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RESEARCH OF COKE WASTEWATER TREATMENT PROCESS WITH GLAUCONITE CLAY

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Abstract

The process of complex purification of coke wastewater from phenols, rhodanides, ammonia, and resinous substances with the use of glauconite clay has been studied. Natural and activated glauconite, glauconite in combination with cationic flocculant brand Extraflock P 70, and activated carbon brand UAF (for comparison of cleaning efficiency) were used in this research. The activation of natural glauconite was carried out with a 7 % solution of HNO₃ at 95–100 °C, at a ratio "mineral sorbent:acid solution" of 1:6 and an activation time of 5 hours. It has been established that acid activation leads to a change in the chemical composition of glauconite and increases the specific surface area from 32 m²/g to 128 m²/g. Based on the results of natural glauconite thermal analysis, a conclusion was made about the phase transformations and chemical reactions that occur in glauconite clay during heating or cooling. Also, the thermal effects that accompany these changes, and some qualitative characteristics of the glauconite mineral were found. It was established that the maximum degree of phenols extraction from industrial effluent is up to 50% and is achieved when glauconite is used in combination with a flocculant. The maximum degree of purification from total ammonia is 57–58 % when using activated glauconite and glauconite with flocculant. The lowest degree of purification is achieved for rhodanides removal, not exceeding 20 % for any adsorbent. The highest degree of purification of 96.8 % is observed when removing resinous substances with glauconite in combination with a flocculant. Activation of glauconite by HNO₃ leads to an increase in sorption capacity by 5–15 % depending on the pollutant. The coke wastewater purification degree of these pollutants with activated carbon is 20 % of phenols, 14 % of rhodanides, 28 % of total ammonia, and 72 % of resinous substances, respectively. Therefore, in industrial practice, it is recommended to use glauconite at a concentration of 2 g/dm³ in combination with 0.1 % solution of cationic flocculant with a volume of 30 cm³/dm³ with the duration of wastewater treatment 20–180 minutes for complex processing of effluents.

Keywords: coke chemical effluents; differential thermogram; phenol; rhodanides; ammonia; resinous substances; glauconite; adsorption isotherm.

ДОСЛІДЖЕННЯ ПРОЦЕСУ ОЧИЩЕННЯ СТИЧНИХ ВОД КОКСОХІМІЧНОГО ВИРОБНИЦТВА ГЛАУКОНІТОВОЮ ГЛИНОЮ

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Анотація

Досліджено процес комплексного очищення коксохімічних стоків від фенолів, роданідів, загального амоніаку та смолистих речовин із використанням глауконітової глини. У роботі використано природний і активований глауконіт, глауконіт в поєднанні з катіонним флокулянтом марки Extraflock P 70 та активоване вугілля марки УАФ (для порівняння ефективності очищення). Активацію природного глауконіту проведено 7 %-им розчином HNO₃ при температурі кипіння – 95–100 °C, співвідношенні «мінеральний сорбент:розчин кислоти» 1:6 та часі активації 5 год. Встановлено, що кислотна активація призводить до зміни хімічного складу глауконіту та збільшенню питомої поверхні з 32 м²/г до 128 м²/г. За результатами термічного аналізу природного глауконіту зроблено висновок про фазові перетворення та хімічні реакції, які протікають у глауконітовій глині при нагріванні або охолодженні, по термічним ефектам, що супроводжують ці зміни та отримати якісну характеристику мінералу глауконіту. Встановлено, що максимальний ступінь очищення фенолів із промислових стоків становить до 50 % і досягається при використанні глауконіту в поєднанні з флокулянтом. Максимальний ступінь очищення від загального амоніаку складає 57–58 % при застосуванні активованого глауконіту та глауконіту з флокулянтом. Найменший ступінь очищення досягається при вилученні роданідів, що не перевищує 20 % для будь-якого адсорбенту. Найбільший ступінь очищення 96.8 % спостерігається при видаленні смолистих речовин глауконітом в поєднанні з флокулянтом.

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Активация глаукониту HNO_3 приводит до збільшення сорбційної ємності на 5–15 % в залежності від поліюганта. Ступінь очищення коксохімічних стоків від наведених поліюгантів активованим вугіллям складає 20 % від фенолів, 14 % від роданидів, 28 % від загального амоніаку та 72 % від смолистих речовин, відповідно. Отже, в промисловій практиці рекомендовано використовувати для комплексної переробки стоків глауконіт концентрацією 2 г/дм³ в поєднанні з 0,1 % розчином катіонного флокулянту об'ємом 30 см³/дм³ за тривалості обробки стоків 20–120 хв.

Ключові слова: коксохімічні стоки; диференційна термограма; феноли; роданиди; амоніак; смолисті речовини; глауконіт; ізотерма адсорбції.

ИССЛЕДОВАНИЕ ПРОЦЕССА ОЧИСТКИ СТОЧНЫХ ВОД КОКСОХИМИЧЕСКОГО ПРОИЗВОДСТВА ГЛАУКОНитОВОЙ ГЛИНОЙ

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Аннотация

Исследован процесс комплексной очистки коксохимических стоков от фенолов, роданидов, общего аммиака и смолистых веществ с использованием глауконитовой глины. В работе использован природный и активированный глауконит, а также глауконит в сочетании с катионным флокулянтом марки Extraflock P 70 и активированный уголь марки УАФ (для сравнения эффективности очистки). Активация природного глауконита проведена 7 %-ным раствором HNO_3 при температуре кипения – 95–100 °С, соотношении «минеральный сорбент : раствор кислоты» 1 : 6 и времени активации 5 ч. Установлено, что кислотная активация приводит к изменению химического состава глауконита и увеличению удельной поверхности с 32 до 128 м²/г. По результатам термического анализа природного глауконита сделан вывод о фазовых превращениях и химических реакциях, протекающих в глауконитовой глине при нагревании или охлаждении, по термическим эффектам, сопровождающим эти изменения и получено качественную характеристику минерала глауконита. Установлено, что максимальная степень извлечения фенолов из промышленных стоков составляет до 50 % и достигается при использовании глауконита в сочетании с флокулянтом. Максимальная степень очистки от общего аммиака составляет 57–58 % при использовании активированного глауконита и глауконита с флокулянтом. Наименьшая степень очистки достигается при извлечении роданидов и не превышает 20% для любого из адсорбентов. Наибольшая степень очистки 96,8 % наблюдается при удалении смолистых веществ глауконитом в сочетании с флокулянтом. Активация глауконита раствором HNO_3 приводит к увеличению сорбционной емкости на 5–15% в зависимости от полиюганта. Степень очистки коксохимических стоков от приведенных полиюгантов активированным углем составляет 20 % от фенолов, 14 % от роданидов, 28 % от общего аммиака и 72 % от смолистых веществ, соответственно. Следовательно, в промышленной практике для комплексной переработки стоков рекомендуется использовать глауконит концентрацией 2 г/дм³ в сочетании с 0,1% раствором катионного флокулянта объемом 30 см³/дм³ при длительности обработки стоков 20–120 мин.

Ключевые слова: коксохимические стоки; дифференциальная термограмма; фенол; роданиды; аммиак; смолистые вещества; глауконит; изотерма адсорбции.

Introduction

On the territory of Kamianske city, there are effectively operating coke-chemical enterprises, in particular PJSC "DKHZ" and PJSC "YUZHKOCS", which specialize in the production of strategic products for Ukraine: coke, resin, ammonium sulfate, and processed products. At the same time, they are polluters of urban ecosystems. Environmental problems caused by environmental pollution by phenols, coal tar, and oils discharged from industrial wastewater are attracting the widespread attention of scientists because of their highly toxic effect on living organisms [1–3]. Phenols and resins have no natural destructors and, being transmitted through food chains, become dangerous to humans. The increased content of phenols in water leads to a deterioration of organoleptic characteristics, causing the appearance of a specific odor. The maximum concentration limit of phenols for sanitary water bodies is 0.001 mg/dm³ [4].

Much of the liquid effluents generated at coke plants are still discharged into water bodies or are insufficiently treated. In addition, periodic salvo emissions of phenols, rhodanides, ammonia, resinous substances occur as a result of technological process violations of capturing coking chemical products, which leads to dilution of wastewater with technical water and increased costs of water treatment. The load on the biochemical plant increases and the required degree of purification is not always achieved. Such discharges are technologically difficult to detect because the control sample is taken only 4 times a day, whereas the discharge duration is up to 2 days. As a result, most pollutants are not removed under the regulatory requirements, which leads to the decrease of phenol-destroying microorganisms in activated sludge [5].

Various substances (apatites, zeolites, clays) are used for the adsorption of phenols, but carbon adsorbents are the most widespread [6]. They are obtained from various raw materials

(lignin, wood, coal) by physical or chemical activation.

According to the known method [7] of extracting phenols from liquid media using activated carbon, phenolic water is either passed through a carbon filter or the smallest particles are added directly to the liquid waste. However, the service life of activated carbon is short, and regeneration and removal of retained phenols are quite difficult. It is necessary to flush the load with benzene or other phenolic solvents, followed by the removal of pollutants with lime or distillation. These factors lead to the fact that the method of sorption of phenols on activated carbon is costly, so it is difficult to apply in practice. It is known that 2 g of activated carbon sorbent can absorb 40 mg of phenols, which is not enough for high concentrations of pollutants and is economically unprofitable due to significant operating costs [8].

The inevitable condition for the development of purification technology based on the sorption method is to determine the ability of each material to absorb the pollutant. At present of interest is wastewater treatment with natural sorbents, which include glauconite. There is a promising possibility of using glauconite in the treatment of coke wastewater.

Glauconite itself is a promising mineral of various uses. Significant advantages of this mineral are wide distribution, cheapness, availability, granular structure, heat resistance, good ion exchange, and filtration properties, as well as the ability to purposefully change the technological parameters through chemical modification [9–11]. When interacting with resinous substances in coke wastewater, glauconite is operational in a wide range of temperatures from -20 to $+100$ °C.

In [12–14] it is noted that glauconite is a natural mineral of variable composition. The chemical formula of glauconite – $(K, H_2O)(Fe^{3+}, Al^{3+}, Fe^{2+}, Mg^{2+}) \cdot 2[Si_2AlO_{10}](OH)_2 \cdot nH_2O$. This mineral belongs to the layered alum-iron-magnesium silicates with a porous structure of 2:1 type (between two grids of tetrahedra is one mesh of octahedra). Homogeneous layers are separated by layers of K^+ cations, water, and exchangeable cations). Silicon ions in tetrahedra can be replaced by aluminum ions, resulting in a positive charge.

Due to the layered structure, glauconite has good sorption and ion exchange properties. This mineral is a multifunctional sorbent that effectively removes aniline, phenol, heavy metal

ions Cu^{2+} , Fe^{2+} , Pb^{2+} , cations Ca^{2+} , Mg^{2+} from aqueous solutions [15–17].

Glauconite is called a catalytic destructor due to its unique composition and properties, e.g. [18]:

- high dispersion and hydrophilicity, formation of moistened sol-gel phases, which determine the cohesive-adhesive properties of stickiness and plasticity;

- high physical and chemical activity, characterized by the absorption capacity and the presence of a complex absorption complex.

Glauconite analogs include shungite, rubble, zeolites, bentonites, etc. A distinctive feature of glauconite from others minerals is its well-developed surface structure and the fact that it has not a scaffold, but a layered structure. In this case, part of the intramolecular forces is not balanced by the interaction with ions located in the cavity of one such layer of chemicals contained in solutions and air. As a result, they accumulate on the active surfaces of the plates that make up the total crystal [19–21].

Due to its ion-exchange properties, glauconite can release mobile elements (K, Na) into the liquid. At the same time, it "plants" others substances in its vacated energy centers, as a rule, more mobile and dangerous. The presence of a layered structure explains the high sorption properties of glauconite to petroleum products, phenols, heavy metals, radionuclides. Physico-chemical parameters of glauconite: hardness – 1.7–1.8; density 2000–2900 kg/m³; cation exchange capacity – 15 mg·eq; the capacity of the monolayer – 1.73 mmol/g [22].

An important feature of natural clays is the possibility of chemical modification by acids (hydrochloric, sulfuric, acetic, etc.), salts, alkalis, as well as heat treatment. Clay activation is based on the change of their electrokinetic potential (replacement of Si^{4+} ions by Ca^{2+} , Mg^{2+} , Fe^{3+} , Al^{3+} in the diffuse layer of the clay particle) in the crystal lattice of the mineral. Decationation of glauconites, which begins with the formation of hydrogen, breaks Si-O-Al bonds in adjacent tetrahedra, resulting in the formation of groups (OH-) associated with the silicon atom, and coordinated aluminum atoms [23].

In [24] it was shown that the textural characteristics of the natural and activated glauconite differ significantly. Thus, activated glauconite has a greater value of the specific surface area and total pore volume. Natural glauconite possesses a specific surface area of 21.06 m²/g, while the activated – 35.04 m²/g.

In Ukraine, the significant production of glauconite is located in the Adamiv deposit of the Khmelnytsky region. Glauconite of Adamiv deposit has the following mineral composition, %: glauconite – ≤70; quartz – ≤10; montmorillonite – 5–25; phosphorites and other minerals – ≤10 [25].

Therefore, it is advisable to evaluate the sorption properties of glauconite of the Adamiv deposit to further use it for wastewater treatment. Based on this, the following tasks were set:

- to perform thermal analysis of a glauconite sample from the Adamiv deposit;
- to activate glauconite clay by 7 % HNO₃ solution to study its sorption efficiency;
- to determine the effectiveness of coke wastewater treatment from phenol, rhodanides,

resinous substances, and ammonia with natural glauconite and in combination with cationic flocculant, activated glauconite, and carbon;

- to obtain the adsorption isotherms of natural and activated glauconite to determine the specific surface area of the mineral.

Experimental

Natural and HNO₃-activated glauconite clay samples from the Adamiv deposit were used in the study of coke wastewater treatment. The chemical composition of samples was determined on the X-ray spectrometer "Elvax" using X-ray fluorescence analysis (Table 1).

Table 1

Chemical composition of natural and activated glauconite clay from the Adamiv deposit, % wt.

Component	Content, % wt.	
	Natural	Activated by HNO ₃
Al ₂ O ₃	7.72	3.82
SiO ₂	64.79	79.51
Na ₂ O	1.79	0.046
K ₂ O	5.0	2.02
CaO	2.92	1.39
MgO	2.16	0.16
Fe ₂ O ₃	12.56	11.19
FeO	0.5	0.1
MnO	0.01	0.004
P ₂ O ₅	2.43	1.73
TiO ₂	0.12	0.03

Thermal analysis of glauconite from the Adamiv deposit was performed on the asynchronous thermal analyzer STA 409 PC (NETZSCH, Germany). The initial material was quartered, wiped through a sieve with mesh cell 0.1 mm. The powder was moistened and formed into a "tablet". The sample was dried at temperature 100–110 °C for 20 hours in the oven. Mode of analysis: heating to a temperature of 300 °C at a rate of 10 deg/min.

Acid activation of glauconite clay with nitric acid was performed according to the following method. The adsorbent and 7 % HNO₃ solution were loaded into a heat-resistant glass reflux flask. The ratio "mineral sorbent:acid solution" was 1:6. Activation time – 5 hours. Boiling at 95–100 °C ensured good mixing of the mixture. Immediately after activation with the acid solution, the sorbent was washed with water until the neutral reaction. Then the sorbent was

dried at a temperature of 100–110 °C for 2 hours in an oven.

To conduct experimental studies of the process of wastewater treatment of coke production from phenols and related pollutants a laboratory installation was used (Fig. 1). Due to the presence of the separate partition in the proposed design with the formation of the separation chamber, air-saturated water from the flotation chamber and added sorbents, form flotation complexes with pollutants that float to the flotation open surface and are removed with sludge, reducing the concentration of pollutants. Pollutants are concentrated on the surface of the bubbles and removed with foam. Since the outlet pipe is equipped with a control valve for sludge removal, it is possible to keep the adsorbents in the flotation process in a controlled time interval with subsequent unloading and disposal of sludge.

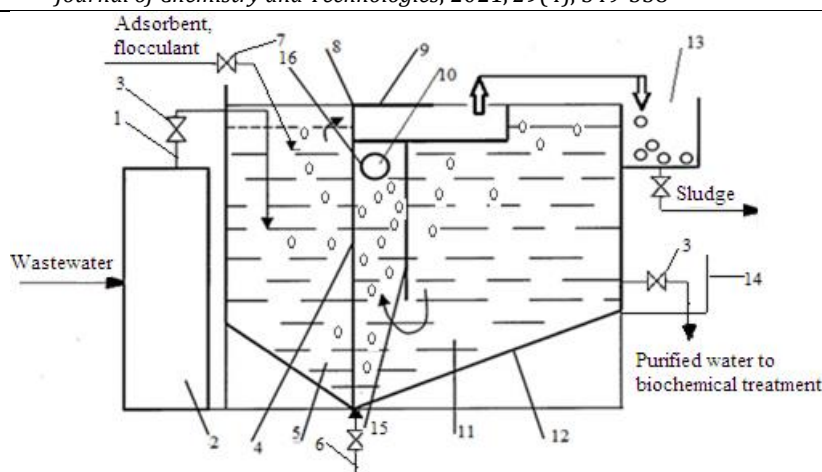


Fig. 1. Installation of liquid waste treatment from phenols and related pollutants: 1, 14, 16 - pipelines; 2 - wastewater tank; 3 - valve; 4 - distribution partition; 5 - flotation chamber; 6 - air blower; 7 - dosing device; 8 - flow distributor; 9 - limiting plate; 10 - window; 11 - separation chamber; 12 - flotor; 13 - sludge pocket; 14 - drain pocket; 15 - loading partition

Coke chemical effluent through pipeline 1 was fed to the flotation chamber 5. The flotation chamber had an inlet pipe equipped with a dispenser for supplying adsorbents and flocculants through the dosing device 7. Sludge pocket 13 made an annular outside the cylindrical body and equipped with a scraper for removing foam. In the central flotation chamber 5 there is a dividing partition, which separates chamber 11, in which the outlet of the central flotation chamber 5 has a flow distributor 8 adjacent to the upper part of the dividing partition and made in the form of a block of rectangular channels closed from above. An air supercharger 6 is installed in the bottom of the flotation chamber 5.

The determination of ammonia, rhodanides, and phenol in coke wastewater was performed by photocolometric method on a KFK-2 spectrophotometer. The mass concentration of resinous substances was determined at a wavelength of 400 nm using petroleum ether as an extractant (detection limit 3 mg/dm³) [2]. The content of phenol and its homologs were evaluated by photocolometric method with 4-aminoantipyrine in the presence of potassium hexacyanoferrate at pH 10.3±0.2 at a wavelength of 540 nm [2] Detection limit – 0.05 mg/dm³. The mass concentration of rhodanide ions (SCN⁻) was measured using iron (III) chloride at a wavelength of 440 nm according to a known method [2]. The detection limit is 0.2–0.4 mg/dm³. Total ammonia was determined with Nessler's reagent at pH 10.3±0.2 at a wavelength of 420 nm according to a known method [2]. Detection limit – 0.05 mg/dm³.

The commercial product Extraflock P 70 cationic type flocculant based on polyacrylamide

was used (JSC PCC "Coagulant" TU U 24.1-19155069-014-2011) with the dosage of 30 cm³/dm³ and the concentration of the working solution 0.1%.

An important role is played by the optimal consumption of flocculant, which is added, following the regulations of the enterprise, because at low and high concentrations the dispersed system stabilization can be observed. With a small consumption of flocculant in water, there are not enough macromolecules to bind the liquid phase under the flocs, and with excessive - a spatial network of associated polymer molecules is formed, which prevents the convergence and aggregation of particles.

The initial content of phenol in wastewater was 410 mg/dm³, total ammonia – 1200 mg/dm³, rhodanides – 224 mg/dm³, resinous substances – 312.5 mg/dm³. According to the previous studies [27], it was found that the clay dose of 2 g/dm³ is optimal and most economically feasible in the complex extraction of coke-chemical pollutants. Therefore, the adsorbents were added to the reactor in an amount of 2 g/dm³. Wastewater was floated for 20–180 minutes.

The Langmuir equation was used for comparative estimation of the capacity of the monolayer of adsorbents. For the studied adsorbents, the value of the capacity of the monolayer a_{∞} allows estimating the specific pore surface of the natural and activated glauconite available for phenol [28].

The value of phenol adsorption Γ (mol/g) was determined by the formula:

$$\Gamma = (C_0 - C) \cdot V / m, \quad (1)$$

where V is the volume of the solution, dm³;

m is the mass of the adsorbent, g;
 C_0 is the initial concentration of phenols, mol/dm³.

The specific surface area of the adsorbents was determined by the formula [28]:

$$S = a_{\infty} N_A \omega \cdot 10^{-18}, \quad (2)$$

where S is the specific surface area of the adsorbent, m²/g;

a_{∞} is the adsorption limit value (capacity of the monolayer), mol/g;

N_A is the Avogadro's number, 6,022·10²³ mol⁻¹;

ω is the area of the adsorbate molecule (elementary "landing" site), nm².

The calculation of the site per molecule in the fulfilled monolayer on the surface of glauconite was performed according to the formula proposed by Brunauer and Emmett [28]:

$$\omega = 1,091 \left(\frac{M}{N_A \rho} \right)^{2/3}, \quad (3)$$

where M is the molar mass of the adsorbate, g/mol; ρ is the density of the adsorbate in the liquid state, g/cm³.

The calculated value of ω for phenol (0.65 nm²) is consistent with previously obtained experimental data [27] for other organic aromatic substances with similar structures.

Adsorption concentration isotherms were represented in $\Gamma - C$ coordinates (Γ is the amount of change in the amount of test ion in the solution caused by the sorbent, mmol/g, C is the equilibrium concentration of the studied ions in the system, mol/dm³).

Results and discussion

The thermogram of the sample of natural glauconite of the Adamiv deposit is presented in Fig. 2.

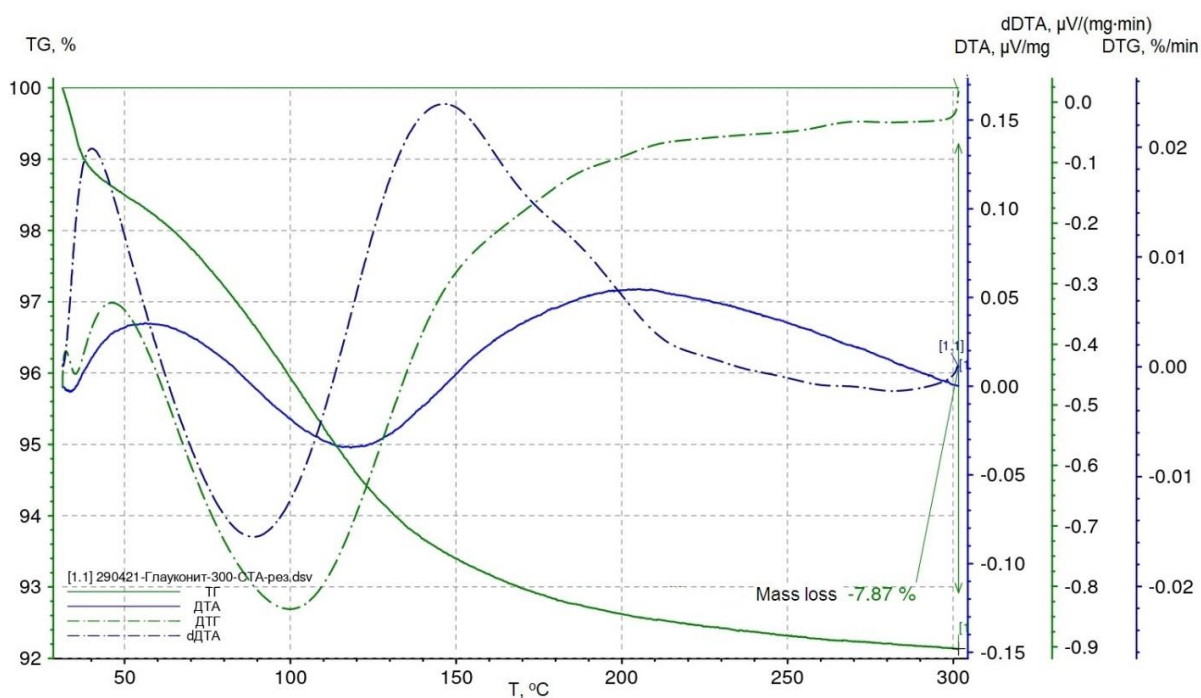


Fig. 2. Thermogram of glauconite from the Adamivskoye deposit:

1 – differential-thermal curve (DTA), 2 – the first derivative of the DTA curve (rate of phase transformations) (dDTA), 3 – mass loss curve (TG), 4 – the first derivative of the TG curve (speed) weight loss) (DTG).

The reduction of the mass of the substance when heated is possible during such processes as evaporation, for example, removal of interlayer water from montmorillonite and hydromica, as well as dehydration. Thus, using a thermogram, it is possible to obtain a qualitative characteristic of the mineral type of the substance [26].

Heating glauconite in the temperature range 120–200 °C leads to moisture loss. Dehydration is characterized by an endothermic effect with a

maximum at a temperature of 120 °C. The course of the DTA curve indicates the occurrence of a single endothermic process in the temperature range 70–200 °C. It characterizes the removal of hygroscopic moisture from the sample, as well as interlayer molecular water from the crystal structure of the mineral. During this process, weight losses of 7.5% occur. Further increase in temperature leads to slower weight loss, as

evidenced by the appearance on the curve of the sloping area.

Fig. 3 shows the experimental dependences of the degree of extraction of phenol from coke wastewater at a dose of adsorbents 2 g/dm^3 for a treatment duration of 180 minutes.

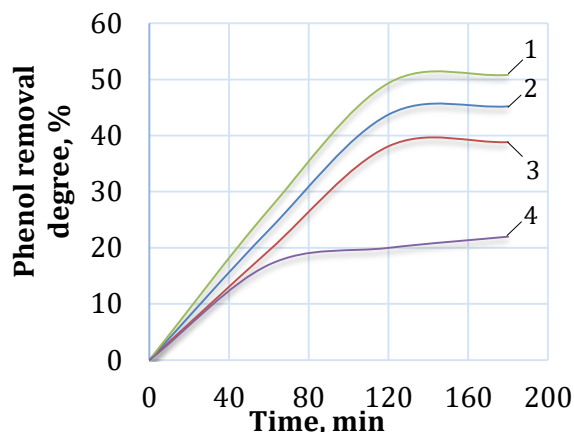


Fig. 3. Changing the phenol removal degree over time: 1 - glauconite with cationic flocculant; 2 - acid-activated glauconite; 3 - glauconite; 4 - activated carbon

Fig. 3 shows that when using acid-activated glauconite, the degree of phenol removal reaches 43.7 %, natural glauconite - 38 %, while glauconite with cationic flocculant was much more effective - up to 50 %. The degree of phenol removal by activated carbon is about 20 %. A combination of glauconite with cationic flocculant proved to be the most effective method.

Fig. 4 shows the degree of extraction of the total of ammonia in coke wastewater at a dose of adsorbents 2 g/dm^3 for a treatment duration of 180 minutes.

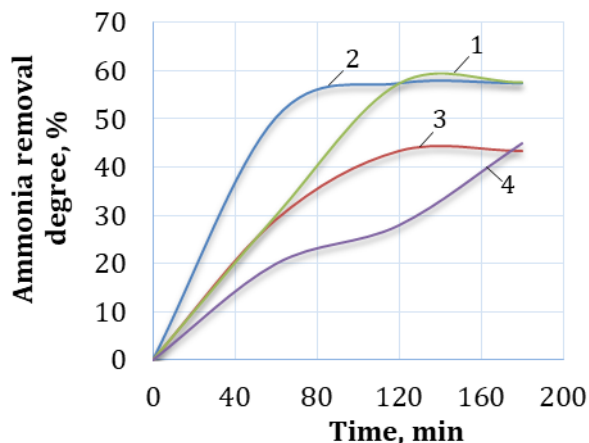


Fig. 4. Changing the ammonia removal degree over time: 1 - glauconite with cationic flocculant; 2 - activated glauconite; 3 - glauconite; 4 - activated carbon

During the experiment, it was found that after 120 min the total ammonia content decreased from 1200 mg/dm^3 to 511 mg/dm^3 when using acid-activated glauconite and glauconite with cationic flocculant - up to 507 mg/dm^3 , with a recovery rate of up to 58 %. The efficiency of treatment with natural glauconite is up to 681 mg/dm^3 (56.8 %), whereas activated carbon is less efficient - up to 864 mg/dm^3 (28 %). It confirms the effectiveness of glauconite mineral in the complex purification of effluent compared to others adsorbents. This can be explained by the microporous structure of the acid-activated glauconite, which can adsorb inorganic substances like ammonia.

Fig. 5 presents the degree of extraction rhodanides in coke wastewater at a dose of adsorbents 2 g/dm^3 for a duration of treatment of 180 minutes.

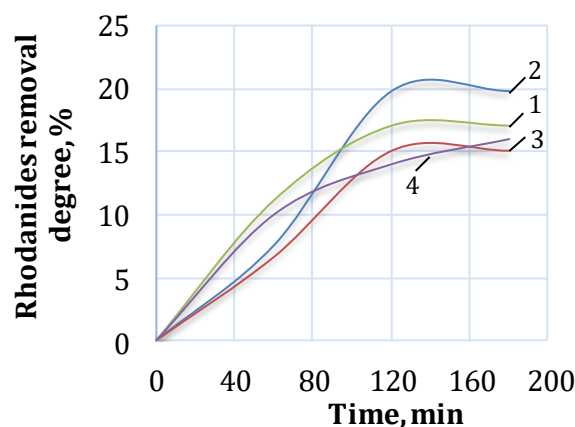


Fig. 5. Changing the rodanides removal degree over time: 1 - glauconite with cationic flocculant; 2 - activated glauconite; 3 - glauconite; 4 - activated carbon

It was found that when using acid-activated glauconite the content of rhodanides from the initial concentration of 224 mg/dm^3 decreases to 180 mg/dm^3 (19.6 %), glauconite with cationic flocculant - up to 187 mg/dm^3 (16.5 %), activated carbon - up to 192.64 mg/dm^3 (14 %). The use of sorbents in the extraction of rhodanide ions leads to bringing the content of pollutants to regulatory standards after biological treatment of industrial effluents ($< 5 \text{ mg/dm}^3$).

Fig. 6 presents the degree of extraction of resinous substances in industrial wastewater at a dose of adsorbents 2 g/dm^3 for a treatment duration of 180 minutes.

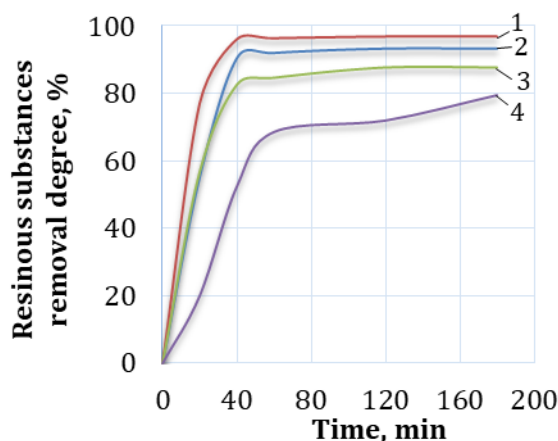


Fig. 6. Changing the resinous substances removal degree over time: 1 - gluconite with cationic flocculant; 2 - activated gluconite; 3 - gluconite; 4 - activated carbon

Fig. 6 shows that the adsorption of residual resins and oils decreases to a concentration of 140 mg/dm^3 within 20 min and reaches the regulatory standard before the mechanical stage of biochemical treatment which is 25 mg/dm^3 (92 %), within 45 min, while gluconite in combination with 0.1 % flocculant - 96.8 %. This standard was not reached when using activated gluconite within 40 min, the concentration of resinous substances was - 39 mg/dm^3 (87.5 %) and for activated carbon - 87.5 mg/dm^3 (72 %).

Therefore, the maximum treatment efficiency when using gluconite in combination with cationic flocculant is 50-96.8% depending on the pollutant and its initial concentration. However, it should be noted, that in this study we used effluents with higher contaminants content. Treatment efficiency was mostly dominated by activated and natural gluconite with the addition of flocculant than the classic sorbent activated carbon.

Probably, during the adsorption treatment of effluent with gluconite clay, there was the formation of agglomerates of "glauconite-

flocculant chains", which effectively bound and adsorbed pollutant molecules. It was noted that the combined effect of all coke-chemical contaminants causing the specific brown color of coke wastewater, almost completely disappeared when we used gluconite with the addition of flocculant. The addition of a cationic flocculant to gluconite increases the rate of deposition of agglomerates by connecting them by polymer bridges. As a result, the formation of sediment induced noticeable clarification of coke water.

The use of gluconite as a sorbent is quite rational because there is no release of toxic impurities into the aqueous phase, and this mineral has a low cost, suitable for modification with further improvement of its sorption properties.

The specific surface area of the natural and activated gluconite samples during the extraction of phenols from the effluent was determined. Adsorption isotherms are presented in Fig. 7 (glauconite dose 2 g/dm^3 ; adsorption duration 180 min).

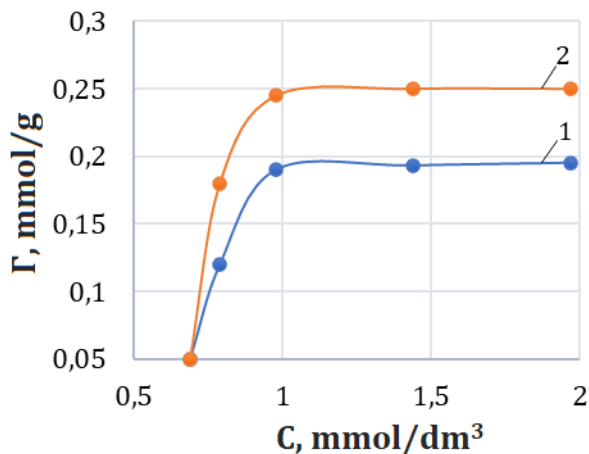


Fig. 7. Adsorption isotherms of phenols onto gluconite samples: 1 - natural; 2 - activated

A similar type of sorption isotherms indicates the same nature of the interaction of phenols in the system "aqueous solution – glauconite sorbent".

The linearity of the isotherm in the Langmuir coordinates is essential for proving the validity of the theory of monomolecular adsorption. To find the coefficients of the Langmuir equation, we used the known method of graphical processing of the corresponding isotherm [28]. From Fig. 7 follows:

- for natural glauconite:

$$a_{\infty} = \Delta C / \Delta(C/\Gamma) = 0.28 / 3.43 = 0.082 \text{ mmol/g.}$$

Thus $S_m = 32 \text{ m}^2/\text{g}$;

- for activated glauconite: $a_{\infty} = \Delta C / \Delta(C/\Gamma) = 1.27 / 3.90 = 0.326 \text{ mmol/g.}$

Thus $S_m = 128 \text{ m}^2/\text{g}$.

The data obtained indicate that the process of acid activation of glauconite clay leads to a significant increase in its sorption capacity.

Glauconite is characterized by a developed surface and the presence of functional groups (silanol, siloxane) capable of binding ions of different nature, including pollutants of coke wastewater, as previously shown in [7].

Thus, glauconite can be recommended for use in the complex treatment of effluents of coke plants, e.g. PJSC "DKHZ", PJSC "YUZHKOCS" at the stage of mechanical treatment, thereby, reducing the activated sludge loading at the stage of biological treatment, also, eliminating the need for dilution due to high concentrations of pollutants. This method brings pollutants content to the regulatory standard, e.g.: resinous substances $< 25 \text{ mg/dm}^3$, total ammonia $< 960 \text{ mg/dm}^3$, rhodanides $< 400 \text{ mg/dm}^3$, and phenols $< 415 \text{ mg/dm}^3$. Application of the proposed method for effluent treatment could significantly improve the overall effectiveness of the mechanical purification stage and reduce the concentration of toxicants after the biological treatment stage.

Conclusions

The adsorption properties of glauconite of the Adamiv deposit towards phenol, resinous substances, rhodanides, and total ammonia of coke-chemical wastewater have been studied.

A thermogram of glauconite from the Adamiv deposit was obtained. The method of activation of glauconite clay with 7% HNO_3 solution was studied and the chemical composition of the mineral before and after activation was determined.

The phenol extraction degree from effluents at an initial content of 410 mg/dm^3 reaches up to 50

% when using natural glauconite with a concentration of 2 g/dm^3 in combination with cationic flocculant, while the classic sorbent (activated carbon) at these concentrations gives only 20 %. It was found that when using acid-activated glauconite and glauconite in combination with cationic flocculant concentration of 2 g/dm^3 and contact duration of 180 min, the degree of removal of total ammonia at an initial concentration of 1200 mg/dm^3 is up to 58 %, sorbent in native form – 56 %. The rhodanides removal degree by the activated mineral at the initial concentration of 224 mg/dm^3 was achieved up to 19.6 % compared to native glauconite – up to 16.5 %. When using activated carbon, the degree of removal of rhodanides was 14 %. The normative concentration of rhodanides has been brought to regulatory standard at the mechanical stage of biochemical treatment. The extraction efficiency of resinous substances was 93.3 % for natural glauconite, 96.8 % for glauconite with cationic flocculant, 87.5 % for activated glauconite, and 72 % for activated carbon.

The values of the specific surface area of glauconite samples were determined: natural – $32 \text{ m}^2/\text{g}$; activated – $128 \text{ m}^2/\text{g}$. These data indicate that the process of acid activation of glauconite clay leads to a significant increase in sorption capacity. Thus, the usage of glauconite clay at consumption of 2 g/dm^3 and a treatment time of 180 min for wastewater treatment of coke plants seems promising, considering the low cost and availability of glauconite, as well its ability to effectively remove various pollutants at high concentrations.

References

- [1] Klymenko, I., Yelatontsev, D., Ivanchenko, A., Dupenko, O., Voloshyn, N. (2016). Developing of effective treatment technology of the phenolic wastewater. Eastern-European Journal of Enterprise Technologies, 3(10(81)), 29-34. <https://doi.org/10.15587/1729-4061.2016.72410>
- [2] Kagasov, V. M., Derbysheva, E. K. (2003). Wastewater treatment of coke-chemical enterprises. Yekaterinburg, Russian Federation: Polygraphist (in Russian).
- [3] Yelatontsev, D., Suprunchuk, V., Voloshin, M. (2017). Sedimentation of pollutant-containing aggregates during purification of wastewater from coking plants. Eastern-European Journal of Enterprise Technologies, 6(10(90)), 38-44. <https://doi.org/10.15587/1729-4061.2017.119064>
- [4] Koganovsky, A. M. (1983). Adsorption and ion exchange in the processes of water treatment and wastewater treatment. Kyiv: Naukova dumka (in Russian).

- [5] Smirnov, A. D. (1982). Sorption water purification. USSR, Leningrad: Khimiya (in Russian).
- [6] Badmaeva, S. V., Khankhasaeva, S. T. (2015). Regularities of phenol adsorption from aqueous solutions on carbon-mineral materials obtained from bentonite clay. *Colloid J.*, 77(6), 685–691. <https://doi.org/10.1134/s1061933x15060034>
- [7] Klimov, E.S., Buzaeva, M.V. (2011). Natural sorbents and complexones in wastewater treatment. Ulyanovsk: UGTU (in Russian).
- [8] Feng, J., Qiao, K., Pei, L., Lv, J., Xie, S. (2015). Using activated carbon prepared from *Typha orientalis* Presl to remove phenol from aqueous solutions. *Ecol. Eng.*, 84, 209–217.
- [9] Lygina, T. Z., Mikhailova, O. A., Khatsrinov, A. I. [et al.] (2009). Technologies of chemical activation of inorganic natural mineral sorbents. Kazan, Russian Federation: KSTU (in Russian).
- [10] Ivanchenko, A. V., Karlash, V. I., Yelatontsev, D. O., Danelska, A. S. (2018). Application of Acid-Activated Zeolith in the Technology of Cleaning Wastewater from Nitrates. *Bull. Vinnytsia Polytech. Inst.*, 5, 13–17. <https://doi.org/10.31649/1997-9266-2018-140-5-13-17> (in Ukrainian).
- [11] Chen, Y., Ye, W., Zhang, K. (2011). Factors affecting phenol adsorption on clay-solidified grouting curtain. *J. Cent. Sou. Univ. Tech.*, 18(3), 854–858. <https://doi.org/10.1007/s11771-011-0773-8>
- [12] Djebbar, M., Djafri, F., Bouchekara, M., Djafri, A. (2012). Adsorption of phenol on natural clay. *Appl. Wat. Sci.*, 2(2), 77–86. <https://doi.org/10.1007/s13201-012-0031-8>
- [13] Gładysz-Płaska, A., Majdan, M., Pikus, S., Sternik, D. (2012). Simultaneous adsorption of chromium(VI) and phenol on natural red clay modified by HDTMA. *Chem. Eng. J.*, 179, 140–150. <https://doi.org/10.1016/j.cej.2011.10.071>
- [14] Mirmohamadsadeghi, S., Kaghazchi, T., Soleimani, M., Asasian, N. (2012). An efficient method for clay modification and its application for phenol removal from wastewater. *Appl. Clay Sci.*, 59-60, 8–12. <https://doi.org/10.1016/j.clay.2012.02.016>
- [15] Carvalho, M. N., de Abreu, C. A. M., Benachour, M., Sales, D. C. S., Baraúna, O. S., da Motta Sobrinho, M. A. (2012). Applying Combined Langmuir-Freundlich Model to the Multi-Component Adsorption of BTEX and Phenol on Smectite Clay. *Adsorption Sci. Tech.*, 30(8-9), 691–699. <https://doi.org/10.1260/0263-6174.30.8-9.691>
- [16] Ahmedzeki, N. S., Rashid, H. A., Alnaama, A. A., Alhasani, M. H., Abdulhussain, Z. (2013). Removal of 4-nitrophenol from wastewater using synthetic zeolite and kaolin clay. *Kor. J. Chem. Eng.*, 30(12), 2213–2218. <https://doi.org/10.1007/s11814-013-0165-x>
- [17] Nayak, P. S., Singh, B. K. (2010). Sorption kinetics for phenol and nitro-substituted toxic phenols from aqueous solution using clay as sorbent material. *Int. J. Environ. Waste Manag.*, 5(3/4), 286. <https://doi.org/10.1504/ijewm.2010.032009>
- [18] Kadhum, S. T., Alkindi, G. Y., Albayati, T. M. (2020). Eco friendly adsorbents for removal of phenol from aqueous solution employing nanoparticle zero-valent iron synthesized from modified green tea bio-waste and supported on silty clay. *Chi. J. Chem. Eng.* <https://doi.org/10.1016/j.cjche.2020.07.031>
- [19] Wang, S., Qiao, N., Yu, J., Huang, X., Hu, M., Ma, H. (2014). Effect of ionic strength on the adsorption behavior of phenol over modified activated clay. *Desal. Wat. Treat.*, 57(9), 4174–4182. <https://doi.org/10.1080/19443994.2014.989269>
- [20] Cavalcanti, J. V. F. L., Abreu, C. A. M., Baraúna, O. S., da Motta, M. (2013). Phenol adsorption by modified clay from Northeastern Brazil. *Canadian J. Chem. Eng.*, 92(2), 355–361. <https://doi.org/10.1002/cjce.21934>
- [21] Yakub, E., Agarry, S. E., Omoruwou, F., Owabor, C. N. (2019). Comparative study of the batch adsorption kinetics and mass transfer in phenol-sand and phenol-clay adsorption systems. *Particulate Sci. Tech.*, 1–11. <https://doi.org/10.1080/02726351.2019.1616862>
- [22] Yousef, R. I., El-Eswed, B., Al-Muhtaseb, A. H. (2011). Adsorption characteristics of natural zeolites as solid adsorbents for phenol removal from aqueous solutions: Kinetics, mechanism, and thermodynamics studies. *Chem. Eng. J.*, 171(3), 1143–1149. <https://doi.org/10.1016/j.cej.2011.05.012>
- [23] Mandal, A., Dey, B. B., Das, S. K. (2020). Thermodynamics, kinetics, and isotherms for phenol removal from wastewater using Red Mud. *Wat. Pr. Tech.*, 15(3), 705–722. <https://doi.org/10.2166/wpt.2020.056>
- [24] Gładysz-Płaska, A. (2017). Application of modified clay for removal of phenol and PO43- ions from aqueous solutions. *Adsorption Sci. Tech.*, 35(7-8), 692–699. <https://doi.org/10.1177/0263617417704774>
- [25] Ivanchenko, A. V., Khavikova, K. E., Voloshin, M. D. (2020). Sedimentation analysis of the dispersed phase in the treatment of phenolic wastewater from coke production by glauconite. *Coll. scholar. paper. Dniprovsk State Technical University (Tech. Sci.)*, 37(2), 93–100. <https://doi.org/10.31319/2519-2884.37.2020.17> (in Ukrainian).
- [26] Khabas, T.A., Kulinich, Ye.A., Yegorova, Ye.Yu. (2011). Thermogravimetric analysis of silicate materials. Toms: TPU (in Russian).
- [27] Ivanchenko, A., Khavikova, K., Trukilo, A. (2020). Mathematical modeling of the processes of wastewater purification from phenols and rhodanides using glauconite. *Sci. Bull. National Mining University*, 4, 111–116. <https://doi.org/10.33271/nvngu/2020-4/111>
- [28] Kel'tsev, N. V. (1984). Basics of adsorption technology. Moscow: Khimiya (in Russian).