

## NONLINEAR ISOTHERM ADSORPTION MODELLING FOR COPPER REMOVAL FROM WASTEWATER BY NATURAL AND MODIFIED CLINOPTILOLITE AND GLAUCONITE

Roman Konanets<sup>1</sup>, Kateryna Stepova<sup>1,✉</sup>

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**Abstract.** The paper presents the results of the Cu<sup>2+</sup> adsorption on natural and thermally/microwave-treated clinoptilolite and glauconite. XPS experiments were performed. The relationship between the adsorbed matter and the equilibrium concentration in wastewater is described by four two-parameter isotherm models and four three-parameter adsorption isotherm models.

**Keywords:** adsorption, wastewater, non-linear fitting, equilibrium isotherm, error analysis.

### 1. Introduction

Copper, being one of the most important industrial metals, finds application in the casing of mortars, artillery, rockets, targeting equipment, and shell casings. Specifically, a significant accumulation of copper has been observed in battlefields, small-arm shooting ranges, artillery, mortar and rocket ranges, and grenade courts. The excessive presence of copper in casings and bullet jackets results in an abundance of copper in soils.<sup>1</sup> The continuous discharge of excessive Cu(II) ions into the ecosystem seriously threatens human health and ecosystem structure due to their non-biodegradability and high toxicity. The removal of copper ions from water is a challenging problem. Modern water purification methods from copper ions include various reagents, electrochemical sorption, ion exchange, biological methods, etc.<sup>2</sup> Among them, the adsorption method receives considerable attention due to its affordability, simplicity of use, and high purification efficiency.<sup>3</sup>

Numerous adsorbents have been investigated for both the purification of water from copper ions and its

identification in solutions. Among these sorbents are activated carbon,<sup>4</sup> magnetically susceptible carbon sorbents,<sup>5</sup> mesoporous silica nanoparticles,<sup>6</sup> anionite,<sup>7</sup> and natural minerals.<sup>8,9</sup> Adsorbents based on natural minerals have become the center of research in this area due to their advantages, such as non-toxicity, availability, and low cost. In addition to copper, they are used to purify aqueous solutions from chromium,<sup>10</sup> zinc, and nickel ions<sup>11</sup> and several other contaminants.

Clinoptilolite is the most prevalent natural zeolite used for the purification of contaminated water.<sup>12</sup> Numerous studies have investigated the removal of heavy metals, namely copper from aqueous solutions using clinoptilolite.<sup>4,13</sup> Glauconite solids are supposed to be effective adsorbents for the removal of metals from water. In 1978 in the studies of Spoljaric and Crawford<sup>14,15</sup> it was found that a glauconitic greensand filter removes a significant amount of heavy metals' cations from polluted waters. The efficiency of thermal and microwave treatment of natural minerals for improving their heavy metals adsorption capacity was described earlier.<sup>16,17</sup>

This paper presents the results of the adsorption of Cu ions from aqueous solutions. Adsorption equilibrium information is the most important data for a proper understanding of the process. It provides the background for the improvement of the adsorption parameters and efficient equipment design. Along with the development of computer technologies, nonlinear isotherm fitting has become widely used, having several advantages over the linear method. This study aims to determine which of the several isotherm models fits best. In this research, the relationship between the adsorbed matter and the equilibrium concentration in wastewater is described by four two-parameter isotherm models: Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich and four three-parameter adsorption isotherm models: Langmuir-Freundlich, Redlich-Peterson, Toth, and Aranovich.

<sup>1</sup> Department of Environmental Safety, Lviv State University of Life Safety, 35 Kleparivska St., Lviv, 79007, Ukraine  
✉ [kateryna.stepova@gmail.com](mailto:kateryna.stepova@gmail.com)

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## 2. Experimental

### 2.1. Adsorbents

The adsorbents used were natural clinoptilolite (pH of aqueous extract – 7.75; bulk density – 947 kg/m<sup>3</sup>) and glauconite (pH of aqueous extract – 8.6; bulk density – 1049,85 kg/m<sup>3</sup>). Samples were pre-washed, levigated, and dried at 80 °C until constant weight. After drying, the samples were sieved. A particle size fraction of 0.8-1.2 mm was chosen for research.

For improving the adsorption properties the natural samples were pre-treated as follows: calcination at 550 °C for 3 hours or microwave treatment for 10 min at 790 W.

The following natural and pre-treated sorbents were chosen for sorption studies:

- 1) Cl\_nat – natural clinoptilolite;
- 2) Cl\_thermo – calcinated clinoptilolite;
- 3) Cl\_MW – microwaved clinoptilolite;
- 4) G\_nat – natural glauconite;
- 5) G\_thermo – calcinated glauconite;
- 6) G\_MW – microwaved glauconite.

### 2.2. Adsorbate

The sorption properties of the samples were investigated under static conditions. The 67 mg/L CuCl<sub>2</sub> solution was used to determine the equilibrium contact time. For each sample type, eight jars of fixed volume (0.1 L) of Cu<sup>2+</sup> solutions were prepared and contacted with 1 g adsorbent, then stirred and left for 24 hours. The

solutions were analysed for the content of Cu<sup>2+</sup> ions. The content of Cu<sup>2+</sup> ions in the solutions was determined by direct potentiometry (Ionometer AI-125). All experiments were repeated three times.

The amount of adsorbed Cu<sup>2+</sup> ions onto the sorbent, mg/g, was calculated as follows:

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

where C<sub>0</sub> – initial concentration of Cu<sup>2+</sup> ions, mg/L; C<sub>e</sub> – equilibrium concentration of Cu<sup>2+</sup> ions in solution, mg/L; V – volume of solution, L; m – mass of adsorbent, g.

### 2.3. XPS

XPS experiments were performed using an Elvax Light SDD according to the requirements of ISO 29581.

### 2.4. Isotherm Adsorption Study

Four two-parameter and four three-parameter isotherm models were chosen to describe the adsorption of copper ions. Table 1 summarizes the corresponding models used in this study.

As linear modelling is unsuitable for three-parameter isotherms, five different error functions, such as SAE, ARE, SSE, HYBRID, MPSD presented in Table 2, were used to evaluate the SNE values. The "Solver" add-in in the MS Excel spreadsheet was used for solving the isotherm equations by minimizing the error functions between the calculated q<sub>e</sub> value and the experimental data. Based on the minimum SNE values optimum parameters sets for the best isotherm model were evaluated.

**Table 1.** Isotherm models equations

Parameter No.	Isotherm model	Formula	Equation number	Reference
Two	Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	2	18
	Fraundlich	$q_e = K_F C_e^{1/n}$	3	19
	Temkin	$q_e = \frac{RT}{b} \ln(K_T C_e)$	4	20
	Dubinin-Radushkevich	$q_e = q_m \exp(-Be^2)$ $e = RT \ln \left( 1 + \frac{1}{C_e} \right)$	5	21
Three	Langmuir-Freundlich	$q_e = \frac{q_m (K_{LF} C_e)^{n_{LF}}}{1 + (K_{LF} C_e)^{n_{LF}}}$	6	22
	Redlich-Peterson	$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^\beta}$	7	23
	Toth	$q_e = \frac{q_m b_T C_e}{(1 + b_T C_e^{n_T})^{1/n_T}}$	8	24
	Aranovich	$q_e = \frac{q_m C_{Ar} \frac{C_e}{C_s}}{\left(1 - \frac{C_e}{C_s}\right)^{1/2} \left(1 + C_{Ar} \frac{C_e}{C_s}\right)}$	9	25

**Table 2.** Error functions equations<sup>26</sup>

Error function	Formula	Equation number
The sum of absolute errors (SAE)	$\sum_{i=1}^n  q_{e\_exp} - q_{e\_calc} _i$	10
The sum of square errors (SSE)	$\sum_{i=1}^n (q_{e\_exp} - q_{e\_calc})_i^2$	11
Average relative error (ARE)	$\frac{100}{n} \sum_{i=1}^n \left  \frac{q_{e\_exp} - q_{e\_calc}}{q_{e\_exp}} \right _i$	12
Hybrid fractional error function (HYBRID)	$\frac{100}{n-p} \sum_{i=1}^n \left( \frac{(q_{e\_exp} - q_{e\_calc})_i^2}{q_{e\_exp}} \right)_i$	13
Marquard's percent standard deviation (MPSD)	$100 \sqrt{\frac{1}{n-p} \sum_{i=1}^n \left( \frac{q_{e\_exp} - q_{e\_calc}}{q_{e\_exp}} \right)_i^2}$	14

The values of isotherm models' parameters are summarized in Table 4. Values in bold type indicate an error function with the minimum SNE value for each model fitted to experimental results obtained for appropriate adsorbent and the minimum SNE for the set of chosen models for each sample.

The results were expressed as plots of solid-phase  $\text{Cu}^{2+}$  concentration against liquid-phase  $\text{Cu}^{2+}$  concentration. As previously mentioned, this study aimed to select the best descriptive isotherm model.

### 3. Results and Discussion

#### 3.1. XPS

In general, the content of iron oxides in glauconite (13.66 %) is significantly higher than in clinoptilolite (2.4 %), while clinoptilolite is richer in silicon and aluminum oxides.

High temperature causes dehydroxylation of the surface and, as a result, changes in the distribution of active centers of various types. As shown by the results of X-ray fluorescence analysis (Fig. 1) of calcined natural clinoptilolite, heat treatment at 550 °C leads to an increase in the relative content of aluminum oxides from 13.85 to 20.5 %, along with a decrease in the content of silicon oxides from 77.5 to 69.63 %. Such changes in the  $\text{Al}_2\text{O}_3/\text{SiO}_2$  ratio can have a significant impact on the selectivity of the studied material. Instead, the calcination of natural glauconite leads to an increase in the content of silicon oxide from 66.0 to 72.25 % and a decrease in the relative content of iron oxides from 13.66 to 10.61 %.

#### 3.2. Isotherm Fitting

The adsorption isotherm characterizes the distribution of the molecules between liquid and solid phases when the adsorption process reaches the equilibrium state. Its main task is to establish the maximum adsorption capacity of the sample, mg/g of adsorbent, depending on the initial concentration in the solution. Besides, the shape of the isotherm indicates the sorption mechanism and dominative pore structure of the adsorbent. The isotherms depicted in Fig. 2 clearly identified the difference between adsorption processes taking place on clinoptilolite and glauconite. The clinoptilolite isotherms by their shape are similar to the isotherm type 3.<sup>27</sup> It is obtained when the formation of mono and polylayers take place simultaneously, resulting in an almost exponential increase in the amount of adsorption. Instead, the glauconite isotherms correspond to isotherm type 1,<sup>27</sup> that predicts the formation of one surface layer until the saturation of the sample. In this case we may assume that the pore sizes are not much larger than the molecular diameter of the adsorbate.

It is evident from Fig. 2 that heat and microwave treatment significantly increases the adsorption capacity of clinoptilolite for copper ions while reducing that of glauconite. It is confirmed by  $q_m$  values of the Langmuir, Dubinin-Radushkevich, Langmuir-Freundlich, Toth, and Aranovich models.

It is clear that the Langmuir-Freundlich and Freundlich models have the best performance for fitting with experimental data of natural and microwaved samples. The Toth model fits well only the adsorption on calcinated samples. It combines the characteristics of Langmuir (at low concentration limit) and Freundlich isotherms (at high concentrations).<sup>28</sup>

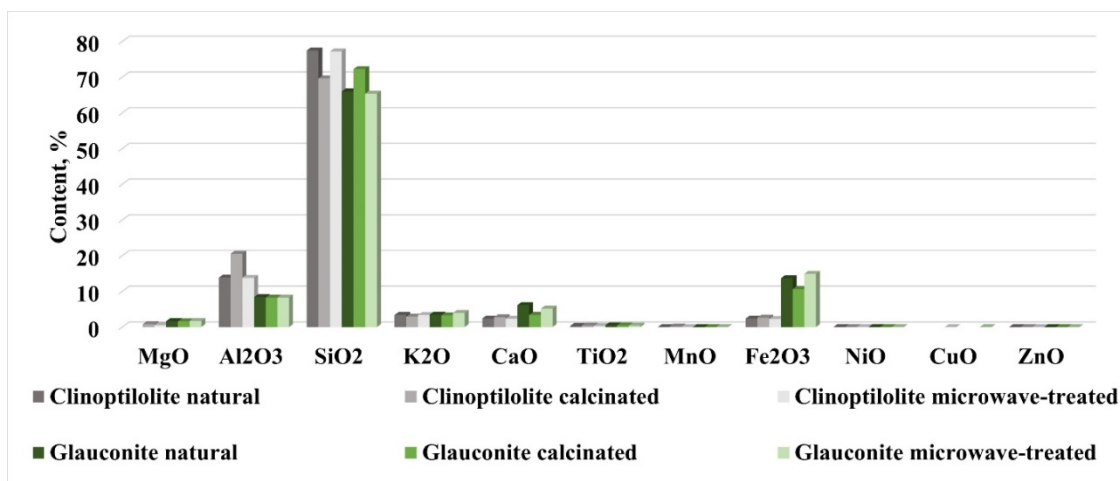
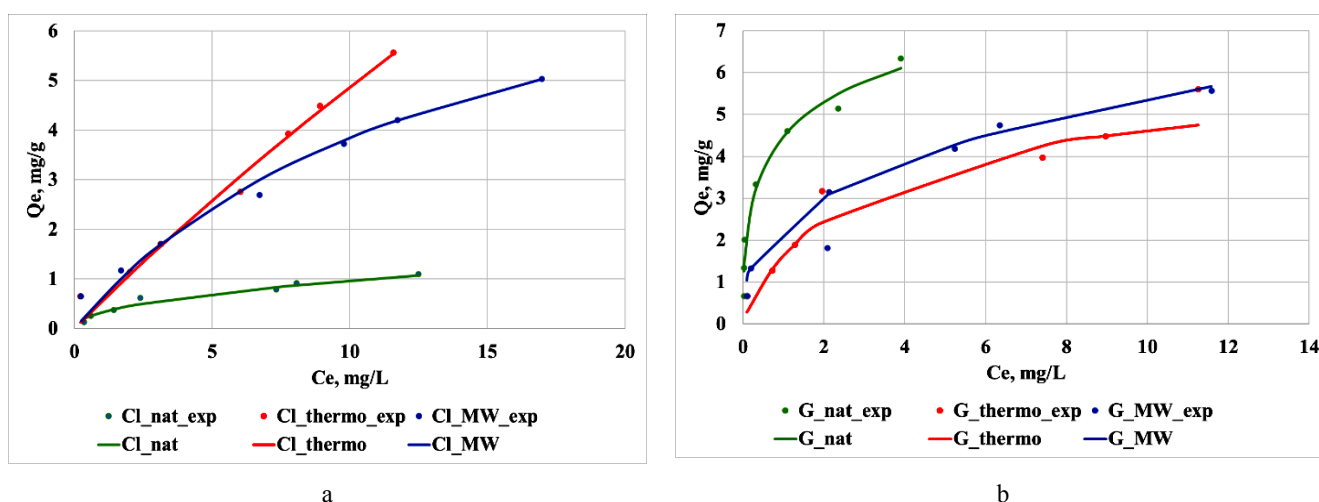


Fig. 1. XPS results of the studied samples


 Fig. 2. Isotherm of  $\text{Cu}^{2+}$  on a) clinoptilolite and b) glaucosite samples

According to the error values of SNE, we may classify the fitting degree of isotherm models in the following order:

– *Natural clinoptilolite*: Freundlich – Toth – Langmuir-Freundlich – Redlich-Peterson – Langmuir – Aranovich – Temkin – Dubinin-Radushkevich;

– *Calcinated clinoptilolite*: Toth – Langmuir-Freundlich – Redlich-Peterson – Freundlich – Langmuir – Aranovich – Dubinin-Radushkevich – Temkin;

– *Microwaved clinoptilolite*: Langmuir-Freundlich – Toth – Langmuir – Redlich-Peterson – Freundlich – Aranovich – Temkin – Dubinin-Radushkevich;

– *Natural glaucosite*: Langmuir-Freundlich (Aranovich) – Freundlich – Toth – Redlich-Peterson – Langmuir – Temkin – Dubinin-Radushkevich;

– *Calcinated glaucosite*: Toth – Langmuir-Freundlich – Langmuir – Freundlich – Redlich-Peterson – Aranovich – Dubinin-Radushkevich – Temkin;

– *Microwaved glaucosite*: Langmuir-Freundlich (Freundlich) – Toth – Langmuir – Aranovich – Redlich-Peterson – Temkin – Dubinin-Radushkevich.

These results showed that the three-parameter models fits better than the two-parameter models.

The Langmuir equation<sup>18</sup> is valid for monolayer sorption on a surface with a finite number of identical sites. The values of maximum adsorption capacity determined by the Langmuir model are 1.272, 31.051, and 9.047 mg/g for natural, calcinated, and microwaved clinoptilolite, respectively. It's evident that thermal and microwave treatment led to a sufficient increase in adsorption capacity. Instead,  $q_{max}$  values for natural, calcinated, and microwaved glaucosite are 5.369, 5.77, and 7.367 mg/g, respectively. Therefore, the adsorption capacity of natural clinoptilolite is lower than natural glaucosite, but the pre-treatment considerably enhances it. However, the pre-treatment of glaucosite doesn't change it much.

The essential feature of the Langmuir isotherm can be expressed by the separation factor or equilibrium parameter of “ $R_L$ ”. It is defined by the following relationship:<sup>29</sup>

$$R_L = \frac{1}{1 + K_L C_0} \quad (15)$$

where  $K_L$  and  $C_0$  (mg/l) are the Langmuir constant and the highest initial Cu concentration respectively. As the “ $R_L$ ” value for studied samples lies between 0 and 1, the ongoing adsorption process is favorable.

The values of “ $R_L$ ” calculated according to the Langmuir model for untreated clinoptilolite and glauconite for initial concentration of  $\text{Cu}^{2+}$  in the solution ( $C_0 = 67.28$  mg/l) are 0.045 and 0.0015, respectively. The lower value of “ $R_L$ ” for glauconite than for clinoptilolite indicates that the adsorption of copper on natural glauconite is more favorable than on clinoptilolite. It is confirmed by experimental data: the adsorption capacity of glauconite is greater than that of clinoptilolite (Fig.2).

The same conclusion can be made from the Freundlich model fitting results. In a favorable adsorption process, the value of the exponent, “ $1/n$ ”,

should be in the range of 0-1.<sup>29</sup> In this study, the values of  $1/n$  vary in the range of 0.3 to 0.9 values which indicates that this adsorption is favorable. Since the value of  $n$  is the above unity, the adsorption is favorable and of physical nature.<sup>30</sup>

The widely used Langmuir and Freundlich models do not give any information about the adsorption mechanism. The Dubinin-Radushkevich isotherm is used to distinguish physical and chemical adsorption.<sup>21</sup> The Dubinin-Radushkevich isotherm is more general because it does not assume a homogeneous surface or constant adsorption potential. It indicates the nature of the adsorption of adsorbate on the adsorbent and can be used to calculate the average free energy of adsorption:

$$E = \frac{1}{\sqrt{2B}} \quad (16)$$

If the  $E$  value is between 8 and 16 kJ/mol then it is assumed that the adsorption process is an ion exchange process, and if it is less than 8 kJ/mol then the adsorption process is of physical nature. The calculated values of free energy of adsorption  $E$  for the samples vary from 0.18 to 5, indicating the physical nature of the copper interaction with the adsorbents (Table 3).

**Table 3.** The energy of adsorption values for studied samples

	Type of the sample					
	Cl_nat	Cl_thermo	Cl_MW	G_nat	G_thermo	G_MW
E, kJ/mol	1.70	0.51	0.61	5	0.18	0.74

The advantage of Temkin isotherm is its feature to ignore the extremely low and high values of the concentrations and the assumption that the heat of adsorption of all molecules in the layer would decrease linearly.<sup>31</sup> The constant “ $b$ ” related to the variation of adsorption energy concluded from Temkin isotherm, is positive for all the studied samples. These indicate the adsorption reaction is exothermic.<sup>26</sup>

The Langmuir-Freundlich isotherm includes the knowledge of the adsorption on heterogeneous surfaces. It describes the distribution of adsorption energy onto the heterogeneous surface of the adsorbent.<sup>32</sup> At low concentrations, this model agrees with the Freundlich isotherm model, while at high concentrations, it concurs with the Langmuir isotherm.

The Langmuir-Freundlich isotherm is a universal model that combines the features of the Freundlich and Langmuir models.<sup>22</sup> At low and high adsorbate concentrations, the Langmuir-Freundlich isotherm model becomes the Freundlich isotherm model and Langmuir isotherms model respectively.<sup>33</sup> The Langmuir-Freundlich isotherm has shown the best-fit copper adsorption on natural glauconite and both microwaved samples.

The Redlich-Peterson isotherm<sup>34</sup> is an integral isotherm that combines the Langmuir and Freundlich

models, which include three parameters in an empirical equation. This equation is suitable for representing adsorption equilibrium over a wide range of concentrations. The value of the exponent  $\beta$  lies between 0 and 1. When the value of  $\beta$  tends to zero, the Redlich-Peterson isotherm follows the Freundlich model at high concentrations, while when the value of  $\beta$  is close to 1, the model approaches the Langmuir model at low concentrations. It can be concluded that the surface of clinoptilolite became more heterogeneous after calcination as the  $\beta$  value changes from 0.818 to 0.179. On the contrary, after calcination of glauconite, its surface becomes homogenous as the  $\beta$  value changes from 0.784 to 0.965 i.e. all adsorption sites are equal. The  $\beta$  value of all other samples indicates that the surface is homogeneous.

According to Toth isotherm when  $n_t = 1$ , this equation reduces to Langmuir isotherm equation. Therefore, the parameter  $n_t$  characterizes the heterogeneity of the adsorption system<sup>35</sup> and if it deviates further away from the unity, then the system is said to be heterogeneous. The values of exponent “ $n_t$ ” of all six samples vary in the range from 0.182 to 0.749 (Table 4) so the process occurs on a homogeneous surface.

The Aranovich model is of an empirical nature and thus has less theoretical explanatory power, but it

fits and works in a wider range of data. The original Aranovich equation is the product of the Langmuir monolayer isotherm multiplied by a factor that accounts for adsorption in higher layers.<sup>25</sup> Aranovich conjectured that higher adsorption layers do not affect the monolayer, *i.e.* the interaction of molecules in the first adsorption layer with molecules in higher adsorption layers is negligible in comparison with their interaction with the adsorbent surface. The Aranovich model, along with the Langmuir-Freundlich

isotherm, describes the process occurring on natural glauconite with high accuracy, unlike all other studied samples with a lower maximum sorption capacity. It can therefore be concluded that after thermal and microwave treatment of glauconite, the interaction of molecules in the first adsorption layer becomes commensurate with the interaction forces in higher adsorption layers. For clinoptilolite samples, the Aranovich model is less suitable than the other three-parameter models.

**Table 4.** Isotherm parameters for the removal of Cu<sup>2+</sup> from simulated wastewater on natural, microwave-treated, and calcinated clinoptilolite and glauconite

Index	Natural clinoptilolite	Calcinated clinoptilolite	Microwave-treated clinoptilolite	Natural glauconite	Calcinated glauconite	Microwave-treated glauconite
1	2	3	4	5	6	7
<b>Two-parameter models</b>						
Langmuir model						
q <sub>m</sub>	1.272	31.051	9.047	5.369	5.770	7.367
K <sub>L</sub>	0.317	0.018	0.074	9.779	0.390	0.264
SAE	0.324	1.178	<b>1.041</b>	3.434	<b>2.353</b>	2.990
SSE	0.024	0.419	0.365	2.457	1.553	2.086
ARE	<b>8.227</b>	14.576	14.729	21.063	16.031	29.959
HYBRID	0.761	<b>9.347</b>	8.552	<b>15.812</b>	11.899	29.678
MPSD	12.579	36.319	34.647	29.442	31.7198	50.193
SNE	4.215	3.577	3.655	3.974	3.632	4.0
Freundlich model						
n	2.123	1.106	1.585	3.442	2.257	2.806
K <sub>F</sub>	0.326	0.608	0.843	4.245	1.698	2.370
SAE	<b>0.320</b>	<b>0.972</b>	<b>0.843</b>	2.026	<b>1.907</b>	<b>2.073</b>
SSE	0.027	0.361	0.184	<b>0.917</b>	1.250	1.828
ARE	13.135	13.013	8.928	21.721	9.101	19.726
HYBRID	1.460	8.254	3.304	18.482	7.136	22.747
MPSD	27.058	34.208	21.119	49.643	15.405	41.036
SNE	<b>3.975</b>	3.547	3.757	3.468	3.718	<b>3.80</b>
Temkin model						
b	10.01	3.74	3.08	2.44	2.43	2.70
K <sub>T</sub>	4.84	12.00	6.42	108.30	10.37	20.59
SAE	0.331	6.421	4.568	2.331	<b>3.360</b>	2.934
SSE	0.026	10.138	3.839	0.996	2.221	3.094
ARE	<b>7.369</b>	<b>31.201</b>	30.180	16.741	29.600	<b>17.105</b>
HYBRID	0.817	54.488	<b>28.094</b>	10.047	26.093	29.538
MPSD	12.594	47.407	40.784	<b>25.661</b>	49.107	39.291
SNE	19.67	142.71	100.95	50.53	104.77	86.25
Dubinin-Radushkevich model						
q <sub>m</sub>	0.71	4.72	3.99	5.06	2.87	5.42
B	0.173	1.915	1.344	0.020	14.77	0.92
SAE	0.894	3.784	3.896	3.696	3.650	4.102
SSE	0.237	2.956	2.868	2.944	2.916	<b>3.324</b>
ARE	18.673	30.358	32.414	21.006	24.695	38.804
HYBRID	5.461	<b>27.682</b>	<b>29.121</b>	17.554	<b>21.491</b>	47.827
MPSD	<b>28.014</b>	50.879	52.166	<b>28.805</b>	36.405	65.780
SNE	50.188	109.92	114.69	67.426	82.96	154.038

Continuation of Table 4

1	2	3	4	5	6	7
<b>Three-parameter models</b>						
Langmuir-Freundlich model						
$q_m$	1.765	53.474	9.509	11.157	6.483	11.609
$K_{LF}$	0.136	0.0095	0.065	0.395	0.282	0.070
$n_{LF}$	0.738	0.978	0.955	0.432	0.871	0.521
SAE	0.306	1.130	<b>1.030</b>	1.850	<b>2.274</b>	<b>2.046</b>
SSE	<b>0.020</b>	<b>0.389</b>	0.323	<b>0.778</b>	1.497	1.855
ARE	10.873	14.708	14.035	18.926	14.819	17.180
HYBRID	1.012	11.426	9.697	17.159	13.284	26.073
MPSD	19.382	40.413	37.153	46.422	31.436	39.271
SNE	4.100	3.435	<b>3.51</b>	<b>3.406</b>	3.549	<b>3.80</b>
Redlich-Peterson model						
$\lambda$	0.818	0.179	0.546	0.784	0.965	0.572
$a_{RP}$	0.52	0.88	0.74	30.69	0.44	1494.00
$K_{RP}$	0.443	1.138	1.320	141.422	2.317	2988.777
SAE	0.284	0.975	<b>0.936</b>	1.688	<b>2.321</b>	2.337
SSE	0.025	0.371	0.238	<b>0.665</b>	1.532	<b>1.289</b>
ARE	<b>7.748</b>	<b>13.146</b>	11.791	17.727	15.821	16.404
HYBRID	1.112	10.554	6.996	14.792	14.746	16.411
MPSD	11.731	29.215	24.008	32.517	26.592	22.965
SNE	4.210	3.523	3.744	3.76	3.927	4.204
Toth model						
$q_m$	1.19	11.477	6.152	260.92	5.50	86.73
$b_T$	0.41	0.080	0.346	3.179	0.508	1.049
$n_T$	0.675	0.182	0.302	0.275	0.749	0.187
SAE	0.290	<b>0.975</b>	<b>0.892</b>	1.877	<b>2.281</b>	7.679
SSE	0.024	0.379	0.227	<b>0.769</b>	1.499	12.495
ARE	<b>7.929</b>	13.251	11.143	18.142	15.314	40.677
HYBRID	1.050	10.742	6.384	14.728	14.011	86.318
MPSD	15.105	38.953	30.022	41.390	33.335	<b>60.107</b>
SNE	4.035	<b>3.38</b>	3.563	3.501	<b>3.351</b>	3.856
Aranovich model						
$q_m$	0.998	5.352	3.947	6.203	3.441	4.409
$C_{Ar}$	15.831	2.40	7.233	8.66	19.69	91.18
$C_S$	34.376	17.398	27.780	9.438	16.909	52.587
SAE	0.281	1.505	1.490	7.020	1.803	3.570
SSE	0.016	0.444	0.391	10.422	<b>0.679</b>	4.008
ARE	8.415	15.685	14.637	<b>50.375</b>	15.545	<b>20.983</b>
HYBRID	0.692	<b>10.677</b>	<b>8.335</b>	116.296	9.304	46.873
MPSD	<b>9.548</b>	28.868	24.790	62.256	20.979	37.287
SNE	5.28	6.50	6.22	<b>3.406</b>	5.41	4.03

## 4. Conclusions

The heat treatment of clinoptilolite at 550 °C leads to an increase in the relative content of aluminum oxides from 13.85 to 20.5 %, along with a decrease in the content of silicon oxides from 77.5 to 69.63 %. Instead, the calcination of natural glauconite leads to an increase in the content of silicon oxide from 66.0 to 72.25 % and a decrease in the relative content of iron

oxides from 13.66 to 10.61 %. That can have a significant impact on the selectivity of the studied material.

The Langmuir-Freundlich and Freundlich models have the best performance for fitting with experimental data of natural and microwaved samples. The Toth model fits well only the adsorption on calcinated samples.

The adsorption of copper on natural glauconite is more favorable than on clinoptilolite, which is confirmed by experimental data: the adsorption capacity of glauconite is greater than that of clinoptilolite.

The heat and microwave treatment significantly increases the adsorption capacity of clinoptilolite for copper ions while reducing that of glauconite. It is confirmed by  $q_m$  values of the Langmuir, Dubinin-Radushkevich, Langmuir-Freundlich, Toth, and Aranovich models.

The values of maximum adsorption capacity determined by the Langmuir model are 1.272, 31.051, and 9.047 mg/g for natural, calcinated, and microwaved clinoptilolite, respectively. Instead,  $q_{max}$  values for natural, calcinated, and microwaved glauconite are 5.369, 5.77, and 7.367 mg/g, respectively. Therefore, the adsorption capacity of natural clinoptilolite is lower than natural glauconite but the pre-treatment considerably enhances it. However, the pre-treatment of glauconite doesn't change it much.

The physical nature of the interaction of copper with the adsorbents is confirmed by values of the Freundlich constant  $n$  and the free energy of adsorption  $E$  calculated from Dubinin-Radushkevich model.

The Temkin isotherm constant  $b$  indicates the adsorption reaction is exothermic. The values of Toth and Redlich-Peterson models' constants of all six samples confirm that the copper adsorption occurs on homogeneous surfaces.

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## References

- [1] Barker, A. J.; Clausen, J. L.; Douglas, T. A.; Bednar, A. J.; Griggs, C. S.; Martin, W. A. Environmental Impact of Metals Resulting from Military Training Activities: A Review. *Chemosphere* **2021**, *265*, 129110. <https://doi.org/10.1016/j.chemosphere.2020.129110>
- [2] Liu, Y.; Wang, H.; Cui, Y.; Chen, N. Removal of Copper Ions from Wastewater: A Review. *Int. J. Environ. Res. Public Health* **2023**, *20*, 3885. <https://doi.org/10.3390/ijerph20053885>
- [3] Rathi, B. S.; Kumar, P. S. Application of Adsorption Process for Effective Removal of Emerging Contaminants from Water and Wastewater. *Environ. Pollut.* **2021**, *280*, 116995. <https://doi.org/10.1016/j.envpol.2021.116995>
- [4] Fu, F.; Wang, Q. Removal of Heavy Metal Ions from Wastewaters: A Review. *J. Environ. Manage.* **2011**, *92*, 407–418. <https://doi.org/10.1016/j.jenvman.2010.11.011>
- [5] Soloviy, Ch.; Malovanyy, M.; Bordun, I.; Ivashchyshyn, F.; Borysiuk, A.; Kulyk, Y. Structural, Magnetic and Adsorption Characteristics of Magnetically Susceptible Carbon Sorbents Based on Natural Raw Materials. *J. Water Land Dev.* **2020**, *47*(X–XII), 160–168. <https://doi.org/10.24425/jwld.2020.135043>
- [6] Amin, K. F.; Gulshan, F.; Asrafuzzaman, F. N. U.; Das, H., Rashid; R., Manjura Hoque, S. Synthesis of Mesoporous Silica and Chitosan-Coated Magnetite Nanoparticles for Heavy Metal Adsorption from Wastewater. *Environ. Nanotechnol. Monit. Manag.* **2023**, *20*, 100801. <https://doi.org/10.1016/j.enmm.2023.100801>
- [7] Kostenko, E.; Melnyk, L.; Matko, S.; Malovanyy, M. The Use of Sulphophtalein Dyes Immobilized on Anionite AB-17X8 to Determine the Contents of Pb(II), Cu(II), Hg(II) and Zn(II) in Liquid Medium. *Chem. Chem. Technol.* **2017**, *11*, 117–124. <https://doi.org/10.23939/chcht11.01.117>
- [8] Djebbar, M.; Djafri, F. Adsorption of Zinc Ions in Water on Natural and Treated Clay. *Chem. Chem. Technol.* **2018**, *12*, 272–278. <https://doi.org/10.23939/chcht12.02.272>
- [9] Gumnitsky, J.; Sabadash, V.; Matsuska, O.; Lyuta, O.; Hyvlud, A.; Venger, L. Dynamics of Adsorption of Copper Ions in Fixed-Bed Column and Mathematical Interpretation of the First Stage of the Process. *Chem. Chem. Technol.* **2022**, *16*, 267–273. <https://doi.org/10.23939/chcht16.02.267>
- [10] Malovanyy, M., Sakalova, H. Vasylynych, T., Palamarchuk, O., Semchuk, J. Treatment of Effluents from Ions of Heavy Metals as Display of Environmentally Responsible Activity of Modern Businessman. *J. Ecol. Eng.* **2019**, *20*, 167–176. <http://dx.doi.org/10.12911/22998993/102841>
- [11] Petrushka, I.; Petrushka, K.; Bliatnyk, B. Improvement of Adsorption Processes of Wastewater Treatment from Nickel Ions. *Environ. Probl.* **2020**, *5*, 83–87. <https://doi.org/10.23939/ep2020.02.083>
- [12] Kabuba, J.; Banza, M. Ion-Exchange Process for the Removal of Ni (II) and Co (II) from Wastewater Using Modified Clinoptilolite: Modeling by Response Surface Methodology and Artificial Neural Network. *Results Eng.* **2020**, *8*, 100189. <https://doi.org/10.1016/j.rineng.2020.100189>
- [13] Zanin, E.; Scapinello, J.; de Oliveira, M.; Rambo, C. L.; Francescon, F.; Freitas, L.; de Mello, J. M.; Fiori, M. A.; Oliveira, J. V.; Dal Magro, J. Adsorption of Heavy Metals from Wastewater Graphic Industry Using Clinoptilolite Zeolite as Adsorbent. *Process Saf. Environ. Prot.* **2017**, *105*, 194–200. <https://doi.org/10.1016/j.psep.2016.11.008>
- [14] Spoljaric, N.; Crawford, W. A. Glauconitic Greensand: A Possible Filter of Heavy Metal Cations from Polluted Waters. *Environ. Geol.* **1978**, *2*, 215–221. <https://doi.org/10.1007/BF02380487>
- [15] Spoljaric, N.; Crawford, W. A. Removal of Contaminants from Landfill Leachates by Filtration through Glauconitic Greensands. *Environ. Geol.* **1978**, *2*, 359–363. <https://doi.org/10.1007/BF02380510>
- [16] Sysa, L. V.; Stepova, K. V.; Petrova, M. A.; Kontsur, A. Z. Microwave-Treated Bentonite for Removal of Lead from Wastewater. *Vopr. Khimii i Khimicheskoi Tekhnologii* **2019**, *5*, 126–134. <https://doi.org/10.32434/0321-4095-2019-126-5-126-134>
- [17] Kontsur, A.; Sysa, L.; Petrova, M. Investigation of Copper Adsorption on Natural and Microwave-Treated Bentonite. *EasternEuropean J. Enterp. Technol.* **2017**, *6/6* (90), 26–32. <https://doi.org/10.15587/1729-4061.2017.116090>
- [18] Langmuir, I. The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. *J. Am. Chem. Soc.* **1918**, *40*, 1361–1403. <https://doi.org/10.1021/ja02242a004>



- [19] Freundlich, H.M.F. Over the Adsorption in Solution. *J. Phys. Chem.* **1906**, *57*, 385–471.
- [20] Hansen, J.B. Kinetics of Ammonia Synthesis and Decomposition on Heterogeneous Catalysts. In *Ammonia*. Nielsen, A., Ed; Springer: Berlin, Heidelberg, 1995; pp 149–190. [https://doi.org/10.1007/978-3-642-79197-0\\_4](https://doi.org/10.1007/978-3-642-79197-0_4)
- [21] Kielbasa, K.; Kamińska, A.; Niedoba, O.; Michalkiewicz, B. CO<sub>2</sub> Adsorption on Activated Carbons Prepared from Molasses: A Comparison of Two and Three Parametric Models. *Materials* **2021**, *14*, 7458. <https://doi.org/10.3390/ma14237458>
- [22] Jeppu, G.; Clement, P. A Modified Langmuir-Freundlich Isotherm Model for Simulating pH-dependent Adsorption Effects. *J. Contam. Hydrol.* **2012**, *129-130*, 46–53. <https://doi.org/10.1016/j.jconhyd.2011.12.001>
- [23] Redlich, O.; Peterson, D.L. A Useful Adsorption Isotherm. *J. Phys. Chem.* **1959**, *63*, 1024–1026. <https://doi.org/10.1021/j150576a611>
- [24] Toth, J. State Equations of the Solid-Gas Interface Layer. *Acta Chim. Hung.* **1971**, *69*, 311–317.
- [25] Aranovich, G.L. The Theory of Polymolecular Adsorption. *Langmuir* **1992**, *8*, 736–739. <https://doi.org/10.1021/la00038a071>
- [26] Hadi, M.; Samarghandi, M. R.; McKay, G. Equilibrium Two-Parameter Isotherms of Acid Dyes Sorption by Activated Carbons: Study of Residual Errors. *Chem. Eng. J.* **2010**, *160*, 408–416. <https://doi.org/10.1016/j.cej.2010.03.016>
- [27] Kajama, M. N. Hydrogen Permeation Using Nanostructured Silica Membranes. *WIT Trans. Ecol. Environ.* **2015**, *192*, 447–456. <https://doi.org/10.2495/SDP150381>
- [28] Dhaouadi, H.; M'Henni, F. Vat Dye Sorption onto Crude Dehydrated Sewage Sludge. *J. Hazard. Mater.* **2009**, *164*, 448–458. <https://doi.org/10.1016/j.jhazmat.2008.08.029>
- [29] Ozdes, D.; Duran, C.; Senturk, H. B.; Avan, H.; Bicer, B. Kinetics, Thermodynamics, and Equilibrium Evaluation of Adsorptive Removal of Methylene Blue onto Natural Illitic Clay Mineral. *Desalin. Water Treat.* **2013**, *52*, 208–218. <https://doi.org/10.1080/19443994.2013.787554>
- [30] Özcan, A. S.; Erdem, B.; Özcan, A. Adsorption of Acid Blue 193 from Aqueous Solutions onto BTMA-Bentonite. *J. Colloid Interface Sci.* **2005**, *266*, 73–81. <https://doi.org/10.1016/j.jcis.2004.07.035>
- [31] Aharoni, C.; Tompkins, F. C. Kinetics of Adsorption and Desorption and the Elovich Equation. *Adv. Catal.* **1970**, *21*, 1–49. [https://doi.org/10.1016/S0360-0564\(08\)60563-5](https://doi.org/10.1016/S0360-0564(08)60563-5)
- [32] Koble, R. A.; Corrigan, T. E. Adsorption Isotherms for Pure Hydrocarbons. *Ind. Eng. Chem.* **1952**, *44*, 383–387. <https://doi.org/10.1021/ie50506a049>
- [33] Ayawei, N.; Ebelegi, A. N.; Wankasi, D. Modelling and Interpretation of Adsorption Isotherms. *J. Chem.* **2017**, *2017*, 3039817. <https://doi.org/10.1155/2017/3039817>
- [34] Le, N. C.; Van Phuc, D. Sorption of Lead (II), Cobalt (II) and Copper (II) Ions from Aqueous Solutions by  $\gamma$ -MnO<sub>2</sub> Nanostructure. *Advances in Natural Sciences: Nanoscience and Nanotechnology* **2015**, *6*, 025014. <https://doi.org/10.1088/2043-6262/6/2/025014>
- [35] Jafari Behbahani, T.J.; Jafari Behbahani, Z. A New Study on Asphaltene Adsorption in Porous Media. *Pet. Coal* **2014**, *56*, 459–466.

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### НЕЛІНІЙНЕ МОДЕЛЮВАННЯ ІЗОТЕРМИ АДСОРБЦІЇ ДЛЯ МІДІ ЗІ СТИЧНИХ ВОД ПРИРОДНИМ ТА МОДИФІКОВАНИМ КЛИНОПТИЛОЛІТОМ І ГЛАУКОНІТОМ

**Анотація.** Представлено результати адсорбції іонів  $\text{Cu}^{2+}$  на природному та термічно обробленому та НВЧ-опроміненому клиноптилоліті та глауконіті. Проведено експерименти з рентгенівської фотоелектронної спектроскопії зразків. Залежність між адсорбованою речовиною та рівноважною концентрацією в стічних водах описано чотирма двопараметричними та чотирма трипараметричними моделями ізоTERM адсорбції.

**Ключові слова:** адсорбція, стічні води, нелінійне моделювання, ізоTERMA рівноваги, аналіз похибок.