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Use of Microwaves to Activate Bentonite in the Processes of Sorption of Nickel Ions from Concentrated Aqueous Solutions

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The physicochemical parameters of the process of sorption water purification from compounds of Nickel with clay sorbent in static conditions are studied. The absorption isotherm of ions of this metal from concentrated aqueous solutions on samples of bentonite using ultrahigh-frequency irradiation (microwave) is analyzed. Most correctly, it is described by the linear equation of Langmuir. It is shown that irradiation of this sorbent by microwaves in the process of nickel ion sorting almost 2 times increases the value of the marginal sorption capacity for this metal (in comparison with the method of "stimulation" - preliminary washing of bentonite with pure water under the action of microwaves). The results of the study of spent bentonite by scanning electron microscopy, energy dispersion and X-ray diffraction analysis indicate that the metal under action of the microwave is deposited on the surface of the bentonite not only in the form of an adsorbed monolayer of ions, but also in the form of a separate crystalline phase, nickel silicate. Changes in the acidity of the medium during sorption purification under the action of microwave are observed: from pH \approx 5.7 ... 6.5 (before exposure) to pH \approx 6.7 ... 7.1 (after irradiation). Confirmed assumption about that under the action of microwaves in the aqueous medium there is a partial destruction of the silicate framework of clay sorbents with the release of silicon ions SiO_3^{2-} . These ions undergo hydrolysis, as a result of which the pH of the solution increases. Also, the direct discontinuity of the Si-O bonds in the near-surface groups $\equiv\text{Si-OH}$ is not excluded, which leads to an increase in the number of "free" hydroxyl groups.

Keywords: aqueous solutions, nickel, purification, sorbent, bentonite, activation, microwave.

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Introduction

The problem of sewage and natural water treatment has been and remains relevant. In this regard, sorption is one of the main methods of water purification from pollutants. An important problem of such a method is the search for cheap, but high-performance sorbents.

Significant amounts of energy and reagents for pre-purification, activation and regeneration of synthetic sorbents increase the cost of water purification. In view of this, the use of clay natural materials with high sorption characteristics is a promising scientific and practical direction [1].

Among other natural sorbents, bentonite clay is used in sorption purification processes for a long time - both for industrial and domestic purposes [2].

The general physical and chemical characteristics of bentonite clays have a high specific surface area and high dispersion, which results in good adsorption performance. The general formula of these minerals can be represented as



where MeO_k - metal oxides (iron, alkaline and alkaline earth metals, etc.). By chemical nature and phase composition bentonites are compositions of aluminosilicate minerals: montmorillonite, chlorite, hydromicans, etc.

In order to enhance the valuable properties of bentonites are subject to activation or modification, which uses a variety of physical and chemical procedures. As a rule, it is calcination, chemical activation with soda, acids, organic reagents, etc. [3].

In recent decades, the promising direction of increasing the efficiency of the process of sorption water purification is the use of ultrahigh-frequency electromagnetic radiation (UHF EMR, or "microwave") [4, 5]. However, the effect of microwave EMR on the sorption properties of precisely clay materials was studied very little.

Among heavy metals, pollutants of wastewater, Nickel occupies a special place. He is involved in the process of hematopoiesis and is a member of the red blood cells. In addition, its role in the oxidative-reducing

processes of the body is important.

At the same time, Nickel is a dangerous component of natural water. In river contaminated and poorly contaminated waters, the concentration of Nickel varies normally from 0.8 to 10 $\mu\text{g}/\text{dm}^3$; in heavily contaminated it is several tens of micrograms in 1 dm^3 .

Many scientific and technical developments of specialists and researchers in the field of water purification are now focused on finding and improving the most effective methods of water purification from excess heavy metal ions, including Nickel.

The presented work is a continuation of a series of previous studies of authors, which studied the change in the sorption parameters of bentonite under the influence of microwave EMR [6 - 8]. Among other water pollutants, the object of the study also acted Nickel compounds. In particular, in the previous series of works, the authors investigated the effect of microwaves on the sorption of Nickel ions by bentonite from dilute aqueous solutions [9].

The purpose of this work was to continue the study of the parameters of sorption of Nickel ions from water systems on bentonite using microwave EMR, but now from more concentrated solutions and the modified technique.

I. Methodology for conducting research

In the present series of experiments, model solutions of Nickel salts, similar in size to the actual waste water of industrial enterprises of the metallurgical sector, were used. In addition, the sorbent treatment procedure was changed by microwaves, and the sorbent itself was investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersion analysis (EDA) methods before and after contact with solutions.

For the production of a model solution of Ni^{2+} salt ("models"), Nickel (II) chloride hexahydrate was used, dried at 90 °C for 2 hours. From this model solution a series of working solutions in the range of concentrations of Ni^{2+} ions from 720 to 140 mg/dm^3 was obtained by stepwise dilution of it in 1,3 times. Such a distribution of concentrations is selected in order to have its lower values partially overlap with higher values of concentrations of working solutions in the previous series of studies [9]. This made it possible to compare the results obtained with the front series now and to deduce certain patterns.

The basic sorption parameters of bentonite (maximum sorption capacity and the constant of sorption equilibrium), as in the previous series, were studied under static conditions. The study was subjected to both a native sample (without irradiation of the microwave EMD) and activated by a new, modified method: the working solution was irradiated by microwaves directly during the sorption process.

In particular, the samples of the "Nat" series were studied as follows: the native ("commercial") bentonite weights of 1.0 g were placed in 250 ml glass bottles and poured 100 ml of the working solutions of Nickel (II) chloride. After several stirring (at intervals of about 1

hour) and maintaining the suspensions obtained (about 12 hours), the purified working solutions were gently drained and their residues removed from the sorbent using a vacuum pump. The solutions were filtered and small amounts of nitric acid were added to them until pH = 2 was obtained to stabilize Ni^{2+} ions. Preparation and sorption purification of the working mixtures was carried out at room temperature, and the spent bentonite after pouring the solutions was placed together with the flask in the oven at 90 °C.

In a series of specimens "DIR" (*Direct Irradiation*), the native sorbent was not washed with water, as in previous work [9], but immediately filled with a working solution of Nickel (II) chloride. The flask was shaken and placed with the suspension in a microwave oven. In it there was a "direct irradiation" of the working suspension for 300 seconds (with intermittent mixing). After cooling, as in the "Nat" series, the working solutions were carefully drained off, the residues were removed from the sorbent by means of a vacuum pump, filtered and added acid. The spent bentonite was placed together with the flask in a drying oven at 90 °C.

Preparation and sorption purification of "Nat" working solutions were carried out at room temperature. At the same time, sorption purification of solutions of the series "DIR" occurred at higher temperatures due to heating the solution in microwaves.

A detailed study of the dependence of the sorption parameters of bentonite on the temperature of the working solution under the conditions of the "DIR" series is difficult, since the heating of the working suspension of microwaves occurs very quickly and unevenly. In particular, after 300 seconds of irradiation, one suspension was heated to a boil, while the other - to a hot but not boiling state.

The same applies to the study of the dependence of the sorption parameters of bentonite on the acidity of the medium. As already mentioned above, the working solutions were obtained from the model by multiple dilutions with distilled water. At the same time, the acidity of the solutions changed significantly: from pH = 5.7 (concentrated "model") to pH = 6.5 (diluted working solution).

A detailed study of these issues - dependences of sorption parameters of bentonite "direct irradiation" on the power of microwaves, the time of irradiation, the frequency and ways of mixing the suspension, temperature and acidity of the environment, etc. - the authors plan to devote a separate series of studies.

As in previous works [6, 9], as a source of microwave electromagnetic waves, an author-made generator was used, executed on a magnetron of the model M-10; the radiation range - 2.45 GHz; output power - 790 Watts.

The equilibrium concentrations of Ni^{2+} ions in model and working solutions were determined by the atomic absorption method on the C-115.M-1 spectrometer [10]. For the implementation of intra-laboratory control, individual samples of working solutions were studied on the content of Nickel ions by electricphotocolormeter KFK-2 (reaction with dimethylglyoxime [11]).

All stages of the preparation of sorbent, the manufacture of model and working solutions, as well as

the process of their sorption purification, were carried out in eco-safety laboratory Lviv State University of Life Safety. Here also carried out photometric work. Atomic absorption studies of solutions before and after sorption were performed at the laboratory of industrial toxicology of the Danylo Halytsky Lviv National Medical University.

For the construction of isotherms of adsorption, their graphical and analytical processing, calculations of sorption parameters, etc., the classical methods of Langmuir (formulas 1 and 2), Freundlich, Dubinin-Radushkevich and others are used [12]. The models that most accurately describe each isotherm are selected according to the numerical values of the criteria for statistical estimation.

$$q_e = \frac{C_0 - C_e}{m} V \quad (1)$$

$$\frac{C_e}{q_e} = \frac{1}{q_\infty K} + \frac{1}{q_\infty} C_e \quad (2),$$

where q_e is the equilibrium sorption capacity, mmol/g; q_∞ - limiting sorption capacitance (monolayer), mmol/g; C_0 and C_e - concentration of ions of Nickel before and after sorption, mmol/dm³; m - mass of bentonite, g; V - volume of solution, dm³; K is the constant of sorption equilibrium.

Investigation of the microstructure of bentonite samples was carried out on the basis of a raster microscope of electronic microanalyser REMMA-102-02. Scanning of the surface of the samples was carried out using an electron beam with a diameter of several nanometers and an electron energy of 0.2 - 40 kV. The range of the change in the multiplicity of the increase was 10 - 20.000; the resolution was about 5.0 nm.

The main images obtained from an electron microscope were images of elastically reflected (back-scattered, BSE) and secondary (SE) electrons. Two types of BSE - topological (TOPO) and compositional (COMPO) - have been applied. In TOPO mode, the relief of the investigated surface was observed, in COMPO - phase contrast, where each phase of the sample has a brightness of light proportional to its averaged atomic number.

At the same microscope samples of bentonite were investigated on the elemental composition. As is well-known [13], with the help of an electron beam, a spectrum of characteristic radiation is obtained, whose lines are detected by the presence of chemical elements (high-quality EDA). Comparison of the intensities of the corresponding lines for the sample and for the standard allows for quantitative EDA. The range of the analyzed elements - from number 5 (boron) to number 92 (uranium). The probes in the microanalysis were 1 to 2 nA, the accelerating voltage was 20 kV.

The XRD bentonite samples obtained after sorption of Nickel in both variants were carried out by the powder method by the values of the reflection angles of the diffractogram (2θ , degrees), the interplanar distances (d , Å), and the relative intensities (I_{rel}) of the diffraction peaks (hkl), using the standard interplanar tables distances of minerals. For the correlation of the areas of the corresponding peaks of hkl to their total area, the

quantitative content of the main phases in the sample (% at.) is calculated [14].

The diffractogram was recorded on a DRON-3 (copper-filtered radiation) diffractometer, in the $\theta/2\theta$ scan mode, at a rate of 1 deg/min.

II. Results and discussion

In fig. 1 shows a graph of the dependence of adsorption of Nickel ions on their equilibrium concentration, obtained in the present series (dark markers). Near (light markers), a part of the results of the previous series of works [9] is depicted, where more dilute solutions and other sorbent activation procedure were used.

Comparing these two graphs, you can note the following. In the previous series, bentonite was used, preliminary washed with pure water under the action of the microwave EMB (so-called "stimulated"). In this case, the isotherm adsorption is faster than saturation, but the value of the maximum sorption capacity of such a sorbent is lower than in the new series.

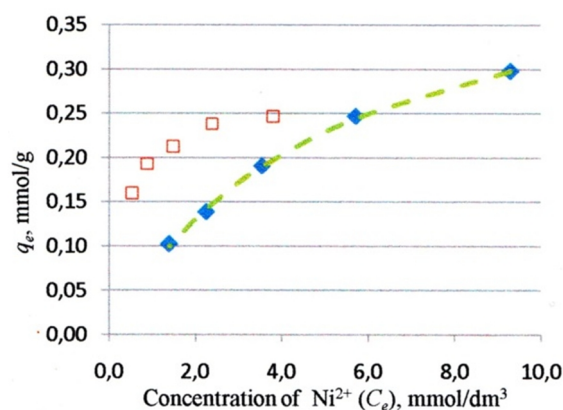


Fig. 1. Dependence of adsorption of Nickel ions on their equilibrium concentration on "stimulated" bentonite [9] and after "direct irradiation".

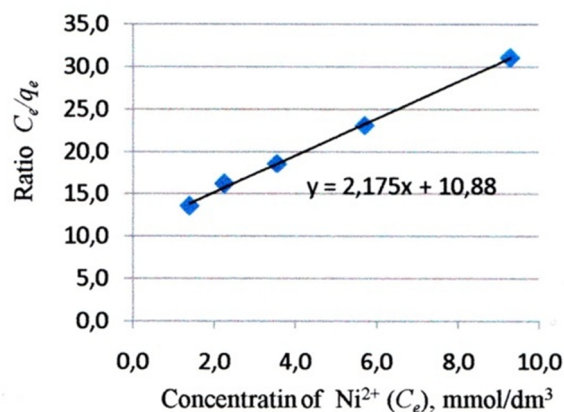
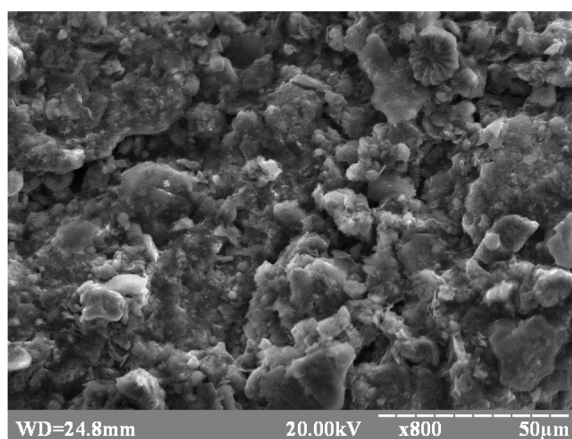
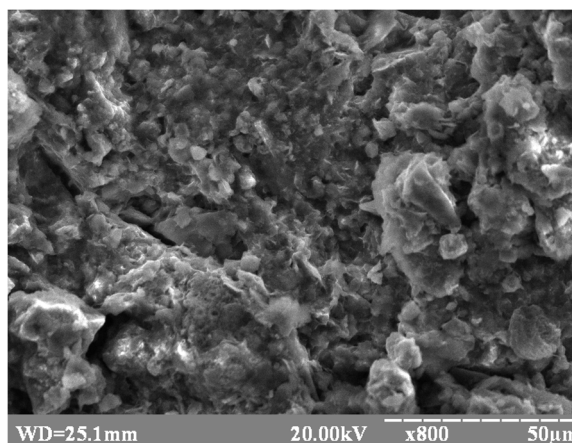


Fig. 2. Linearization of adsorption graph of Nickel ions on bentonite "direct irradiation" by model Langmuir.



a)



b)

Fig. 3. Microphotos of the bentonite surface: a - native; b - "direct irradiation" in a solution of Nickel salt.

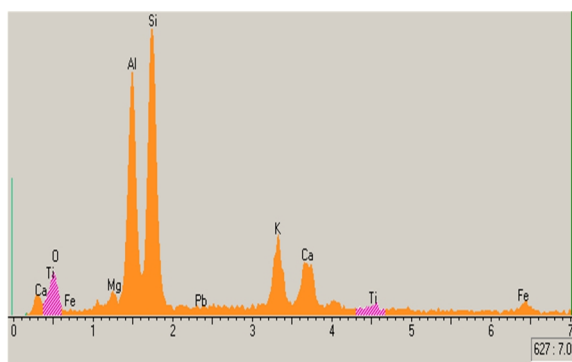


Fig. 4. The spectrum of qualitative EDA of "dark" part of microphotographs of a sample of bentonite from a series of "direct irradiation".

To confirm this fact, the calculations of the "direct exposure" bentonite sorption parameters were performed on several well-known models [12]. The clearest dependence was shown by the processing of the current adsorption curve obtained by the classical linear equation Langmuir (formulas 1 and 2, fig. 2).

The value of the limiting sorption capacitance for Nickel bentonite "direct irradiation" obtained from these calculations is $q_e = 26.9$ mg/g (0.49 mmol/g), which is

almost twice as much as in the case of "stimulated" bentonite [9].

Such a difference could be explained by an increase in the number and size of the micropores on the bentonite surface after irradiation by microwaves in the aqueous medium. However, the same procedures were used in the series of "stimulated" bentonite. Obviously, the key to changing the sorption parameters of this material in the case of "direct irradiation" is precisely the presence of metal ions in the process of action of microwaves on the aluminosilicate surface.

To solve this issue, a number of additional studies on native and worked out samples of bentonite were carried out using the methods of SEM, EDA and XRD.

Among the significant number of articles obtained by the authors of the microphotographs bentonite of different degrees of processing, the greatest interest was caused by the image of bentonite samples of a series of "direct irradiation". They can be seen in separate white microcrystals of light color, which were not in the microphotographs of native bentonite.

In fig. 3 microphotographs of these samples of bentonite are presented: a) - without activation (series "Nat"); b) - after activation by "direct irradiation" of the sorbent in a solution of Nickel salts (series "DIR"). The magnification of the image and the scale ruler are shown below the microphotos.

When shooting in the COMPO mode, these microcrystals looked more "light" (the presence of heavy elements - for example, Nickel) on the general "dark" background of the aluminosilicate phase (light elements).

On the basis of this fact, we suggested that the sorption exclusion of Nickel from aqueous solutions under the action of the microwave occurs not only by the classical adsorption mechanisms (deposition of the surface monolayer ions), but also by the formation of microcrystals of a single Ni-containing phase or of an individual chemical compound of Nickel.

The EDA spectra obtained on the same microanalyzer showed that the main part of the material of the "DIR" series samples is classical aluminosilicates with a significant content of Mg, Ca, K and Fe ("dark" background, fig. 4), and "light" microcrystals are the phase with significant content of Nickel. The results of quantitative elemental EDA (excluding Oxygen) indicated the presence in this phase of more than 80% wt. of Nickel.

That is, the results of the EDA confirmed that "light" microcrystals on the surface of the bentonite after deposition on it Nickel under the action of a microwave is an individual chemical compound of this metal. Taking into account the noticeable quantities of these crystals, the authors suggested that they would be detected by an X-ray diffraction analysis, whose sensitivity is approx. 5% at.

In relation to the diffractograms of the native sample of bentonite (series "Nat"), given in the previous publication of the authors [9], the distribution of peaks was slightly changed on the diffractogram of the spent bentonite of the "DIR" series. In particular, by changing the intensity of the corresponding reflections hkl , it can be argued that in the irradiated sorbent the relative content of montmorillonite (up to 33% at.) and quartz (up

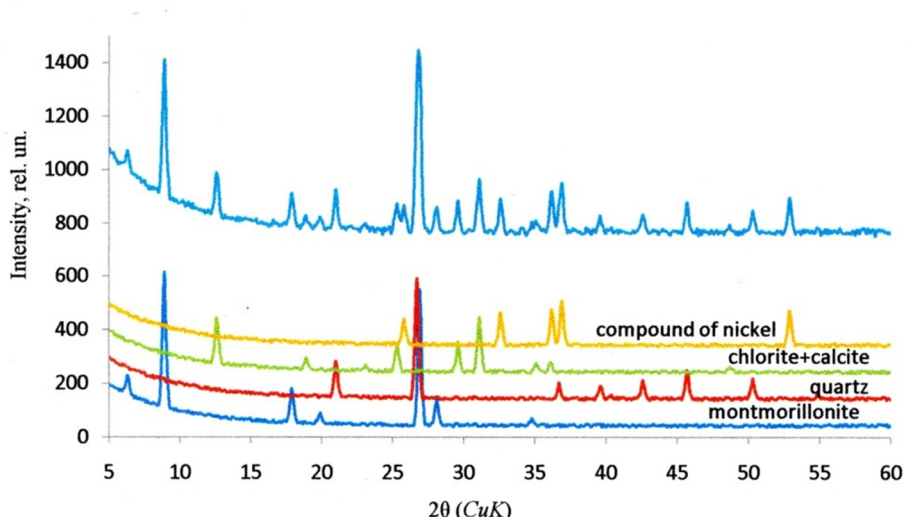


Fig. 5. Results of the XRD analysis of diffractograms of the bentonite sample of the "DIR" series after interaction with the solution of Nickel salt.

to 30% at.) increased, while the intensity of such phases as chlorite and calcite decreased. And most importantly - small, but noticeable peaks of a new phase appeared: at 25.8; 32.6; 36.3; 36.8 and 52.9 degrees (2θ).

The phase analysis of the diffractograms of the spent bentonite of the "DIR" series after the sorption purification of the aqueous solution of Nickel salts is shown in fig. 5.

Having developed a database of crystalline structures of probable new phases, which may include Nickel, Silicon, Chlorine, Oxygen and Hydrogen (correspondingly, chloride, silicate, Nickel hydroxide or their hydrated forms) and constructing the corresponding theoretical diffraction patterns [14], the authors determined that these new peaks may belong to the compound $Ni_2[SiO_4]_2$.

That is, the precipitation of Nickel on bentonite can occur not only by sorption precipitation or ion substitution, but also in the form of microcrystals of an individual compound - insoluble Nickel silicate.

Another important point concerns the change in the acidity of the medium in the working solutions before and after exposure. The pH of the suspensions of the "DIR" series after the end of sorption increased significantly with respect to the initial values: from pH \approx 5.7 ... 6.5 (as stated above) to pH \approx 6.7 ... 7.1.

This fact confirms the assumption by many authors [4, 5, 15, etc.] that under the action of microwaves in the aqueous medium there is a partial destruction of the silicate frame of clay sorbents with the release of SiO_3^{2-} silicate ions. These ions are hydrolyzed, as a result of which the pH of the solution increases.

In addition, the direct discontinuity of the Si-O bonds in the near-surface groups $\equiv Si-OH$ can not be excluded, which leads to an increase in the number of "free" hydroxyl groups.

Under such conditions, additional adsorption of Nickel on bentonite may be due to stimulated

crystallization microwaves on the surface of a sorbent of insoluble silicates or hydroxysilicates of this metal. Also, one can not reject the probability that under the action of the microwave EMR, in the presence of polar water molecules, there are favorable conditions for the formation of centers of crystallization of the salts of sufficiently active metals on the surface of the inert aluminosilicate phase.

Conclusions

1. The absorption isotherm of Nickel ions from concentrated aqueous solutions on samples of bentonite using ultrahigh-frequency irradiation is analyzed. Most correctly, it is described by the linear equation of Langmuir.

2. It is shown that the irradiation of this sorbent of microwave in the process of Nickel ion sorting almost 2 times increases the value of the marginal sorption capacity for this metal, as compared with the method of "stimulation" - preliminary washing of bentonite with pure water under the action of a microwave.

3. The results of the study of spent bentonite by scanning electron microscopy, energy dispersion and X-ray diffraction analysis indicate that the metal under action of the microwave is deposited on the surface of bentonite not only in the form of an adsorbed monolayer of ions, but also in the form of a separate crystalline phase - Nickel silicate.

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Використання мікрохвиль для активації бентоніту у процесах сорбції іонів нікелю з концентрованих водних розчинів

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Вивчено фізико-хімічні параметри процесу сорбційного очищення води від сполук Нікелю глинистим сорбентом у статичних умовах. Проаналізовано ізотерму абсорбції іонів цього металу з концентрованих водних розчинів на зразках бентоніту з використанням надвисокочастотного опромінення (мікрохвиль). Найбільш коректно вона описується лінійним рівнянням Ленгмюра. Показано, що опромінення цього сорбенту мікрохвилями у процесі сорбування іонів Нікелю майже у 2 рази збільшує значення граничної сорбційної ємності за цим металом (у порівнянні з методом «стимуляції» - попередньої промивки бентоніту чистою водою під дією мікрохвиль). Результати вивчення відпрацьованого бентоніту методами скануючої електронної мікроскопії, енергодисперсійного та рентгенофазового аналізу вказують на те, що згаданий метал під дією мікрохвиль осаджується на поверхні бентоніту не тільки у вигляді адсорбованого моношару іонів, але й у формі окремої кристалічної фази – силікату Нікелю. Спостерігаються зміни кислотності середовища в процесі сорбційної очистки під дією мікрохвиль: від рН $\approx 5,7 \dots 6,5$ (перед опроміненням) до рН $\approx 6,7 \dots 7,1$ (після опромінення). Підтверджено припущення про те, що під дією мікрохвиль у водному середовищі відбувається часткове руйнування силікатного каркасу глинистих сорбентів з вивільненням силікат-іонів SiO_3^{2-} . Ці іони зазнають гідролізу, внаслідок чого рН розчину зростає. Також, не виключений прямий розрив зв'язків Si—O в приповерхневих угрупованнях $\equiv\text{Si—OH}$, що призводить до збільшення кількості «вільних» гідроксильних груп.

Ключові слова: стічні води, нікель, очистка, сорбент, бентоніт, активація, мікрохвилі.