^{4+}. Характер кривых сорбции определяется природой сорбируемого катина. По эффективности поглощения природным монтмориллонитом ионы располагаются в следующем порядке: $Ni^{2+} \geq Co^{2+} > Mn^{2+} > V^{4+}$. Результаты проведенных исследований свидетельствуют о возможности эффективного применения бентонитовых глин Таганского месторождении в очистке сточных вод от катионов тяжелых металлов.

Ключевые слова: сорбция, природный монтмориллонит, тяжелые металлы, сорбция, катионы.

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