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Проведено інтерпретацію адсорбції міді на природному та стимульованому магнітним випромінюванням бентоніті в рамках моделей адсорбції. На природному бентоніті процес описується ізотермою Ленгмюра, а на стимульованому зразку – Ленгмюра-Фрейндліха. Розраховано максимальну адсорбційну ємність, яка становить 11,82 (бентоніт) та 25,74 мг/г (стимульований бентоніт). Адсорбція на стимульованому зразку проходить внаслідок утворення нових адсорбційних центрів

Ключові слова: модифіковані глини, мікрохвильове випромінювання, очищення стоків, моделювання адсорбції, нелінійне моделювання

Проведена интерпретация адсорбции меди на природном и стимулированном магнитным излучением бентоните в рамках моделей адсорбции. На природном бентоните процесс описывается изотермой Ленгмюра, а на стимулированном – Ленгмюра-Фрейндлиха. Рассчитана максимальная адсорбционная емкость: 11,82 мг/г (бентонит) и 25,74 мг/г (стимулированный бентонит). Адсорбция на стимулированном образце проходит вследствие образования новых адсорбционных центров

Ключевые слова: модифицированные глины, микроволновое излучение, очистка стоков, моделирование адсорбции, нелинейное моделирование

INVESTIGATION OF COPPER ADSORPTION ON NATURAL AND MICROWAVE-TREATED BENTONITE

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1. Introduction

The humanity entered XXI century with the significant advances in technology & industry and severe environmental issues. The industrial production causes the extensive use of resources, including water. As a result, large volumes of wastewater are formed. Freshwater is a valuable resource for a comfortable life of humanity, and it is vital for survival. Hence, the issue of wastewater treatment is of particular concern for the modern science [1]. Various mechanical, physicochemical and biological methods are used for the natural and wastewater purification (aeration, sedimentation, filtration, sorption with synthetic and natural materials, etc.). The main requirements for the wastewater treatment are as follow: high recovery rate, the absence of secondary pollution, cost-efficiency, and simple application technology [2].

The adsorption process fulfills the abovementioned requirements. The adsorption process also supports sustainable development: there are many safe and efficient adsorbents, which can be regenerated or re-utilized. Numerous research efforts [3] are dedicated to development and study of properties of the efficient and low-cost adsorbents. Taking into account the large volumes of wastewater to be treated, the natural adsorbents are of special interest for large-scale industrial processes. However, they often underperform in pollutants removal rate. These facts indicate that the adsorption properties enhancement with non-reagent methods is a relevant scientific task.

2. Literature review and problem statement

The natural clay minerals have been widely applied in adsorption technologies, and their properties are well studied. However, the natural minerals typically reveal low adsorption capacities, so the efficient and low-cost methods for adsorption capacity enhancement are significant [4].

Bentonites are promising agents because of their high adsorption capacity and susceptibility to surface modification [6]. The general formula of these minerals can be represented as $[x(\text{Al}_2\text{O}_3)\cdot y(\text{SiO}_2)]\cdot z(\text{OH})\cdot m(\text{H}_2\text{O})\cdot n(\text{MeOx})$, where MeOx is the metal oxides; x and y are the coefficients that characterize the type of a mineral [5].

According to the atomic structure, bentonite is an aluminosilicate material with a negatively charged three-dimensional aluminosilicate framework with a strictly regular structure. The hydrated positive ions of alkali and alkaline earth metals, which compensate the charge of the carcass, along with water molecules, are located in the intervals of this frame. Because of this, only molecules of substances with the critical size smaller than the effective size of the frame are adsorbed into the adsorption cavities of aluminosilicate [6].

The general physicochemical characteristics of bentonite clays are the specific surface area, dispersity (particle size), bentonite number (swelling capacity), adsorption index, thermal stability, etc. To enhance the valuable properties of bentonites (primarily adsorption capacity), they are often activated or modified with a variety of physical and chemical methods [7]. Due to the activation, the chemical composi-

tion of bentonites partially changes; this leads to an increase in the specific surface area and its acidity, an increase in the specific pore volume, and an improvement in thermal stability. The natural clay minerals are highly susceptible to thermal treatment, and the recent works [5] report improvement of the adsorption capacity for heavy metals related to thermal treatment.

The work [6] presents the detailed review of the past decade achievements in adsorption on clay minerals. Having studied over 200 recent publications, the author concludes that the primary mechanism of adsorption on montmorillonite-based minerals is ion-exchange, with sodium or calcium acting as exchanging cations. As a result of the process, Cu-bentonite surface complex forms. The author also collected data on Cu²⁺ adsorption on various types of clay minerals. The highest capacities among the non-modified minerals are reported for Na-montmorillonite, montmorillonite-illite, natural clay, goethite, smectite (33.33, 30.99, 44.84, 37.25, 42.43 mg/g, respectively). At the same time, many natural adsorbents (montmorillonite, Na-montmorillonite, kaolinite, siderite, etc.) reveal low capacities, which did not exceed 20 mg/g [5–7].

A contemporary review of montmorillonite-based materials [5] suggests the possible mechanisms of adsorption. Removal on natural and modified montmorillonite is caused by cation exchange, specific adsorption, and surface precipitation. The authors also emphasize that the selective adsorption of heavy metals does not follow any universal rules.

A promising direction to increase the efficiency of adsorption purification and subsequent regeneration of adsorbents is the use of microwave electromagnetic radiation (EMR). At present, few research papers have reported the application of this method for adsorption improvement. The attempt to improve the competitive adsorption of H₂O/CO₂, H₂O/Toluene on zeolites from gas media has been made [8]. Critically, the microwave irradiation has shown no preference over thermal treatment, and no selectivity improvement has been achieved. The method is promising only for adsorbent regeneration, and is not applicable for adsorption enhancement.

The paper [9] reported the use of microwave-enhanced sorption for dye removal on organobentonite. The process reveals 71–84 % decolorization rate for three dyestuffs, whereas the efficiency of the conventional process is only 18 %. The authors [9] explained the effect of microwave radiation by the increase of zeta potential of clay particles; as a result, the adsorption rate increases and separation of clay particles elevates. The microwave radiation caused microstructure changes in sodium silicate/bentonite composite [10]. Hence, microwave-enhanced sorption is a promising area of research. However, the research efforts in this area are not extensive, and we were not able to find any other papers except the abovementioned works [8–10] related to microwave-enhanced adsorption. Furthermore, none of the papers reported the influence of microwave radiation on adsorption removal of copper or other heavy metals. The current work aims to contribute to microwave-enhanced adsorption studies and investigate the adsorption properties of bentonite treated with microwave radiation for copper removal.

3. The aim and objectives of the study

The study aims to assess the influence of electromagnetic microwave radiation on the adsorption capacity of bentonite

clay towards Cu²⁺ ions. This will be a scientific basis for elaboration of the simple, sustainable, and efficient wastewater treatment method, which is superior to adsorption with chemically modified adsorbent because it does not require the involvement of additional reagents.

To achieve this aim, the following objectives have to be solved:

- to study the crystalline structure of the natural bentonite adsorbent employing X-ray diffractometry;
- to perform the experimental investigation of Cu²⁺ adsorption on the natural and EMR-stimulated bentonite;
- to fit the experimental data with the theoretical isotherms and obtain the maximal adsorption capacities of the natural and EMR-stimulated adsorbents;
- to suggest possible adsorption mechanisms on the natural and EMR-stimulated adsorbents.

4. Methodology of bentonite structure investigation, adsorption properties, and isotherm fitting studies

The commercial bentonite of fine grinding was purchased in the general trading network. The natural sample was ground to powder and applied without any other treatment.

X-ray phase analysis was used to explore the structure of bentonite. The diffractograms were obtained by the powder method on DRON-3 diffractometer using copper filtered radiation. The qualitative phase composition was determined by indexing the peaks of the corresponding minerals using FM-MINERAL software.

The modified sample was obtained by bentonite treatment with EMR. An EMR generator had been designed by the authors and assembled on M-10 magnetron. The standard switching circuit was used (without pulse modulation); the radiation range was 2.45 GHz with the output power 790 W. The horn antenna was applied for better distribution and concentration of radiation [11].

The bentonite sample (1.0 g) was placed in a glass flask and 25 ml of bidistilled water was added. The sample was exposed to medium-power microwave EMR for 120 sec. After sedimentation, the water was carefully decanted. The sample was dried at 105 °C until the constant weight was reached.

The sorption properties of bentonite were studied under static conditions. A stock solution of copper sulfate was prepared from dry CuSO₄ and bidistilled water. To stabilize Cu²⁺ ions, a drop of nitric acid was added to obtain pH-2. The working solutions were prepared from the stock solution by multiple dilutions with bidistilled water. The bentonite samples (1 g) were added to simulated wastewater (250 ml). The suspension was mixed and left to settle, and the procedure was repeated three times. The contact time was 24 hours. The concentration of Cu²⁺ ions was determined by the atomic absorption method (AAC-115-M-1 spectrometer). All the experiments were performed in triplicates.

Adsorption removal was assessed as a percentage of removed Cu²⁺ ions:

$$S = \frac{C_i - C_e}{C_i} \cdot 100 \%, \quad (1)$$

where C_i – initial concentration, mg/l; C_e – equilibrium concentration, mg/l.

The magnitude of adsorption capacity improvement by EMR was assessed by the multiple regression analysis per-

formed in R. The linear regression models for $S=f(C_i)$ were constructed; the residuals were normally distributed and homoscedastic.

Adsorption capacity was calculated by the decrease of Cu^{2+} ions in solution:

$$q_e = (C_i - C_e) \cdot \frac{V}{m}, \tag{2}$$

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

The experimental results were fitted with Langmuir, Freundlich, Redlich-Peterson, Toth, and Langmuir-Freundlich isotherms:

– Langmuir [12]:

$$q_e = \frac{q_m K C_e}{1 + K C_e}, \tag{3}$$

where q_m is the maximal adsorption capacity, mg/g; K , a , and n are the isotherm constants;

– Freundlich [13]:

$$q_e = K C_e^{1/n}, \tag{4}$$

– Redlich-Peterson [14]:

$$q_e = \frac{K C_e}{1 + a C_e^n}; \tag{5}$$

– Toth [15]:

$$q_e = \frac{q_m a C_e}{(1 + a C_e^n)^{1/n}}; \tag{6}$$

– Langmuir-Freundlich [16]:

$$q_e = \frac{q_m (K C_e)^n}{1 + (K C_e)^n}. \tag{7}$$

Langmuir’s isotherm (3) assumes that adsorption sites are homogenous and thus the probability of adsorption on each site is equal [12]. The Freundlich’s theory (4) [13] suggests that the surface has heterogeneous sites, and the distribution of adsorption heat on the surface is non-uniform. Redlich-Peterson isotherm (5) is often referred to as a combination of Langmuir and Freundlich isotherms to describe adsorption in a wide range of concentrations [14]. Langmuir-Freundlich model (7) is well fitted with the data that follow the symmetrical quasi-gaussian distribution of adsorption energy, where sites with low and high adsorption energy are present [16]. When the low-energy adsorption sites prevail, the data are well fitted with Toth isotherm (6) [17].

The isotherms were fitted using the non-linear fitting method performed by Python programming code. Although the non-linear fitting is more complicated, the transformation of non-linear equations to linear forms often changes the error structure and may also disrupt the variance of standard least squares method [18–20]. In the work [21] the higher accuracy and significance of the non-linear fitting compared to the linear method was confirmed. Thus, the determination coefficient of linear regression analysis proves to be incomplete for a choice of

the best-fit model. Besides, linear fitting is not applicable for three-parameter isotherms [18].

The model suitable for experimental data representation was selected by the minimal sum of standardized errors. The following formulae were used for error analysis:

– sum of the absolute errors (SAE) [17]:

$$\sum_{i=1}^n |q_{e_exp} - q_{e_calc}|_i, \tag{8}$$

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

– sum of the squares of the errors (SSE) [18]:

$$\sum_{i=1}^n |q_{e_exp} - q_{e_calc}|_i^2; \tag{9}$$

– average relative error (ARE) [19]:

$$\frac{100}{n} \sum_{i=1}^n \left| \frac{q_{e_exp} - q_{e_calc}}{q_{e_exp}} \right|_i, \tag{10}$$

n is the number of the experimental points;

– hybrid fractional error function (HYBRID) [20]:

$$\frac{100}{n-p} \sum_{i=1}^n \left| \frac{q_{e_exp} - q_{e_calc}}{q_{e_exp}} \right|, \tag{11}$$

p is the number of parameters of the adsorption isotherm.

– Marquardt’s percent standard deviation (MPSD) [21]:

$$100 \sqrt{\frac{1}{n-p} \sum_{i=1}^n \left(\frac{q_{e_exp} - q_{e_calc}}{q_{e_exp}} \right)_i^2}. \tag{12}$$

The optimal model was selected by performing the following steps. For each model, the isotherm parameters were calculated by minimizing the error functions, calculating the other error functions, and standardized errors sum (SES). The parameters that showed the minimal sum of standardized errors were set as optimal for the experimental data representation. The model with the minimal sum of the standardized errors and maximal determination coefficient value was selected as the best-fit isotherm and used to obtain the maximal adsorption capacity of the adsorbent.

5. Results of Cu^{2+} adsorption on natural and EMR-stimulated bentonite

Fig. 1 illustrates the XRD pattern after appropriate digital processing and crystal-chemical analysis.

The adsorption efficiency was assessed as a percentage of Cu^{2+} removal from solutions. Fig. 2 shows the effect of the various initial Cu^{2+} concentrations.

The efficiency of adsorption gradually decreases with the increase of the initial concentration. The lines for adsorption on natural and stimulated samples are almost parallel, which indicates the involvement of similar adsorption mechanisms. However, the stimulated sample reveals higher efficiency. Table 1 presents the regression coefficients, their significance, and the determination coefficients.

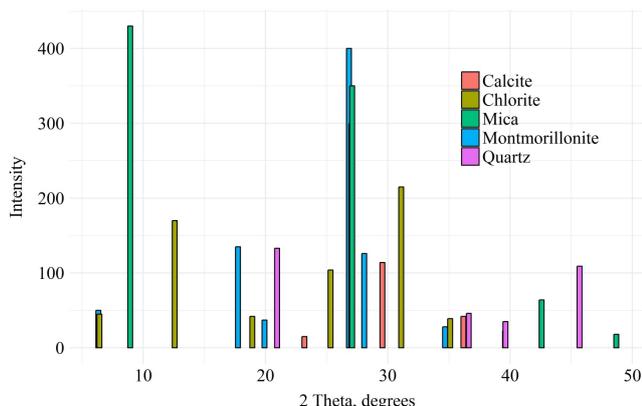


Fig. 1. XRD pattern of natural bentonite (CuKα – corrected)

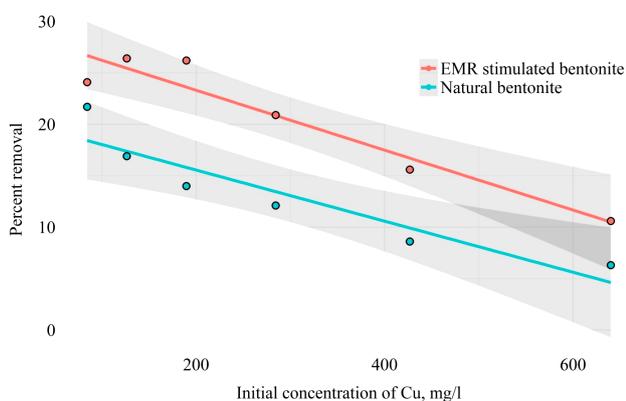


Fig. 2. Adsorption removal of Cu²⁺ by natural and EMR-stimulated bentonite

Table 1

Regression analysis of adsorption removal of Cu²⁺

| Regression parameters | Natural bentonite | | | EMR-stimulated bentonite | | |
|-----------------------|-------------------|-----------------|-----------------------|--------------------------|-----------------------|-----------------------|
| | Coefficients | <i>p</i> -value | <i>R</i> ² | Coefficients | <i>p</i> -value | <i>R</i> ² |
| Intercept | 20.52 | 0.0003 | 0.84 | 29.13 | 3.76·10 ⁻⁵ | 0.90 |
| Ci | -0.02 | 0.007 | | -0.03 | 0.002 | |

The coefficients are significant, and the regression lines fit the experimental data well. The maximal removal rates are 20.5 % for the natural sample, and 29.1 % for EMR-stimulated bentonite. As the initial concentration of the pollutant increases by 100 mg/l, the adsorption efficiency decreases by 2 and 3 %, for natural and EMR-stimulated bentonite, respectively. At higher concentrations, the adsorption efficiencies flatten out, and the lines approach one another.

The adsorption isotherms provide the primary information about the process efficiency and interaction between the adsorbent and adsorbate. Hence, the practical application of adsorbents requires experimental data fitting by theoretical models. The experimental results were fitted by Langmuir, Freundlich, Redlich-Peterson, Toth, and Langmuir-Freundlich isotherms. Fig. 3, 4 illustrate the experimental data of Cu²⁺ adsorption on natural and EMR-stimulated bentonite and their fitting to the theoretical models.

Table 2 presents the sample error analysis for Freundlich isotherm on EMR-stimulated bentonite.

The minimized errors values (Table 2) 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 (Table 3). These data were also used to plot the isotherms.

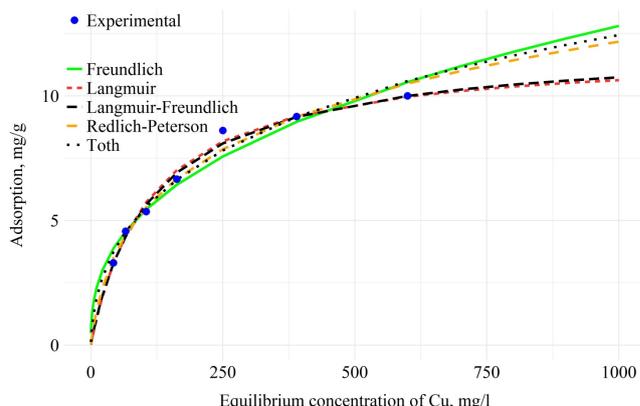


Fig. 3. Isotherms of copper adsorption on natural bentonite

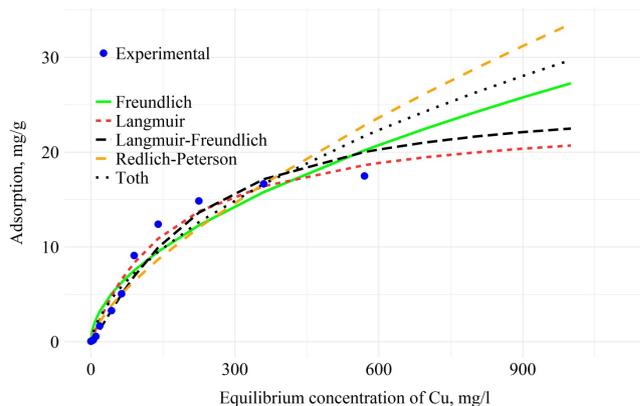


Fig. 4. Isotherms of copper adsorption on EMR-modified bentonite

Table 2

Error analysis of the non-linear isotherm fitting of Cu²⁺ adsorption on EMR-stimulated bentonite*

| Errors | Minimized errors | | | | | SES | Adsorption parameters | |
|-----------------------|------------------|--------------|--------------|--------------|--------------|--------------|-----------------------|----------|
| | ARE | MPSD | HYBRID | SSE | SAE | | <i>n</i> | <i>k</i> |
| SAE | 26.10 | 26.20 | 19.40 | 15.10 | 14.50 | 14.11 | 2.26 | 1.23 |
| SSE | 142.30 | 134.30 | 79.70 | 39.30 | 57.30 | 13.89 | 1.87 | 0.68 |
| ARE | 40.10 | 65.60 | 62.60 | 449.40 | 826.40 | 54.71 | 1.06 | 0.06 |
| HYBRID | 102.50 | 182.00 | 70.20 | 600.80 | 1782.00 | 13.90 | 1.29 | 0.17 |
| MPSD | 48.60 | 65.80 | 95.80 | 602.50 | 1105.10 | 14.13 | 1.07 | 0.07 |
| <i>R</i> ² | 0.89 | 0.89 | 0.92 | 0.95 | 0.92 | – | – | – |

Note: * – the figures in bold represent the minimized errors used to obtain the adsorption parameters

Table 3 Isotherm parameters for the removal of Cu²⁺ from simulated wastewater on natural and EMR-stimulated bentonite

| Isotherm | Isotherm parameters notation | Isotherm parameters values | SES | R ² | Isotherm parameters values | SES | R ² |
|---------------------|------------------------------|----------------------------|-------------|----------------|----------------------------|--------------|----------------|
| | | Natural bentonite | | | EMR-stimulated bentonite | | |
| Langmuir | q _e | 11.82 | 3.96 | 0.99 | 24.28 | 13.30 | 0.98 |
| | K | 0.01 | | | 0.06 | | |
| Freundlich | K | 2.64 | 3.85 | 0.95 | 1.87 | 13.89 | 0.95 |
| | n | 0.93 | | | 0.68 | | |
| Redlich-Peterson | n | 0.92 | 3.82 | 0.93 | 0.32 | 13.36 | 0.93 |
| | a | 0.02 | | | 5.09 | | |
| | K | 0.12 | | | 1.63 | | |
| Toth | q _e | 5.80 | 3.75 | 0.92 | 50.00 | 14.25 | 0.90 |
| | a | 0.51 | | | 0.001 | | |
| | n | 0.22 | | | 0.99 | | |
| Langmuir-Freundlich | q _e | 7.89 | 4.02 | 0.92 | 25.74 | 12.35 | 0.98 |
| | K | 0.01 | | | 0.005 | | |
| | n | 1.90 | | | 1.22 | | |

The progressive saturation of the adsorbent is observed. Thus, the adsorption isotherms of natural and EMR-stimulated bentonite are of the L-type with a strict plateau [16].

The isotherm metrics (R² and SES, Table 3) indicate that the best adjustments were obtained for Langmuir (natural bentonite) and Langmuir-Freundlich isotherms (EMR-stimulated bentonite). Therefore, we can assume that the sites that are active at copper adsorption in the natural bentonite are homogenous, whereas the EMR-modified adsorbent reveals heterogeneity of the sites. 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.

Because the data were fitted by Langmuir and Freundlich isotherms moderately well, the progression of adsorption was assessed with a separation factor [18]. The separation factor indicates that the adsorbents are favorable for copper removal: the values are 0.02 and 0.15 for natural and EMR-stimulated adsorbents, respectively.

The maximal adsorption capacities represent the adsorbent affinity towards copper ions [5]. The isotherms were used to derive the maximal adsorption capacities, which are 11.82 and 25.74 mg/g for natural and EMR-stimulated adsorbents, respectively. The results indicate that the electromagnetic radiation improves the adsorption capacity: the stimulated sample reveals significantly higher capacity compared to the natural one, which shows the values cited for montmorillonite-like minerals [5, 7].

The spent Cu-loaded adsorbent can be used in other wastewater treatment processes. Mekewi et al. [22] report an application of the montmorillonite clays modified with copper nanoparticles for methylene dye degradation. Hence, the spent clay adsorbent can be used for dye removal from wastewater. The authors [23] demonstrated that Cu(II)-bearing montmorillonite has a higher capacity for Cd(II) compared to the natural montmorillonite: 94 % removal rate was achieved.

The results of our study proved that the action of microwave radiation on bentonite with the simultaneous hydrothermal destruction of the surface significantly improves the ability to adsorb ions of heavy metals, particularly copper. In comparison with the natural sample, EMR-stimulated sample revealed a higher adsorption capacity and thus can be a promising material for wastewater purification. The EMR-simulation is superior to chemical modification of natural minerals because it does not require the additional reagents and expensive equipment. The EMR-stimulation unit is reasonably priced and can be re-designed into the industrial assembly.

At present, the study lacks the detailed structural investigations of the natural and EMR-modified bentonite. The analysis of IR- and UF-spectra, as well as thermograv-

The modelling results indicate that the optimal parameters for each isotherm are similar, e.g. the coefficient *K* for Langmuir and Langmuir-Freundlich isotherms (natural bentonite). However, the real values of maximal adsorption capacity are obtained only when using the combination of the determination coefficient and SES.

6. Discussion of Cu²⁺ adsorption on natural and EMR-stimulated bentonite

The XRD phase analysis of the natural sample revealed 4 minerals: hydromica (about 27 % at.), montmorillonite (about 25 % at.), quartz (about 22 % at.), chlorite (about 20 % at.), and some impurities (calcite, sylvinite, and other minerals). Therefore, the natural sample has a similar phase composition as other montmorillonite-containing minerals.

It is likely that the combined action of two factors, namely microwave irradiation and hydrothermal destruction of the surface affects the crystalline structure of clay material, distribution of macro- and micropores causes activation of the adsorbing surface, etc., which leads to sorption characteristics enhancement.

The plot $q_e = f(C_e)$ gives an isotherm of the classical type (a smooth increase in the equilibrium sorption capacity with the increase of the equilibrium concentration) over a wide range of initial Cu²⁺ concentrations (Fig. 3, 4).

imetry, will contribute to understanding the influence of EMR-stimulation. In addition, these studies can be performed with the spent sorbent, which will allow developing the insight on adsorption mechanism. However, the detailed structural investigations are out of the scope of the current paper and call for the self-contained article. The important limitation of the results is related to variability of the natural minerals composition. The prevalence of the certain mineral phase might reveal different adsorption rate, so the relationship between the phase composition and EMR-stimulated adsorption is an important association to be established in the future studies.

7. Conclusions

1. The structural characterization of the natural bentonite has proved that hydromica, montmorillonite, quartz, and chlorite are the main minerals in the natural bentonite sample. The prevalent adsorption mechanism on natural bentonite adsorbent is ion exchange.

2. The adsorption studies in a wide range of initial concentrations (20–640 mg/l) have shown that the natural and EMR-stimulated samples are capable of removing up to

20.5 % and 29.1 % of Cu^{2+} , respectively. The adsorbents have revealed the high adsorption capacity, but limited selectivity.

3. The non-linear fitting of experimental data to the theoretical isotherms of Langmuir, Freundlich, Redlich-Peterson, Toth, and Langmuir-Freundlich have demonstrated that the adsorption on natural bentonite fitted the Langmuir model. The EMR-stimulated bentonite data agreed well with Langmuir-Freundlich isotherm. The isotherm modeling allowed predicting the maximal adsorption capacities: 11.82 and 25.74 mg/g for natural and EMR-stimulated samples, respectively. Therefore, the EMR-stimulation significantly improved the adsorption capacity but had a little effect on selectivity.

4. The experimental investigation and theoretical modeling showed that the adsorption sites of the natural bentonite were homogenous. The fitting to Langmuir-Freundlich isotherm indicated that the EMR-stimulated adsorbent had heterogeneous adsorption sites. Hence, the electromagnetic treatment modified the bentonite surface, stimulated the formation of the new adsorption sites, and improved the pores structure. The new adsorption sites of different nature caused the involvement of the other adsorption mechanisms on the EMR-stimulated adsorbent: specific adsorption and surface precipitation.

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