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ZEOLITES AND CLAYS AS ADSORBENTS FOR SURFACTANTS: INNOVATIVE TECHNOLOGIES FOR ENVIRONMENTAL SAFETY

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This paper investigates natural sorbents, clinoptilolite and glauconite, for the removal of surfactants from wastewater. Surfactants are widely used in various industries, and their excessive presence in wastewater can lead to significant water pollution. Therefore, research into effective and cost-efficient sorbents is of increasing importance. Clinoptilolite and glauconite are non-metallic minerals that can adsorb surfactants from aqueous solutions, thus contributing to environmental sustainability. The influence of thermal and microwave treatment, as well as modification with metal-containing solutions, on the sorption properties of the materials was studied. Experimental results show that zeolites and clays are effective in removing surfactants from aqueous media; moreover, their adsorption capacity can be significantly enhanced through modification. The findings indicate that both types of sorbents are effective in removing dodecyl sulfonate from wastewater. In particular, Fe- and microwave-modified glauconite exhibited higher adsorption capacity compared to natural glauconite, while metal-modified clinoptilolite samples outperformed the unmodified ones.

Keywords: natural sorbents, adsorption, wastewater treatment, surfactants, adsorption isotherms.

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Introduction

In order to prevent the dangerous impact of wastewater on the environmental situation, it is necessary not only to rationally use natural resources, timely carry out demineralization and reclamation, phytomelioration of disturbed lands, etc. [1], but also to introduce effective wastewater treatment technologies, in particular the use of natural sorbents such as clinoptilolite and glauconite [2]. This will reduce emissions of pollutants into the environment, improve water quality and ensure the sustainability of ecosystems, which is important for sustainable development and environmental safety.

According to Mikhailov et al. [3] in the systemic analysis of the mineral resource base of strategic minerals of Ukraine, glauconite is one of the promising non-metallic minerals which are important for industry.

Instead, zeolites are classified as minerals with unclear prospects, which requires additional research and assessment of their potential. This emphasizes the need for further study of zeolites to identify possible areas of their effective use in various industries, such as adsorption technologies for water treatment.

Surfactants are hazardous and harmful compounds that cause destabilization of aquatic flora and fauna. It causes foaming in rivers, which leads to eutrophication of lakes and wastewater treatment plants. Surfactants increase the solubility of some pollutants in aquatic systems, causing eutrophication and threatening planktonic species [4]. Excessive presence of surfactants in water may reduce water quality, cause unpleasant taste and odor, and cause short- and long-term changes in the ecosystem. Surfactants also work synergistically with other toxic compounds present in water [5]. Perfluorinated surfactants were banned by EU Directive 2006/122/EC after they were found in the aquatic environment and human blood. However, a special permit was granted for some industries in which they cannot be replaced [6]. It has been observed that the toxicity of surfactants increases with an increase in their hydrophobicity. An increase in the length of alkyl groups increases the hydrophobicity of surfactants, which leads to an increase in the toxicity of the molecule. Conversely, an increase in the ethylene oxide content in a molecule reduces the hydrophobicity and toxicity of surfactants [7]. This means that an increase in the length of alkyl groups is directly proportional to the toxicity of surfactants, and an increase in the number of ethylene oxide groups is inversely proportional to toxicity.

Zeolites are good adsorbents for removing pollutants from wastewater. Natural Armenian zeolite has a higher adsorption capacity for CTAB (284 mg/g) compared to SDS (113 mg/g) due to the higher hydrophobicity of CTAB [8]. Hydrophobic interactions dominated the adsorption process, and the longer alkyl chain of CTAB contributed to its higher adsorption on the zeolite surface.

The natural Chilean zeolite modified with CTAB surfactant enhanced the adsorption capacity of the zeolite for the anionic surfactant SDBS [9]. Zeolites have shown good efficiency in the removal of surfactants, and modification with cations contributes to its increase.

The adsorption of anionic, cationic, and nonionic surfactants on layered (montmorillonite, illite, muscovite, kaolinite) and nonlayered (sepiolite and polygorskite) clays showed that adsorption on clay minerals depends on the nature of the surfactant and the structure of clay minerals. The anionic surfactant SDS was successfully adsorbed on an anionic clay made of bilayer magnesium hydroxide and aluminum. The adsorption of the surfactant enhanced with increasing temperature (288–308 K) [10].

Clays show good adsorption efficiency of surfactants, moreover it can be improved by forming composites and hybrids with other materials.

The adsorption of the anionic surfactant SDS on the surface of alumina was low (65%) under neutral conditions, but increased under slightly acidic conditions, and in the presence of NaCl, the adsorption increased to 98%. Pure alumina removed 94% of the anionic surfactant SDS from wastewater at an optimum concentration of 120 g/L and an equilibrium time of 1 h [11]. Alumina adsorbs surfactants well, and its efficiency can be improved by modifying its surface properties.

Materials and methods

Clinoptilolite is one of the most common widespread zeolites, first described in 1890. In terms of the volume of free intracrystalline space, clinoptilolite is classified as a medium-porous zeolite, its total porosity is on average 30%, and its specific surface area reaches about 105 cm^2/g. The density of the mineral varies between 2.11 and 2.2 g/cm^3. The water filling the intracrystalline space of clinoptilolite has the ability to be reversibly removed in a wide range of temperatures (from room temperature to 650^0C) without destroying its structure (dehydration) [12].

The mineral glauconite in the broad sense is a random alternation of non-expandable layers of 10Å and expandable montmorillonite layers. The number of the latter can exceed 50%, but it is commonly accepted to limit the name «glauconite» strictly to varieties with less than 10% of expandable layers. The difference in the number of expandable layers explains many of the observed variations in glauconite properties, including chemical composition (especially potassium content), thermal characteristics, cation exchange capacity, color, refractive index, and specific gravity. It is believed that mineral glauconite is formed by the absorption of potassium and iron by a degraded low-charge layered silicate lattice and the elimination of other types of silicate lattice under appropriate environmental conditions, of which the redox potential is the most critical [13].

The material used for the study was natural clinoptilolite from a deposit in the village of Sokyrnytsia, Khust district, Zakarpattia region (pH of the water extract was 7.75 and the bulk density was 946.7 kg/m^3) and glauconite from a quarry in Yarmolynets district, Khmelnytskyi region (pH of the water extract was 8.6 and the bulk density was 1049.85 kg/m^3).

In order to improve the adsorption properties, the natural samples were pretreated by calcination at 550^0C for 3 hours or microwave treatment at 790 W for 10 minutes.

Preparation of samples for analysis

Samples of natural sorption materials (clinoptilolite and glauconite) for the synthesis were pre-washed, soaked and dried in an oven at 80^0C until a constant weight was reached. After drying, the samples were sieved. A fraction of 0.8–1.2 mm was chosen for research.

In order to improve the sorption properties of the investigated samples, they were exposed to the following types of pretreatment:

1. Calcination in a muffle furnace at 750^{0}C for 3 hours.

2. Microwave irradiation at a power of 790 W for 30 min.

3. Irradiation with microwave radiation in contact with metal solutions: iron (III) chloride (concentration of 20 g/l), copper (II) chloride (concentration of 20 g/l) and calcium chloride (concentration of 20 g/l).

The 500-mL flasks were filled with natural materials (1 g) and filled with the appropriate salt solutions. After that, the samples were exposed to microwave radiation for 10 minutes at a power of 790 W. Subsequently, the samples were washed and dried at 80^{0}C until a constant weight was reached.

Adsorption studies

Ten beakers were filled with 100 ml of working solution of the appropriate concentration, then 1.0 g of sample was added, mixed, and left for 24 hours. The solutions were then filtered and analyzed for NH_4^+, PO_4^{3-}, and surfactant ions.

The removal parameters and the maximum equilibrium adsorption capacity were determined by the ratio between the amount of adsorbed ammonium or phosphate q_e [mg/g] and the equilibrium concentration of C_e [mg/L]. The adsorption isotherms are described by the following mathematical equations [14]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (1)$$

In Eq. (1), K_L is the Langmuir constant, which characterizes the affinity of the adsorbent and adsorbate (dm^3/mg); q_m is the maximum sorption capacity (mg/g of the sorbent); and C_e and q_e are the equilibrium concentrations of the component in the liquid and solid phases, respectively.

The Freundlich model (Eq. (2)) is an exponential equation, this equation allows for an infinite adsorption process.

$$q_e = K_F C_e^{1/n_f} \quad (2)$$

Here, K_F is the constant of the Freundlich isotherm, which characterizes the adsorption capacity, mg/g of sorbent. When the K_F increases, the adsorption capacity increases. n_f is the heterogeneity coefficient, therefore, the Freundlich isotherm model can be used for heterogeneous systems.

The Langmuir-Freundlich isotherm model (Eq. (3)) at low adsorbate concentrations reduces to the Freundlich isotherm. In contrast, at high concentrate ions it predicts the adsorption capacity of the monolayer, which is inherent in the Langmuir isotherm.

$$q_e = \frac{q_m (K_{LF} C_e)^{n_{LF}}}{1 + (K_{LF} C_e)^{n_{LF}}}, \quad (3)$$

where q_m and K_{LF} are the adsorption capacity and affinity constant, respectively; and n_{LF} is the heterogeneity coefficient or a measure of adsorption intensity. If n_{LF}=1, then Eq. (3) reduces to the Langmuir isotherm model.

The Dubinin-Radushkevich isotherm model (Eq. (4)) can be used to describe the sorption mechanism with the distribution of Gaussian energy over a heterogeneous surface, thus allowing to determine the physical or chemical nature of adsorption [15].

$$q_e = q_m \exp(-Be^2), \quad (4)$$

where B is a constant (mol^2/kJ^2); and e is the Polanyi adsorption potential (kJ/mol) determined by the following formula:

$$e = RT \ln(1 + 1/C_e). \quad (5)$$

In contrast to the Langmuir model, this model is more general, since it does not assume surface homogeneity and the constancy of the adsorption potential. The calculation of the free energy, E, according to the Dubinin-Radushkevich model determines the physical or chemical adsorption:

$$E = -(2B)^{-0.5}. \quad (6)$$

Since the conversion of the isotherm into linearized forms leads to a change in the error structure of the experimental data, nonlinear analysis has become essential because it provides an accurate method for determining adsorption parameters without changing the original form of the isothermal equations.

The model was evaluated by the minimum sum of standardized errors. The following errors were used for the analysis [16]:

– the sum of absolute errors (SAE):

$$\sum_{i=1}^{n} \left| q_{e\_\exp} - q_{e\_calc} \right|_i, \quad (7)$$

were q_{e_exp} and q_{e_calc} are the sorbate content in the sorbent determined experimentally and calculated, respectively, mg/g sorbent;

– the sum of squares of absolute errors (SSE):

$$\sum_{i=1}^{n} (q_{e\_\exp} - q_{e\_calc})^2_i; \quad (8)$$

– the sum of relative errors (ARE):

$$\frac{100}{n} \sum_{i=1}^{n} \left| \frac{q_{e\_\exp} - q_{e\_calc}}{q_{e\_\exp}} \right|_i, \quad (9)$$

where n is the number of experimental points;

– the hybrid fractional error (HYBRID):

$$\frac{100}{n-p}\sum_{i=1}^{n}\left(\frac{(q_{e\_exp}-q_{e\_calc})^2}{q_{e\_exp}}\right)_i, \quad (10)$$

where p is the number of model parameters to be determined.

– the standard deviation by Marquardt (MPSD):

$$100\sqrt{\frac{1}{n-p}\sum_{i=1}^{n}\left(\frac{q_{e\_exp}-q_{e\_calc}}{q_{e\_exp}}\right)_i^2}. \quad (11)$$

For a more accurate evaluation of the models, two experimental measurements were made for the experimental values that were not used for isotherm modeling. For each model, the isotherm parameters were calculated by minimizing the errors and calculating other error functions and the standardized error sum (SES). The best-fitting isotherms were selected based on the error bars of the experimental values and were used to establish the adsorption mechanism and to obtain the maximum adsorption capacity of the adsorbent.

Results and discussion

The adsorption isotherms of surfactants on natural and modified clinoptilolite are shown in Figs. 1 and 2.

The shape of the curve reflecting the change in the amount of adsorbed surfactant as a function of pressure corresponds to the type IV isotherm according to the IUPAC classification. The type IV isotherm is usually characteristic of mesoporous adsorbents. The results of nonlinear modeling of experimental tests within the framework of theoretical models are presented in Table 1.

The process of surfactant sorption on clinoptilolite samples, as described by the Langmuir-Freundlich model with a high determination coefficient (R^2=0.94–0.99), indicates a strong correlation between the experimental data and the model. This suggests that sorption occurs on heterogeneous surfaces with varying energy sites, which is characteristic of modified clinoptilolites. Notably, Fe- and Cu-modified clinoptilolite samples exhibit the highest sorption capacity, making them particularly effective for surfactant removal from aqueous solutions. However, thermal and microwave treatments, often applied to enhance adsorptive properties, do not significantly affect the sorption capacity, indicating that structural modifications through heating do not improve clinoptilolite performance in this context.

The results of nonlinear modeling of experimental studies on glauconite samples within the framework of theoretical models are presented in Table 2.

The process of surfactant sorption on glauconite samples obeys both the Dubinin-Radushkevich and Langmuir-Freundlich models, indicating that adsorption occurs on both microporous structures and heterogeneous surface sites. The sorption capacity of glauconite samples for surfactants follows the order: Fe-modified>microwave-treated>natural>Cu-modified>calcined glauconite. This sequence highlights that, while natural glauconite is an effective surfactant absorber compared to clinoptilolite, its performance can be significantly enhanced through modification with iron-containing compounds. Such modification increases active sites and enhances the overall adsorption capacity, making Fe-modified glauconite particularly suitable for water treatment applications

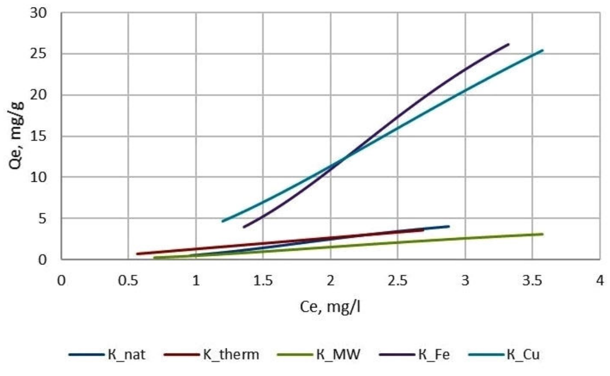

Fig. 1. Surfactant adsorption isotherms on clinoptilolite samples: K_nat – clinoptilolite natural; K_therm – heat-treated clinoptilolite; K_MV – microwave-irradiated clinoptilolite; K_Fe – Fe-modified clinoptilolite; and K_Cu – Cu-modified clinoptilolite

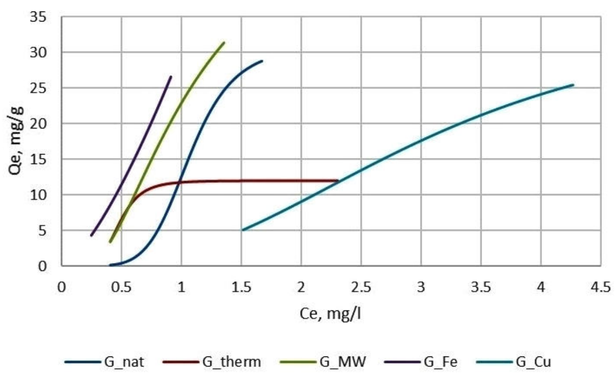

Fig. 2. Surfactant adsorption isotherms on glauconite samples: G_nat – glauconite natural; G_therm – heat-treated glauconite; G_MV – microwave-irradiated glauconite; G_Fe – Fe-modified glauconite; and G_Cu – Cu-modified glauconite

aimed at removing surfactants from contaminated environments.

Conclusions

The experimental results confirm that the modification of natural sorbents, such as clinoptilolite and glauconite, can significantly affect their ability to adsorb surfactants. Modification with various metals, especially iron and copper, can significantly increase the efficiency of surfactant absorption, making these materials promising for use in wastewater treatment technologies. This approach helps to expand the possibilities of using both zeolites and glauconites in practical environmental solutions.

Fe- and Cu-modified clinoptilolite exhibit the highest sorption capacity for surfactants, outperforming untreated samples. This enhanced capacity is attributed to the introduction of metal ions, which create additional active sites for adsorption. However, thermal

Table 1

Parameters of nonlinear modeling of adsorption isotherms

Parameters	Values				
	K_nat	K_therm	K_MW	K_Fe	K_Cu
Langmuir isotherm					
q_m	21394	19627	12340	112385	118318
K_L	$5.651\cdot10^{-5}$	$7.661\cdot10^{-5}$	$6.564\cdot10^{-5}$	$6.072\cdot10^{-5}$	$5.523\cdot10^{-5}$
R^2	0.84	0.90	0.89	0.81	0.91
Freundlich isotherm					
K_F	0.729	1.167	0.549	3.204	4.131
n_F	0.606	0.730	0.726	0.561	0.693
R^2	0.97	0.95	0.93	0.97	0.98
Langmuir-Freundlich isotherm					
q_m	6.263	5.173	5.594	40.000	58.920
K_{FL}	0.428	0.613	0.308	0.368	0.24
n_{FL}	2.765	2.958	2.037	3.178	1.995
R^2	0.98	0.99	0.94	0.98	0.98
Dubinin-Radushkevich isotherm					
q_m	6.649	6.220	4.120	48.090	37.350
β	0.991	0.652	0.934	1.514	1.190
R^2	0.98	0.99	0.93	0.98	0.97

Table 2

Parameters of nonlinear modeling of surfactant adsorption isotherms on glauconite samples

Parameters	Values				
	G_ nat	G_ therm	G_MW	G_Fe	G_Cu
Langmuir isotherm					
q_m	143577	21.95	107431	331336	110220
K_L	$10.41\cdot10^{-5}$	0.660	$19.64\cdot10^{-5}$	$8.142\cdot10^{-5}$	$5.114\cdot10^{-5}$
R^2	0.78	0.59	0.81	0.92	0.90
Freundlich isotherm					
K_F	11.930	8.073	20.97	30.120	3.658
n_F	0.532	1.647	0.679	0.711	0.729
R^2	0.93	0.56	0.89	0.96	0.96
Langmuir-Freundlich isotherm					
q_m	31.000	11.980	–	86583	36.390
K_{FL}	0.933	2.064	–	0.0035	0.325
n_{FL}	5.739	5.373	–	1.406	2.572
R^2	0.99	0.74	–	0.96	0.98
Dubinin-Radushkevich isotherm					
q_m	64.880	15.090	54.320	46.240	35.950
β	0.584	0.142	0.306	0.189	1.421
R^2	0.97	0.67	0.97	0.91	0.98

and microwave treatments, often used to modify the structure of adsorbents, do not lead to any significant changes in the sorption capacity of clinoptilolite, suggesting that these methods do not further improve its performance in surfactant removal.

In contrast, the sorption capacity of glauconite for surfactants follows a different pattern, with Fe-modified samples demonstrating the best performance, followed by microwave-treated, natural, Cu-modified, and calcined glauconite. Natural glauconite proves to be a more efficient sorbent for surfactants than clinoptilolite, and its performance is significantly boosted by modification with iron-containing compounds, which enhances its ability to capture and retain surfactants from aqueous solutions.

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ЦЕОЛІТИ ТА ГЛИНИ ЯК АДСОРБЕНТИ ДЛЯ ПОВЕРХНЕВО-АКТИВНИХ РЕЧОВИН: ІННОВАЦІЙНІ ТЕХНОЛОГІЇ ЕКОЛОГІЧНОЇ БЕЗПЕКИ

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Природні сорбенти, а саме клиноптилоліт і глауконіт, досліджуються в цій роботі для видалення поверхнево-активних речовин (ПАР) зі стічних вод. ПАР широко використовуються в різних галузях промисловості, і їх надлишок у стічних водах може спричиняти значне забруднення водних ресурсів, тому пошук ефективних і економічно вигідних сорбентів набуває актуальності. Клиноптилоліт і глауконіт – це неметалеві мінерали, які можуть бути використані для адсорбції ПАР зі стічних вод, що сприятиме сталому розвитку. У дослідженні вивчено вплив термічної та мікрохвильової обробки, а також модифікації металовмісними розчинами на сорбційні властивості природних матеріалів. Експериментальні дані свідчать, що цеоліти та глини є високоефективними у видаленні ПАР із водного середовища, проте для підвищення їх ефективності застосовується модифікація. Результати показали, що обидва типи сорбентів можуть успішно використовуватися для очищення стічних вод від додецилсульфонату, при цьому глауконіт, модифікований залізом і мікрохвилями, демонструє вищу адсорбційну здатність порівняно з природним зразком, а зразки клиноптилоліту, модифіковані металами, перевершують природний клиноптилоліт.

Ключові слова: природні сорбенти, адсорбція, стічні води, поверхнево-активні речовини, ізотерми адсорбції.

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