

K. Stepova¹, L. Sysa¹, A. Kontsur¹, O. Myakush²

Adsorption of Copper Ions by Microwave Treated Bentonite

¹Lviv State University of Life Safety, Lviv, Ukraine, e-mail: katvastepova@gmail.com

²Ukrainian National Forestry University, Lviv, Ukraine

Changes of bentonite surface structure under the influence of direct microwave irradiation during adsorption of Cu²⁺ from concentrated solutions were investigated by X-ray and EDS analysis. The microwave treated bentonite (MTB) has been proved to have enhanced adsorption capacity for copper due to improved pore structure and some peculiarities of adsorption mechanism. The non-linear fitting of experimental data to the theoretical isotherms have demonstrated that the adsorption on natural bentonite fitted the Toth model, whilst microwave-treated bentonite fitted the Langmuir-Freundlich model. The isotherm modeling allowed predicting the maximal adsorption capacities 44.8 mg/g. XRD and SEM analysis of MTB sample after adsorption indicated formation of microcrystals of individual copper compound. The adsorption on MTB sample takes place not only in pores or in monomolecular layer on the bentonite surface, but the prevalent mechanism is surface-induced coprecipitation of copper as microcrystals of individual copper compound.

Keywords: bentonite; microwave; adsorption; copper; non-linear fitting.

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Introduction

Heavy metal water pollution is an important environmental concern due to its negative impact on human health, plants and animal lives. Heavy metals are toxic and prone to bioaccumulation [1-3]. For instance, Cu is frequently present in industrial wastewater such as mine drainage, galvanizing plants, natural ores and municipal wastewater treatment plants. Copper is not biodegradable and travels through the food chain via bioaccumulation. The increase of Cu (II) in human body causes brain, skin, pancreas and heart diseases [4]. Therefore, the problem of reducing copper content in industrial wastewater is relevant.

The basic requirements for the wastewater treatment are high recovery rate, lack of secondary pollution, economic efficiency and simple technology [3]. Various mechanical, biological and physicochemical methods are used for water purification. The most effective for heavy metals removal are precipitation, ultra-filtration, electro dialysis, reverse osmosis, precipitation and coagulation, ion exchange and adsorption. Adsorption is the most popular due to high efficiency, simplicity of use and availability of various adsorption materials [1].

Natural clay minerals, including bentonite, are potentially good adsorption materials, characterized by a large surface area, layered structure, high cations exchange ability, chemical and mechanical stability and low cost. Bentonite is a potential ionic exchanger for heavy metals due to its low-cost, high abundance, easy manipulation, and harmlessness. Bentonite has a better adsorption capacity for heavy metal ions than other minerals [5]. The general formula of bentonite is $[x(\text{Al}_2\text{O}_3) \cdot y(\text{SiO}_2)] \cdot z(\text{OH}) \cdot m(\text{H}_2\text{O}) \cdot n(\text{MeO}_x)$, where Me – Fe, alkaline and alkaline earth metals [6]. According to the atomic structure, bentonite is a clay material with a negatively charged three-dimensional aluminosilicate framework and a strictly regular structure. In the intervals of the framework hydrated positive ions of alkaline and alkaline earth metals are located. It compensates the charge of the framework and water molecules. For this reason, only molecules of the size smaller than the effective size of the framework are adsorbed into the pores of aluminosilicate [7, 8].

Bentonite is the cost-effective sorbent but its sorption characteristics are somewhat lower in comparison with synthetic materials. The pre-treatment of bentonite sorbents improves their sorption activity [9,

10]. For this purpose, hydrothermal cleaning of sorbent, calcination, washing with soda solutions, inorganic acids, organo-mineral composites and various types of irradiation are used [10]. In recent years, a promising way of pre-treatment of sorbents is the microwave radiation processing. Such investigations have been carried out on natural clays and on synthetic sorbents (activated carbon, ion exchange resins, etc.) [11-18]. According to Surendra and Foletto [14, 16] irradiation of bentonite by microwave radiation leads to a change in the micropores distribution on the surface of the mineral. Under the influence of microwave electromagnetic fields, new microcracks appear and large grains are crushed, which increases the active surface area of the sorbent. In abovementioned investigations the combined activating effect of several factors is used: the addition of mineral acids, heating and microwave irradiation.

Two methods of sorbent microwave treatment without adding acids or other activators were described earlier [19-24]. In so called STIM-method [19, 21, 23, 24] natural bentonite is washed by bidistilled water and simultaneously irradiated with microwaves, later the sorbent is exposed to contact with salt solutions – a two-step procedure for activating the sorbent (i.e. "stimulation"). In the DIR-method (direct irradiation) [20, 22, 23] samples of natural bentonite contacted with aqueous salt solutions under the microwaves irradiation. It is proved [19-24] that both methods of bentonite microwave treatment lead to a significant increase in its maximum adsorption capacity of heavy metal ions Ni [19, 20], Zn [21, 22], Pb [23], Cu [24]. The advantage of DIR-method is the intense spontaneous crystallization of a new phase on the surface of the sorbent [20, 22, 23]. It is believed that the reason for this phenomenon is formation of new crystallization centers due to the redistribution of micropores on the surface of the sorbent under the influence of microwaves. The results of these investigations are presented in Table 1.

Copper adsorption from low concentrated solutions on microwave treated bentonite (MTB) (two-step activation, series STIM) was investigated. It has been shown that the pre-irradiation of bentonite by microwaves causes changes on the surface and improves its sorption parameters [24].

The aim of present research is to investigate the process of Cu adsorption from concentrated solutions by bentonite treated by direct irradiation.

I. Materials and Methods

1.1. Materials

1.1.1. Bentonite

The material used for investigation was a natural powder bentonite purchased in the general trading network in Ukraine. pH of its aqueous extract was 8.92; bulk density – 1244 kg/m³; swelling rate ~2. The powder bentonite applied without treatment.

1.1.2. Simulated standard solution

The stock solution of copper sulfate was prepared from dry CuSO₄ · 5H₂O (1.593 g) and double distilled water (500 ml). The concentration of Cu²⁺ ions was determined by the atomic absorption method. The concentration of metal ions in stock solution is 781.2 mg/dm³. The set of standard solutions was prepared from the stock solution by multiple dilutions with double distilled water.

1.2. Methods

1.2.1. Elemental analysis

Atomic absorption spectrophotometer AAC-115.M-1 was used for determination of Cu²⁺ content.

1.2.2. XRD

The phase analysis of bentonite samples after copper sorption was carried out using X-ray powder diffraction [25]. For the crystal structure determination diffraction data were collected using a θ - 2θ scan technique with steps of 0.01° 2θ and exposition time of 2 sec. at every point (diffractometers DRON-3, CuK α -radiation). The qualitative phase composition was determined by indexing the peaks of the corresponding minerals using FM-MINERAL software.

1.2.3. SEM and EDS (EDX)

Scanning electron microscopy images combined with EDS analysis were obtained on Scanning Electron Microscope – Microanalyzer REMMA-102-02 (JSC Selmi, Ukraine). EDS detection limit is 10-100 ppm.

1.2.4. Adsorption experiments

The sorption properties of bentonite were studied under static conditions. Natural bentonite samples (1 g) were added to 100 ml of each simulated solution. This suspension was exposed to microwave irradiation for 10 min at 800 W. After cooling the suspension was left at room temperature for several hours. Solution was separated from the sorbent by decantation. The sample of spent sorbent was dried at 80°C during 2 hours until the

Table 1

Maximum adsorption capacity of heavy metal ions on natural bentonite (samples Ser. Nat) and microwave-treated bentonite by STIM (Ser. STIM) and DIR-methods (Ser. DIR)

Sample	Maximum adsorption capacity of heavy metal ions (mg/g)						
	^a Ni [19]	^b Ni [20]	^a Zn [21]	^b Zn [22]	^b Pb [23]	^a Cu [24]	^b Cu*
Ser. Nat	5.98	N/A	1.23	N/A	30.95	11.82	N/A
Ser. STIM	16.40	N/A	1.78	23.6	N/A	25.74	N/A
Ser. DIR	N/A	26.9	N/A	21.5	114.7	N/A	44.8

^aadsorption from diluted solutions; ^badsorption from high concentrated solutions; *results of present investigation;

constant weight was reached. The content of Cu²⁺ ions in solutions was determined by the atomic absorption method. All the experiments were performed in triplicates.

1.2.5. Isotherms fitting

Adsorption capacity was calculated by the decrease of in Cu²⁺ ions in solution:

$$q_e = (C_i - C_e) \cdot \frac{V}{m}, \tag{1}$$

where q_e – the equilibrium adsorption capacity, mg/g; V – volume of the solution, ml; m – weight of the dried adsorbent, g.

Due to heterogeneous surface of the adsorbent the adsorption is performed with a mixed mechanism. The aim of adsorption isotherms modelling is to determine an isotherm model that describes the experimental data, and thus gives an opportunity to predict the adsorption mechanism.

The experimental results were fitted with Langmuir, Freundlich (two-parameter isotherms), Redlich-Peterson, Toth, and Langmuir-Freundlich (three-parameter) isotherms using the non-linear fitting method [25]. Besides, linear fitting is not applicable for three-parameter isotherms. While linear fitting is more common for its simplicity for use, nonlinear fitting has also been widely used for its applicability to close the gap between predicted and experimental data.

As the isotherm transformation into linearized forms leads to the usual change of error structure of experimental data, the nonlinear fitting analysis became inevitable, since it provides an accurate method for determining adsorption parameters without change of original form of isotherm equations.

The model has been assessed by the minimal sum of standardized errors. The following errors were used for analysis:

- sum of the absolute errors (SAE) [25]:

$$\sum_{i=1}^n |q_{e_exp} - q_{e_calc}|_i$$

where, q_{e_exp} q_{e_calc} are the experimental and calculated adsorption capacities, respectively;

- sum of the squares of the errors (SSE) [26]:

$$\sum_{i=1}^n (q_{e_exp} - q_{e_calc})_i^2$$

- average relative error (ARE) [27]:

$$\frac{100}{n} \sum_{i=1}^n \left| \frac{q_{e_exp} - q_{e_calc}}{q_{e_exp}} \right|_i$$

n is the number of the experimental points;

- hybrid fractional error function (HYBRID) [28]:

$$\frac{100}{n-p} \sum_{i=1}^n \left(\frac{(q_{e_exp} - q_{e_calc})^2}{q_{e_exp}} \right)_i$$

p is the number of parameters of the adsorption isotherm.

- Marquardt’s percent standard deviation (MPSD) [29]:

$$100 \sqrt{\frac{1}{n-p} \sum_{i=1}^n \left(\frac{q_{e_exp} - q_{e_calc}}{q_{e_exp}} \right)_i^2}$$

For more accurate assessment of the models two experimental measurements were assigned to test points and not used for isotherms fitting. For each model, the isotherm parameters were calculated by minimizing error functions and calculating the other error functions, and standardized errors sum (SES). The best-fit isotherms were selected based on the value of test points errors and used to establish the adsorption mechanism and to obtain the maximal adsorption capacity of the adsorbent.

The detailed description of the procedure of analytical processing of adsorption curves has been presented in our previous publications [23, 24].

II. Results and Discussion

2.1. The surface structure of microwave treated bentonite after adsorption

X-ray diffraction analysis of natural bentonite has been described in detail in our previous work [24]. The XRD phase analysis of the untreated bentonite revealed 4 minerals: hydromica (about 27 % at.), montmorillonite (about 25 % at.), quartz (about 22 % at.), chlorite (about 20 % at.) and some impurities (calcite, sylvinitite and other minerals).

Fig. 1 presents the XRD pattern of microwave-treated bentonite (series DIR) after Cu adsorption. The XRD phase analysis of MTB after adsorption showed an increase in the content of montmorillonite (up to 33 % at.) and quartz (up to 30 % at.). However, the total content of chlorite and carbonates has decreased (in total - up to 21% at.). In addition, new reflections appeared in XRD pattern after adsorption (Fig. 1). Most probably, these were the crystals of Cu (I) sulfate [30] or complex hydroxosilikate Cu₅[Si₄O₁₂][OH]₂ [31].

We cannot definitely say which compound of copper will precipitate on bentonite because the theoretical diffraction patterns of these compounds are difficult to be indexed by powder data. The adsorption on MTB sample takes place not only in pores or in monomolecular layer on the bentonite surface, but the prevalent mechanism is surface-induced co-precipitation of copper as microcrystals of individual copper compound. The formation of microcrystal of individual heavy metal compound (Ni₂[SiO₄]₂,²⁰ Zn₄[Si₂O₇][OH]₂,²² Pb₂Si₄O₁₀[H₂O],²³) on the surface of MTB (ser. DIR) after adsorption from concentrated aqueous solutions is described in our previous works [20, 22, 23].

The SEM images of natural and microwave treated bentonite (series “DIR”) (Fig. 2 a,b) revealed significant changes on the surface morphology. The surface of natural bentonite (Fig. 2 a) can be described as grain-like particles with fluffy appearances and fringed edges. The internal structure of microwave treated bentonite (Fig. 2b) is much more porous and layered. On the smooth grain background well-faceted crystals are

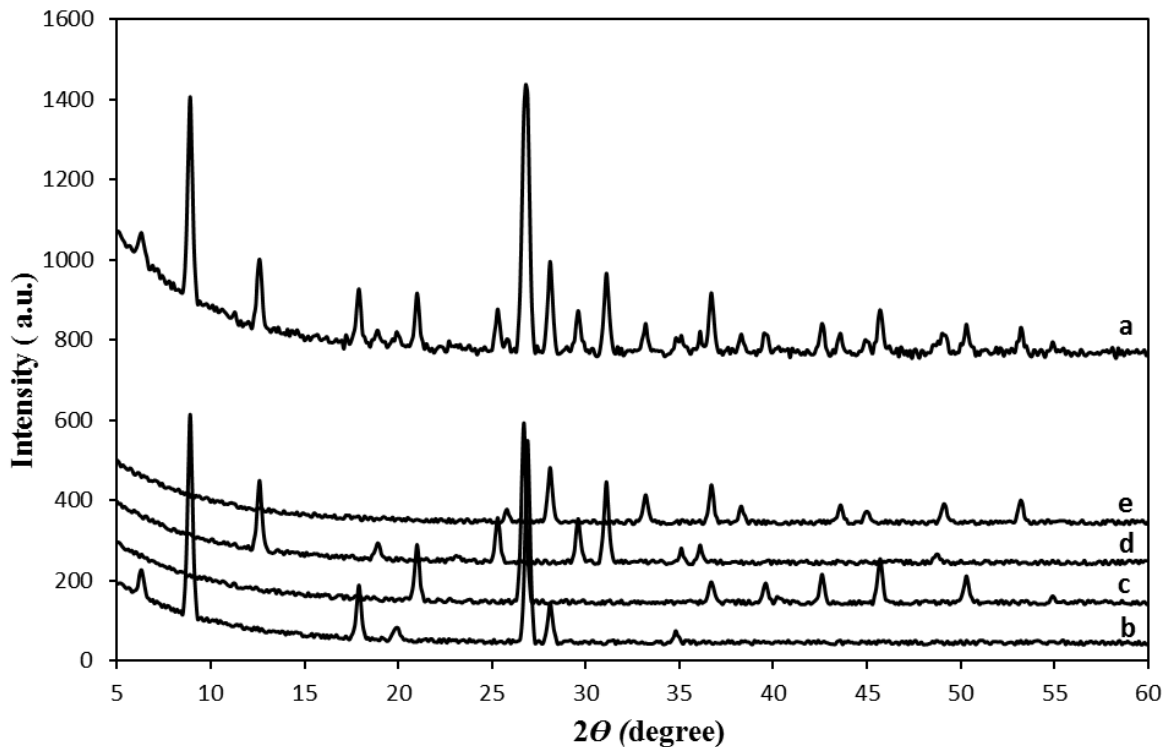


Fig. 1. XRD patterns of a – microwave-treated bentonite (series DIR) after Cu adsorption, b – montmorillonite, c – quartz, d – chlorite and carbonates, e – copper compound.

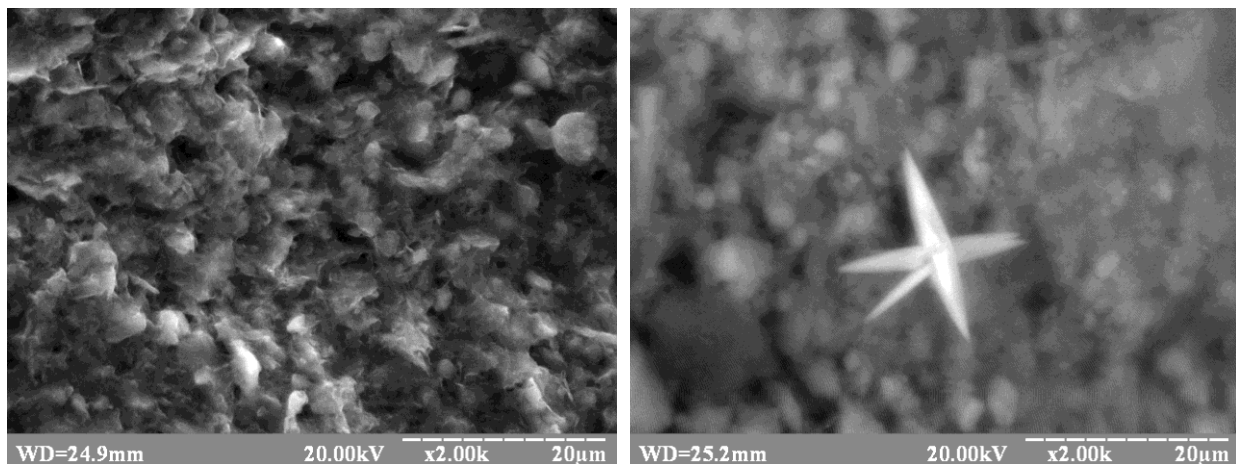


Fig. 2. SEM images: (a) natural bentonite, (b) microwave treated bentonite (series “DIR”).

clearly visible. Dark-field microscopy technique gives an opportunity to see placers of bright crystals (heavy metals) on the dark background (alumosilicates).

Most probably new microcrystals form on the surface of bentonite due to the microwave irradiation. It is supposed to be a separate phase of the individual copper compound. It may be caused by a number of reasons.

The pH of standard solution after adsorption increases from 4.4 to 5.1. It coincides with the statement that microwave processing in aqueous media causes partial destruction of silica skeleton by migration of SiO_4^{2-} ions. These ions hydrolyze and the pH increases. Which is more after distraction of Si-O bonds in surficial $\equiv\text{Si-OH}$ groups the amount of free OH-groups increases. Consequently, it is conceivable that adsorption of Cu^{2+} on the bentonite occurs not only by formation of

Langmuir monolayer of hydrated ions, but also by spontaneous crystallization of neutral poorly soluble copper compounds. A similar phenomenon of the formation of distinct microcrystals on the surface of practically amorphous bentonite phases in the processes of "direct irradiation" of the solution are observed in the corresponding series of our previous studies, where they studied processes of adsorption extraction of zinc [22], nickel [20] and lead [23] from aqueous solutions under similar conditions.

Elemental analysis by EDS shows that the major elements in natural bentonite are Si, Al, Mg, Ca, K, and Fe (Table 2). Elemental composition of the microwave treated sample (series “DIR”) after sorption did not change significantly as it is shown by EDS of dark field that is most probably an alumosilicates (montmorillonite, smectite, chlorite, etc.). EDS spectra of light field of

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MTB sample showed that the major element is copper (up to 45 %).

It is important to note that the Scanning Electron Microscope automatically detected the Cu (I) compound. This fact raises many questions, as the Cu (I) compounds are unstable in aqueous solutions. In addition, significant content of Silicon in this new phase has been identified.

2.2. Adsorption of copper

The adsorption capacity of natural and microwave

treated bentonite was assessed by fitting the data to adsorption isotherms. The isotherms provide the information about the maximal adsorption capacity, as well as the basic information about the adsorption mechanism. The experimental results were fitted by Langmuir, Freundlich, Redlich-Peterson, Toth, and Langmuir-Freundlich isotherms. Fig. 3 and 4 illustrate the experimental data of Cu²⁺ adsorption on natural and microwave treated bentonite and its fitting to the

Table 2

Elemental composition of the samples by EDS

Sample	Elemental composition (%)							
	Mg	Al	Si	K	Fe	S	Cu	Others
Natural bentonite	0.88	12.20	50.98	4.16	1.53	<DL	<DL	Ca, Ti
MTB after sorption (light field)	<DL	1.40	5.10	0.25	0.73	16.45	44.99	Ca, Ti

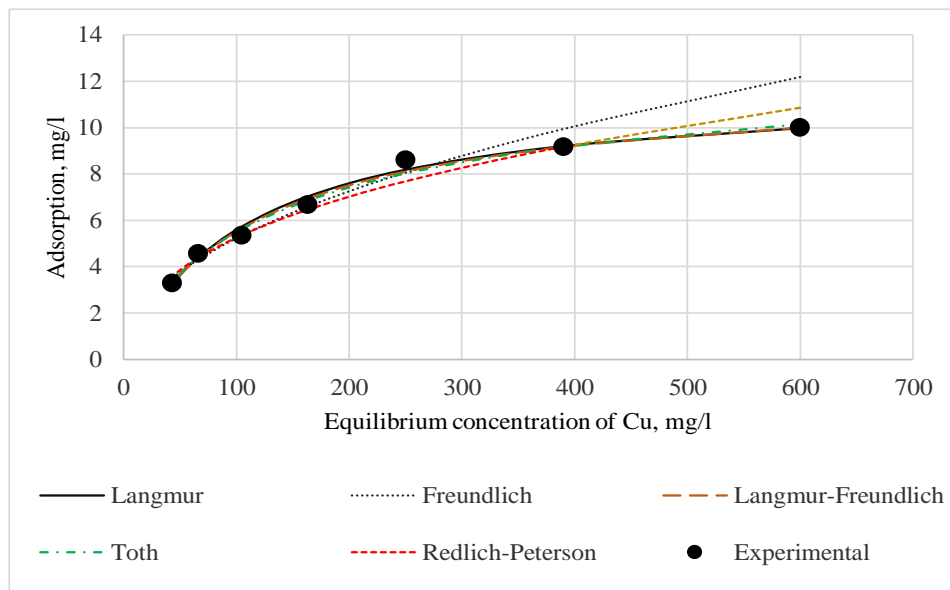


Fig. 3. Isotherms of copper adsorption on natural bentonite.

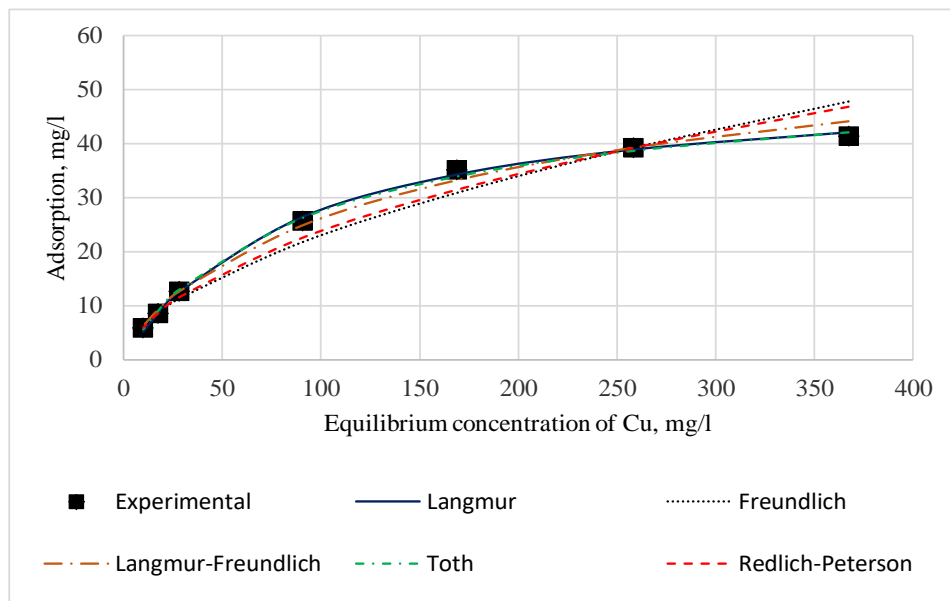


Fig. 4. Isotherms of copper adsorption on microwave treated bentonite.

Table 3

Error analysis of the non-linear isotherm fitting of Cu²⁺ adsorption on MTB

Errors	Minimized errors				
	ARE	MPSD	HYBRID	SSE	SAE
SAE	1.9202	1.4312	1.4657	1.4587	1.7764
SSE	1.1028	0.4976	0.5355	0.5150	0.8994
ARE	3.8559	3.0844	3.1733	3.2383	3.8471
HYBRID	3.3559	1.6997	1.7804	1.7572	2.8797
MPSD	6.6554	4.9909	5.0552	5.0928	6.5140
SES	3.8958	3.7662	3.63188	3.2780	3.7499

Table 4

Error analysis for test points excluded from the set of data used for isotherm fitting of Cu²⁺ adsorption on natural bentonite

Isotherm	Minimized errors					SES
	ARE	MPSD	HYBRID	SSE	SAE	
Langmur	0.0732	0.9540	0.0054	0.9539	0.0698	4.6728
Freundlich	0.4159	5.4201	0.1730	5.4201	2.2544	1.6588
Redlich-Peterson	0.6613	8.6168	0.4373	8.6168	5.6979	7.8190
Toth	0.2608	3.3978	0.0680	3.3978	0.8866	1.5366
Langmur- Freundlich	0.1631	2.1255	0.0266	2.1255	0.3467	3.2685

Table 5

Error analysis for test points excluded from the set of data used for isotherm fitting of Cu²⁺ adsorption on MTB

Isotherm	Minimized errors					SES
	ARE	MPSD	HYBRID	SSE	SAE	
Langmur	0.8875	4.7688	0.7876	4.7688	4.2322	4.1014
Freundlich	3.8709	20.80	14.9836	20.7999	80.5134	6.5470
Redlich-Peterson	3.2681	17.5610	10.6805	17.5610	57.3909	3.9558
Toth	0.7130	3.8311	0.5083	3.8311	2.7315	4.5553
Langmur- Freundlich	1.6669	8.9569	2.7785	8.9569	14.9300	1.8461

theoretical models.

Table 3 presents the sample error analysis for Toth isotherm on natural bentonite. The minimized errors values (Table 3) were obtained by fitting the parameters to the isotherm equation and comparing the theoretical and experimental values. Following the similar procedure, the optimal parameters for isotherms were obtained. These data were also used to plot the isotherms. The plot $q_e=f(C_e)$ gives an isotherm of the classical type over a wide range of initial Cu²⁺ concentrations (Fig. 3, 4).

The progressive saturation of the adsorbent is observed. The isotherm metrics indicate that the best adjustments were obtained for Toth (natural bentonite) and Langmuir-Freundlich isotherms (microwave-treated bentonite). Table 4 and 5 present error analysis for all chosen isotherms to test points excluded from the set of data used for fitting.

Therefore, we can assume that the low-energy adsorption sites prevail in the natural bentonite while copper adsorption [25], whereas the data obtained from the microwave-treated adsorbent follow the symmetrical quasi-gaussian distribution of adsorption energy where sites with low and high adsorption energy are present [32]. This fact indicates that the electromagnetic

treatment stimulates the formation of the new adsorption sites. Possibly, the active sites of the natural sample are Na- or Ca-sites, and ion-exchange is the prevalent adsorption mechanism. The electromagnetic radiation improves the pores structure and influences the surface charge, so the adsorbent becomes benign towards copper ions. Therefore, other mechanisms are also involved, which could be the specific adsorption and surface precipitation.

The adsorption isotherms allow determining the maximal adsorption capacities, which is 0.7 mmol/g (44.8 mg/g) for MTB samples (ser. "DIR"). The maximal adsorption capacities represent the adsorbent affinity towards copper ions. The results of the present study and the data from our previous investigations have shown that direct irradiation to bentonite (DIR) [20, 22, 23] is more advantageous than the procedure for two-step activation of the sorbent (STIM) [19, 21, 24] because it does not require an additional stage of treatment of the sorbent (preliminary washing with double distilled water during irradiation). A smaller amount of technological operations simplify the process, reduce time and, accordingly, reduce the cost of water treatment.

Conclusion

1. The adsorption characteristics, microstructure and phase composition of natural clay sorbent bentonite activated by direct microwaves irradiation in the processes for Cu²⁺ removal from concentrated aqueous solutions was investigated.

2. X-ray diffraction analysis of MTB sample after adsorption indicated formation of microcrystals of individual copper compound. The adsorption on MTB sample takes place not only in pores or in monomolecular layer on the bentonite surface, but the prevalent mechanism is surface-induced co-precipitation of copper as microcrystals of individual copper compound.

3. The microwave treated bentonite has been proved to have enhanced adsorption capacity for copper due to improved pore structure. The non-linear fitting of experimental data to the theoretical isotherms have demonstrated that the adsorption on natural bentonite

fitted the Toth model whereas the microwave-treated bentonite fitted the Lengmur-Freundlich model. The isotherm modeling allowed predicting the maximal adsorption capacities of 44.8 mg/g.

4. The MTB sample reveals high adsorption capacity for copper, and thus is a promising material for wastewater purification. The microwave stimulation is advantageous compared to chemical modification because it does not require the additional reagents and installation of additional stage for treatment.

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Stepova K. - Ph.D., Associate Professor;
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Kontsur A. - postgraduate student;
Myakush O. - Ph.D., Associate Professor.

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К. Степова¹, Л. Сиса¹, А. Концур¹, О. Мякуш²

Адсорбція іонів Купруму бентонітом під дією НВЧ випромінювання

¹Львівський державний університет безпеки життєдіяльності, Львів, Україна, e-mail: katyastepova@gmail.com

²Національний лісотехнічний університет України, Львів, Україна

У статті представлено результати вивчення зміни поверхневої структури бентоніту під впливом прямого НВЧ-опромінювання під час адсорбції Cu^{2+} із концентрованих розчинів за допомогою рентгенофазового та енерго-дисперсійного аналізів. Було доведено, що НВЧ-опромінений бентоніт володіє підвищеною адсорбційною здатністю щодо іонів Купруму за рахунок розвинутої структури пор та деяких особливостей механізму адсорбції. Нелінійне моделювання експериментальних даних в рамках теоретичних моделей ізотерм продемонструвало, що адсорбція нативним бентонітом відповідає моделі Тота, а опроміненим – моделі Ленгмюра-Фрейндліха. Таке моделювання дає змогу передбачити максимальну адсорбційну здатність, що складає 44,8 мг/г. Результати рентгенофазового та мікроструктурного аналізів опроміненого зразка після адсорбції свідчать про утворення мікрокристалів окремої сполуки Купруму. Адсорбція на опроміненому зразку протікає не тільки в мономолекулярному шарі, а переважаючим механізмом є поверхнево-індуковане співосадження іонів міді у складі мікрокристалів окремої сполуки.

Ключові слова: бентоніт; надвисокочастотне випромінювання; адсорбція; мідь; нелінійне моделювання.