Improvement of Sorption Parameters of Nickel Ions on Bentonite in the Result of its Irradiation by Microwaves

L. Sysa, L. Shevchuk, A. Kontsur

The adsorption isotherms of nickel ions from aqueous solutions on bentonite, a natural argillaceous material, previously prepared using ultrahigh-frequency electromagnetic waves ("microwaves") were researched in the article. The phase composition of the sorbent was studied by applying the X-ray powder method. Bentonite sample being pre-wetted and irradiated by microwaves shows 2.7 times better sorption properties than untreated (native) sample, which was shown on the example of adsorption process of nickel ions from model solutions in static conditions. The sorption parameters prepared by using the "microwaved" and the native samples of bentonite were calculated according to the Langmuir adsorption equations. The barrier density of nickel in the irradiated sorbent is 16.4 mg/g (0.28 mmol/g), whereas for native bentonite the value of the analogous parameter is 6.0 mg/g (0.10 mmol/g). The reason for such an increase in sorption properties may be the change in the crystalline structure and distribution of micropores on the surface of the sorbent under the action of "microwaves" in the aqueous medium. It is suggested that the joint action of two factors – microwave irradiation and hydrothermal destruction – affects the near-surface structure of the clay material, distribution of the macro- and micropores, activation of the absorbing surface, which, in turn, leads to a change in the sorption parameters. The determinants in the pre-preparation of sorbent by "microwaves" are ultimate power and time of irradiation.

Keywords: water purification, sorbent, bentonite, nickel, activation, microwaves.

Introduction

Heavy metals, including nickel, are an important but dangerous component of natural water. In river unpolluted and poorly contaminated waters, the concentration of nickel varies normally from 0.8 to 10 μg/dm³; in contaminated it is several tens of micrograms in 1 dm³. The average concentration of nickel in seawater - 2 μg/dm³, in normal groundwater - about 10³ μg/dm³. In underground waters that are washed with nickel-containing rocks, the concentration of nickel sometimes increases to 20 mg/dm³ [1].

As a trace element, nickel is involved, mainly in the process of hematopoiesis and is part of the red blood cells. In addition, its role in the oxidative-reducing processes of the body is important. In tissues and organs is distributed as follows: muscle, liver, lungs, kidneys, pancreas, brain, thyroid gland. These are the bodies in which the basic processes of exchange occur.

Given this, the attention of many specialists and researchers in the field of water treatment is now focused on finding and improving the most effective methods of water treatment from excess heavy metal ions, including Nickel.

Sorption is one of the typical methods of water purification from pollutants, in particular, of the mentioned metals. The main problem of this method is the search for cheap, but high-performance sorbents for use in both the native and after regeneration. Significant energy and reagents for pre-purification, activation and regeneration of synthetic sorbents greatly influence the cost of water purification. In this plan, optimization of methods of using clay natural materials with high sorption characteristics is promising [2].

Bentonite clay is used in the processes of sorption purification for a long time - both for industrial and household purposes [3]. The use of these rocks as sorbents for the treatment of natural and sewage is relevant and of increasing importance as the prevalence of these materials, the simplicity of production and the corresponding low cost make the process of water treatment less costly [4].

A promising direction for increasing the efficiency of the process of sorption water purification and subsequent regeneration of sorbents is the use of ultrahigh-frequency electromagnetic radiation
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Comparison of bentonite sorption parameters of nickel ions from aqueous solutions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method of preparation</th>
<th>Mass ratio &quot;sorbent: solution&quot;</th>
<th>Limit sorption capacity (mg/g)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bentonite of the Zzryansky district (Kurgan region, Russia)</td>
<td>native, dried with 105 °С</td>
<td>1:100</td>
<td>0.12 (pH-7) 1.20 (pH-10)</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>soda activation</td>
<td></td>
<td>5.47 321</td>
<td></td>
</tr>
<tr>
<td>Bentonite of Tagansky district (Kazakhstan)</td>
<td>soda activation</td>
<td>unknown</td>
<td>0.60 35</td>
<td>[7]</td>
</tr>
<tr>
<td>Bentonite of Khakassy district (Altay)</td>
<td>soda activation</td>
<td>unknown</td>
<td>1.11 65</td>
<td>[8]</td>
</tr>
<tr>
<td>Bentonite &quot;commercial&quot; (Russia)</td>
<td>native</td>
<td>1:400</td>
<td>0.10 6.0</td>
<td>[9]</td>
</tr>
<tr>
<td></td>
<td>activated by ultrasound</td>
<td>1:40</td>
<td>0.33 19.2</td>
<td></td>
</tr>
<tr>
<td>The phase of montmorillonite isolated from</td>
<td>native</td>
<td>1:1000</td>
<td>0.44 – 0.56 26 - 33</td>
<td>[10]</td>
</tr>
<tr>
<td>Bentonite Dashukivsky district (Cherkasy region)</td>
<td>soda activation</td>
<td></td>
<td>2.37 – 3.05 139 - 179</td>
<td></td>
</tr>
</tbody>
</table>

I. The state of study of the problem

By chemical nature and phase composition bentonites are compositions of aluminosilicate minerals. The general formula of these minerals can be represented as $\{x(Al_{2}O_{3})\gamma(SiO_{2})\_z(\text{OH})\_m(H_{2}O\_n(\text{MeO})\}$, where MeO is metal oxides (iron, alkaline and alkaline earth metals, etc.).

The main components of bentonites, as a rule, are aluminosilicate materials such as montmorillonite, chlorite, hydromicans, and the like. In crystallochemical terms, they all have a negatively charged three-dimensional aluminosilicate frame with a strictly regular structure.

In the intervals of this framework there are hydrated positive ions of alkaline and alkaline earth metals, which compensate for the charge of the framework, and water molecules. In the adsorption cavities of these materials, only molecules of substances are absorbed, the critical size of which is less than the effective size of the input window [5].

The general physic-chemical characteristics of bentonite clays have a high specific surface area and high dispersion, which results in good adsorption rates, as well as a significant ability to swell (bentonite number), thermal stability, and the like.

In order to enhance the valuable properties (first of all, sorption) bentonites undergo activation or modification, which is used for a variety of physical and chemical procedures. The influence of these procedures on the process of sorption of nickel ions by bentonite was studied by many authors [6 - 10, etc.]. Typically, samples of bentonite without pre-treatment (native) and after chemical activation (soda, acids, organic reagents, etc.) were subjected to comparative study.

In tabl. 1, a small part of the results of the study of the sorption properties of bentonite in relation to nickel ions, obtained by different authors over the past decades, has been summarized. According to their data, the maximum sorption capacity of this sorbent for Nickel is: in the native state - from 6 to 30 mg/g; after activation with a solution of soda - more than 300 mg/g.

It should be noted a significant spread of values of the maximum sorption capacity for samples bentonite from different fields. In the aforementioned articles, the authors do not always indicate the granulometric composition of the samples, although the main reason for such a spread of results may be the difference in the size of the sorbent grains.

The question of the regeneration of popular classical sorbents after their natural and sewage cleaning was studied quite widely [11, etc.], but with regard to natural sorbents, much less attention is paid to scientific literature. Moreover, the effect of microwave EMF on sorption properties and the possibility of regeneration of clay materials were practically not studied.

The authors of this work have begun such studies in their previous publications - the study of sorption processes of biogenic ions on natural and stimulated microwave EMF bentonites [12, 13].

II. Research methodology

There are a number of methods for cleaning natural bentonite, which require considerable time and additional equipment. Since the important task of our research is to minimize the cost of sorption water purification, in this work we used an untreated sorbent sample. In particular,
bentonite of fine grinding, purchased in the general trading network (the so-called "commercial") was investigated.

To clarify the phase composition of the working sample of the sorbent, it was studied by X-ray diffraction analysis. Shooting a diffractogram of the sample of native bentonite (without special processing) was performed by powder method on the DRON-3 diffractometer using copper filtered radiation. The qualitative phase composition of the sample was determined by indexing the peaks of hkl of the corresponding minerals according to their table values d/n; the quantitative phase composition - by the integral intensities (areas) of the corresponding peaks of the diffractogram [14].

Sorption properties of bentonite were studied in static conditions. We investigated both a native ("commercial") and a pre-prepared combination method: washing it with distilled water at the same time as the effect of the microwave EMF.

It is known that the action of "microwaves" on water systems leads to their heating. That is, such a method of pre-treatment of sorbents combines their hydrothermal cleaning with high-frequency irradiation. This process can be considered and clearing of natural contaminants, and activation, and modification, so earlier we were invited to use the term "stimulation" [12].

In particular, for "stimulation" of the native bentonite, its weight gain of 1.0 g was placed in 250 ml glass flasks, poured 30 ml of distilled water and subjected to the action of an UHF EMB of average power for 180 seconds. After defending the resulting suspension, the residual rinsing water was carefully removed from the sorbent using a vacuum pump. In these flasks absorbent cleaning of working solutions was carried out.

As a source of microwave electromagnetic wave, used a generator based on the M-10 magnetron, which was designed and developed by the authors. The standard circuit of the device's inclusion is used - without pulse modulation; the radiation frequency - 2.45 GHz; Output power - 790 Watts. A horn antenna was used to better distribute and concentrate radiation.

Model solutions of nickel sulfate ("models") were made from dried salt qualification "clean" and distilled water. Working solutions were obtained from the model by multiple dilutions with distilled water. The influence of the acidity of the medium of the working solutions in the sorption process on the magnitude of the sorption parameters in this work was not investigated (the sorption process was carried out in a neutral medium, pH = 6). Studies were carried out at room temperature (22 - 24°C).

In a flask with native or microwave-prepared bentonite, 200 ml of the working solution was filled and the sorption purification process was performed: 3 times stirring and settling. The total duration of the contact between the bentonite and the solution was about 24 hours. After settling, the sorbates were carefully drained from the precipitate without filtration, and only then, to stabilize Ni\(^{2+}\) ions, small amounts of nitric acid were added to the solution until pH = 2.

Concentrations of Ni\(^{2+}\) ions in model and working solutions were determined by the atomic absorption method using known techniques on the C-115.M-1 spectrometer. Separate samples of working solutions (intra-laboratory control) were studied on the content of nickel ions by the method of photometric determination of this ion by reaction with dimethylglyoxime using photolorimeter KFK-2 [15].

Preparation of sorbent, making model and working solutions, direct sorption process was carried out in laboratory eco-safety LDU BZD; atomic absorption studies - in the laboratory of industrial toxicology of the Danilo Galitsky Lviv National Medical University.

The development of experimental results - the construction of isotherms of adsorption, their graphical and analytical processing, calculations of sorption parameters - were carried out according to classical methods: Langmuir, Freundlich, Dubinin-Radushkevich, and others. [16]. According to the numerical values of the criteria for statistical estimation, those models that most accurately describe each isotherm are selected.

III. Results and discussion

Phase analysis of the diffractograms of the native sample of bentonite has revealed that it contains 4 minerals in approximately equal amounts: hydromicas (about 27% at.); montmorillonite (about 25% at.); quartz (about 22% at.) and chlorite (about 20% at.); among impurities - calcite, sylvinite and other minerals.

The diffractogram of the native sample of bentonite (CuK\(_\alpha\) - rad.) after the corresponding digital processing is shown in Fig. 1; the results of its phase crystallochemical analysis - in Table. 2.

As a model, an aqueous solution of nickel sulfate with a concentration of 250 mg/dm\(^3\) (by metal) was made. A further series of working solutions in the range of concentrations of Ni\(^{2+}\) ions from 250 to 6.6 mg/dm\(^3\) was obtained by further stepwise dilution of it in 1.5 times.

Analysis of adsorption isotherms of nickel ions from model solutions on samples of bentonite, which did not undergo preliminary processing (native), and irradiated microwave EMF for 180 s in a small amount of water (that is, "stimulated"), showed the following.

The most distinct dependence in both cases was shown by the treatment of isotherms according to the classical Langmuir linear equation (Formulas 1 and 2, Figure 2):

\[
 q_e = \frac{C_\infty - C_e}{m} V \tag{1}
\]

\[
 C_e = \frac{1}{q_m K} + \frac{1}{q_m} C_e \tag{2}
\]

where \(q_e\) is the equilibrium sorption capacity, mmol/g; \(q_m\) - limiting sorption capacitance (monolayer receptivity), mmol/g; \(C_\infty\) and \(C_e\) - concentration of copper ions before and after sorption, mmol/l; \(m\) - mass of bentonite, g; \(V\) - volume of solution, l; \(K\) - is the constant of sorption equilibrium.

The general course of isotherm adsorption in both cases is similar, but the values of sorption parameters are
noticeably different. In particular, the constants of the trend lines calculated by equations (1) and (2) indicate that the total nickel boundary capacity of the "stimulated" sorbent is 2.7 times higher than that of the untreated sample (Table 3). In turn, the constant of the sorption equilibrium of the irradiated sample is 22% less than that of the native one. This suggests that the sorption equilibrium between the solution and the "stimulated" sorbent occurs 1.3 times faster than in the case of a native sample.

As is known, the mechanism of sorption of contaminants on clay materials is quite complex and includes a number of physic-chemical processes, including the Van-der-Waals interaction of sorbate molecules with a developed surface of microcrystals of silicates and electrostatic interaction of polarized sorbate molecules (ions) with positively charged parts of the surface of the sorbent, containing the ions of H⁺, Al³⁺ and others [5]. In addition to the molecular and electrostatic components, the ion exchange mechanism makes a significant contribution to the sorption process in bentonite clay [17].
Clay minerals, which have similar elements of structure (layers of tetrahedra and octahedra), differ in their methods of combining them into packages. In addition, they are distinguished by the nature and energy of communication between these packages, the nature of the settlement of tetrahedral and octahedron nets and a whole set of other, more subtle structural features. Together, all these factors create a huge variety of physical and chemical properties of individual representatives of aluminosilicates, since the properties of any disperse material are largely determined by the structure of its constituent parts.

At present, two main reasons for the cation exchange of clay materials can be distinguished:

1) the replacement of fourvalent silicon with trivalent aluminum in tetrahedral grids and trivalent aluminum with lower valence ions in octahedral grids, which causes the appearance of a negative uncompensated charge of a structural cell;

2) the breakdown of chemical bonds in the tetrahedral and octahedral grids of crystals of clay minerals, which leads to the appearance on their lateral sides of hydroxyl groups, hydrogen atoms in which they are able to enter the exchange reaction.

In the first case, the newly created negative charge of the crystal lattice is counterbalanced by intrastructural changes: for example, the charge opposite to the sign, which arises due to the replacement of some of the structural oxygen atoms with hydroxyl ions. The same effect is created by "own" (intrastructural) cations of metals, which can occupy a part of vacant octahedral positions.

In addition, the excess negative lattice charge can be compensated by non-structural exchange cations. They are most often located on the basal planes of particles of clay material. The energy of the interaction of such ions with the surface depends not only on their valence and size, but also on the location of the lattice charge.

In particular, the charges due to the heterovalent isomorphism in the octahedral grid are farther from the surface of the packets than the charges that arise due to non-stoichiometric substitution in the tetrahedral grids. Accordingly, cations that neutralize the negative charge of the octahedral grid will be bound to the surface by weaker forces compared with cations that neutralize the charge of the tetrahedral grid.

If the charge density of tetrahedral grids of minerals of type 2: 1 is high (1.5 units per element cell and above), but as its compensator stand large single charge cations, then they, except for cations on the basal faces of the crystal, are, in fact, unchangeable (for example, inter-packet ions K⁺ in mica).

In the second case, the main role is played by the properties of the hydroxyl groups themselves. If they are related to cations of the Al³⁺ or Mg²⁺ octahedron layer, then they can, in the first approximation, be equated with OH-groups on the surface of hydrated aluminium or magnesium oxides.

Thus, along with the isomorphic substitution in the crystalline lattice, the source of the cation exchange

### Table 3
Parameters of the sorption process of nickel ions on bentonite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Limit sorption capacity (mmol/g)</th>
<th>Constant of sorption equilibrium (mg/g)</th>
<th>Multiplicity of change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native</td>
<td>0.102</td>
<td>5.98</td>
<td>2.74</td>
</tr>
<tr>
<td>Stimulated</td>
<td>0.279</td>
<td>16.40</td>
<td>1.28</td>
</tr>
</tbody>
</table>
ability of the clay minerals is also the hydroxyl groups located on the lateral faces and edges of their crystals and bound to the silicon atoms. The appearance of a negative charge in the Si-O-grids of these materials due to the isomorphous substitution of Al$^{3+}$ → Si$^{4+}$ in the part of the tetrahedra increases the acidity of the Si-OH groups, and, therefore, the exchange of their protons into other cations becomes considerably facilitated with respect to silica.

In other words, when considering the causes of the cation exchange ability of clay minerals, it is entirely natural to speak not about the choice between the two mechanisms described above for ion exchange, but about the role they play in determining the capacity of this exchange for a particular member of the group of phyllosilicates.

For example, in cases of montmorillonite and vermiculite, isomorphic substitutions create 80% of the total capacity of the cation exchange, and 20% of the capacity is a consequence of the "violation of ties" [5]. Confirmation of this assumption can be the fact that after thermal treatment at 250-300 °C Li-forms of individual samples of montmorillonite, which in the native state practically do not contain isomorphous substitutions in the tetrahedral layers, there was a fall in their exchange capacity by 82-85% [10].

Apparently, in the process of irradiation of the surface of aluminosilicate crystals by "microwaves" in direct contact with water molecules, the sorption mechanism varies (in comparison with the native bentonite). In particular, it is likely that, in addition to the ion exchange mechanism (replacement of Ca$^{2+}$, Mg$^{2+}$ or alkali metals on Ni$^{2+}$), the physical sorption of nickel ions in the newly created micropores also takes effect.

The authors of this article believe that the joint action of two factors (microwave irradiation and hydrothermal destruction of the surface of the sorbent) significantly affects the crystalline structure of the clay material, the distribution of macro and micropores, activation of the absorbing surface, etc., which in turn leads to a change sorption parameters.

Confirm or reject this assumption could be based on the results of precision X-ray diffraction analysis of samples of bentonite, irradiated microwave EMF with simultaneous washing with water, but such works are rather specific and worthy of a separate study.

In any case, it can be argued that in comparison with the raw sample, microwave-irradiated bentonite has the best sorption characteristics of nickel ions, therefore it can be a promising sorbent for the purification of natural and sewage from these pollutants.

The decisive factors in the preliminary preparation of the sorbent with the help of microwave EMF obviously should be the optimum power and dose of radiation. The very process of manufacturing and adjusting the installation for microwave radiation is simple, the cost of electricity during its operation is relatively small, so the economic benefits of using such a method can be tangible.

**Conclusions**

1. The absorption isotherms of nickel ions from aqueous solutions on samples of natural (untreated) and prepared using ultrahigh-frequency irradiation of bentonite have been studied.

2. It is shown that irradiation of this sorbent of microwave EMF simultaneously with washing with its pure water increases the value of the limit sorption capacity by nickel by 2.7 times.

3. The reason for such an improvement in sorption properties may be the change in the crystalline structure of the clay material, the distribution of the macro and micropores, the activation of the adsorbing surface.

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Покращення параметрів сорбції іонів нікелю бентонітом внаслідок опромінення його надвисокочастотними хвилами

Досліджено сорбційні характеристики за Нікелем природного глинистого матеріалу бентоніту, підготовлених спеціальним опроміненням його надвисокочастотними електромагнітними хвилами («мікрохвилами»). Перед початком сорбційної очистки моделей розчинів вивчено фазовий склад вказаного сорбенту рентгенівським методом порошку. На прикладі процесу сорбції іонів Нікелю з водних розчинів у статичних умовах показано, що зразок цього сорбенту, попередньо зволожений та опромінений «мікрохвилами», виявляє у 2,7 раза кращі сорбційні властивості, ніж необроблений (нативний) зразок. Розраховано сорбційні параметри підготовленого з використанням «мікрохвиль» та нативного зразків бентоніту за рівняннями моделі Ленгмюра. Гранічна ємність за Нікелем опроміненого сорбенту становить 16,4 мг/г (0,28 ммоль/г), у той час як для нативного бентоніту значення аналогічного параметру складає 6,0 мг/г (0,10 ммоль/г). Причиною такого посилення сорбційних властивостей може бути зміна кристалічної структури та розподілу мікропор на поверхні сорбенту під дією «мікрохвил» у водному середовищі. Висловлено припущення, що спільна дія двох факторів — опромінення «мікрохвилами» та гідротермальна деструкція — впливає на приповерхневу структуру глинистого матеріалу, розподіл макро- та мікропор, активізацію поглинаючої поверхні, а це, у свою чергу, призводить до зміни сорбційних параметрів. Вирішальними факторами у процесах попередньої підготовки сорбенту за допомогою «мікрохвил» можуть бути оптимальна потужність та час опромінення.

**Ключові слова:** очистка води, сорбент, бентоніт, Нікель, активізація, мікрохвилі.

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