

CHEMISTRY. CHEMICAL ENGINEERING**ХІМІЯ. ХІМТЕХНОЛОГІЯ**

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**DETERMINATION OF THE ADSORBENT SPECIFIC
SURFACE AREA AT TAR REMOVING FROM INDUSTRIAL
WASTE WATER OF AMMONIUM SULPHATE
PRODUCTION**

A.V. Іванченко, Д.О. Єлантєв. **Визначення питомої поверхні адсорбентів при вилученні смолистих речовин з промислових стічних вод виробництва амоній сульфату.** На більшості коксохімічних підприємств України і світу амоній сульфат $(\text{NH}_4)_2\text{SO}_4$, який являє собою аміачне добриво, отримують у відділенні вловлювання хімічних продуктів коксування. У даному відділенні утворюються рідкі відходи – фенольні стічні води, головними забруднюючими агентами яких є смолисті речовини. При виборі промислового адсорбенту для очистки стічних вод визначальною є величина питомої поверхні. Висока вартість сучасних промислових сорбентів зумовлює необхідність пошуку нових, більш доступних їх аналогів, серед яких особливий інтерес мають природні бентонітові глини. **Мета:** Метою дослідження є вивчення закономірностей процесу вилучення смолистих речовин із стічних вод виробництва амоній сульфату з використанням натрієвого і кальцієвого бентонітів, активованого вугілля і торфу, а також визначення питомої поверхні вказаних адсорбентів. **Матеріали і методи:** У дослідженні використовували активоване вугілля марки АГ-5, торф низинний, природну натрієву і кальцієву бентонітову глину. Адсорбцію смолистих речовин досліджували в процесі флотації фенольних стічних вод в умовах, наближених до промислових: тривалість флотації – 20 хв., температура стічної води – 323 К, інтенсивність подачі повітря – 0,15 $\text{дм}^3/\text{год}$. У розрахунках припускали, що адсорбція смолистих речовин носить мономолекулярний характер і описується теорією мономолекулярної адсорбції Ленгмюра. **Результати:** Вперше визначено питому поверхню адсорбентів в процесі сорбції смолистих речовин з фенольних промислових стічних вод, $\text{м}^2/\text{г}$: натрієва бентонітова глина – 1847; активоване вугілля АГ-5 – 1467; кальцієва бентонітова глина – 728; торф низинний – 603. Розраховано граничне значення адсорбції і константу адсорбційної рівноваги для вказаних адсорбентів. Отримані величини свідчать про сильну взаємодію адсорбенту з адсорбатом, особливо бентонітової глини і активованого вугілля. Зважаючи на показники очистки природної лужної бентонітової глини, вона може використовуватися як реагент для інтенсифікації процесу вилучення смолистих речовин зі стічних вод виробництва амоній сульфату під час флотації.

Ключові слова: питома поверхня, бентонітові глини, активоване вугілля, торф, смолисті речовини, ізотерма адсорбції, рівняння Ленгмюра.

A.V. Ivanchenko, D.O. Yelantsev. **Determination of the adsorbent specific surface area at tar removing from industrial waste water of ammonium sulphate production.** At most coke plants of Ukraine and the world, ammonium sulphate $(\text{NH}_4)_2\text{SO}_4$, which is an ammonium fertilizer, get in the department of trapping chemical products of coking. The liquid wastes formed in this department called phenolic wastewater, the main polluting agents of which are tarry substances. When choosing industrial adsorbent for wastewater treatment, the value of specific surface area is a determining factor. The high cost of modern industrial sorbents causes necessity of finding of new, more affordable their analogs, among which of particular interest are natural bentonite clays. **Aim:** The aim of research is to study the regularities of extraction process of tarry substances of manufacturing sewage of a ammonium sulphate with use of sodium and calcium bentonites, an absorbite and peat, and definition of a specific surface area of the specified adsorbents. **Materials and Methods:** In this study the absorbite AG-5, valley peat and natural sodium and calcium bentonite clays are used as sorbents. The adsorption of tar substances had been researched during the flotation process of phenolic wastewater in conditions close to industrial: the duration of flotation is 20 min; the wastewater temperature is 323 K; the intensity of air supply – 0.15 dm^3/h . The calculations suggested that the adsorption of tarry substances is monomolecular in nature and described by the Langmuir's theory of monomolecular adsorption. **Results:** The specific surface area of the adsorbents during the adsorption process of tarry substances from a phenolic industrial wastewater defined for the first time are following (m^2/g): sodium bentonite clay – 1847; absorbite AG-5 – 1467; calcium bentonite clay – 728; valley peat – 603. For these adsorbents was also calculated the limit value of adsorption and constant of adsorption equilibria. The obtained values indicate a strong interaction between adsorbent and adsorbate, especially significant for the bentonite clay and absorbite. It was found, that sodium bentonite is more effective on all counts compared with absorbite, and recommended thus for industrial application.

Keywords: surface area, bentonite clay, absorbite, peat, tar substances, adsorption isotherms, Langmuir equation.

Introduction. Ammonium sulphate is efficient ammoniac fertilizer, is widely used in agriculture under grain, commercial and vegetable crops both for a preseeding treatment and for top-dressing.

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At most the coke-chemical enterprises of Ukraine and of the world an ammonium sulfate is obtained in departments of catching of volatile products of coking (Fig. 1).

In the course of catching of volatile products of coking at the first stage there is a cooling of gas and devaporation with extraction of tar and tar-water. To cool gas quickly, the tar-water is injected into the gas collector 2 and struts which transfer gas from cameras from a coke oven. Due to this, the temperature of gas decreases from 700 °C (gas temperature at cameras output) to 80...85 °C. In the gas collector the majority of tar is condensed and coal and coking dust, soot and other mechanical impurities (so-called fusa) are removed. For final cooling to 25...30 °C the gas in gas pipeline 3 goes to pipe coolers 5 and 6, in tubes where cold water flows. Liquid which is formed as a result of condensation of vapors when cooling gas separates in a fusa-separator 4 from where goes to settlers 7. Here liquid is separated to two layers: heavier tar (density 1.18...1.23 g/cm³) forms a sublayer at the bottom of storage. In the high water layer, a part of ammonia of coke-oven gas is dissolved. This high layer is called tar-water or ammoniacaliquor. Ammoniacaliquor absorbs carbon oxide and hydrogen sulfide from gas with formation of carbonic and sulphurous salts. Tar and ammoniacaliquor after settling are separately sent to storages 8 and 9 respectively. For further use and processing, the cooled coke-oven gas is carefully purified of fluidized droplets of condensate (fog) in electric filters.

Removal of gas from furnaces and its movement via the condensation and catching equipment is carried out by a turboblower 10 which creates a pressure about 1.5...2.5 mm of water column. Each exhaust blower forces up to 7×10⁴ m³/hour. The condensate emitted from gas in an exhaust blower and electric filters also comes to a settler 7.

Part of ammonia, which is formed when coking remains, after cooling in gas, is partially dissolved in water condensate which is emitted from gas at its cooling. Ammoniacaliquor which is formed at the same time contains ammonia in the form of NH₄OH, and also as soluble volatile salts (carbonates and sulfides) and nonvolatile compounds.

For further processing the ammonia (gaseous and soluble) is aggregated, for this purpose in columns 12 and 13 the NH₃ is flashed off from ammoniacaliquor. In a column 12 all "volatile" ammonia is flashed off, and then ammoniacaliquor goes for unit 14 for extraction of the dissolved phenols. Then, the water comes back to the bottom of a column 12 where mixes up with lime cream, and flows in a column 13. Here ammonia which is allocated from nonvolatile salts of an ammonium at decomposition them with hydroxide of calcium of Ca(OH)₂ is flashed off. Ammonia which is flashed off, moves in the gas pipeline before a saturator 16. Ammonia of coke-oven gas is used to obtain an ammonium sulphate. The manufactory for production of this fertilizer is equipped with saturators 16 in which NH₃ is caught by sulfuric acid, centrifuges 15, dryers and other devices. Tar-waters are formed from ammoniac columns. They together with blowthrough waters of a boiler room from the heatpower manufactory and household-domestic waters move to biochemical cleaning shop.

At the first stage in the biochemical cleaning shop the coal oils and tars (tarry substances) are removed which can be considered as aromatic analogs of oil products. The analysis of component

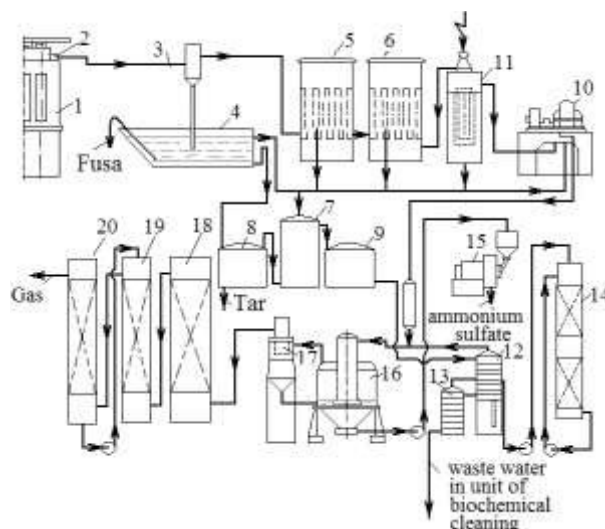


Fig. 1. Scheme of catching of volatile products of coking: 1 – coke oven; 2 – gas collector; 3 – gas pipeline; 4 – settler–fluxing agent separator; 5, 6 – pipe coolers 7 – condensate settler; 8 – tar tank; 9 – ammonium hydroxide tank; 10 – turboblower; 11 – electric filter; 12, 13 – ammoniac columns; 14 – phenolic unit; 15 – centrifuge; 16 – saturator; 17 – entrainment separator; 18 – oil refrigerator; 19, 20 – scrubbers

composition of sewage of this production showed that it is necessary to understand the sum of the polycyclic aromatic hydrocarbons (PAH) as the term “tarry substances”, mainly naphthalene and its derivatives, diphenyl, indene, an anthracene and phenanthrene [1]. Physical and chemical properties of these connections cause low speed of biological degradation and toxic influence that is explained by ability of these hydrocarbons to form films which interfere with the subsequent aerobic biooxidation. Eventually it leads to violation in operation of biochemical cleaning unit (BCU) in general and to excess of threshold limit value (TLV) of phenols and other harmful compounds in treated waters. Lack of an efficient method of cleaning of drains of tarry substances on PJSC “EVRAZ Dneprodzerzhynskii KHZ” (Kamianske) which sewage was chosen as a research object, gives to this phenomenon systematic character (at this moment the low efficient reagentless pressure flotation in combination with considerable dilution of drains is applied).

Coal tar as a disperse system includes not only two liquid phases (actually water and tar), but also solid at which the mechanical impurities of coal and coke, and also a particle of a furnaces setting act. The content of a solid phase in tar generally depends on grinding degree of coal fusion mixture. Unlike oil tars, emulsions of coal tars have the increased stability, consist of aromatic compounds with different degree of condensity and different polarity, and also contain various stabilizers of emulsions (carbon cinder particles, products of a secondary pyrolysis of steam-gaseous mix, etc. which are taken out from the coking camera). Substantially, to this promotes the fact that phenolic waste water contains significant amounts of chlorides, thiocyanides, H_2S , CO_2 , HCN and other compounds.

Finding of an efficient method of extraction of tarry substances from the phenolic manufacturing sewage is topical issue which requires the scientific solution.

Ganzyuk *et al.* [2] showed that one of efficient methods of purification of the manufacturing sewage of tarry substances is adsorption. Its large-scale implementation is substantially caused by the right choice of inexpensive and scarce adsorbents. The greatest distribution in this direction was gained by an absorbite and the industrial adsorbents based on coking wastage.

Klymenko *et al.* [3] in turn suggested using adsorbents of a natural origin for cleaning of drains: minerals on the basis of zeolites or silicates, and also peat and bentonite clays. The research of processes of a sewage disposal of ammonium sulphate manufacturing with use of bentonite clay as an adsorbent with additive of cationic flocculant allowed revealing a number of the idiosyncrasies caused by specific properties of both phases and kinetics of their interaction during the hashing and flotation which define effectiveness of realization of these processes. Results of the beforehand executed experiments [4] cause expediency of use of bentonite clay for a sewage disposal of coke-chemical production from coal tars and oils. This expediency is also supported with existence of the considerable reserves of bentonites in fields in all territory of Ukraine [5].

The aim of this research is to study the regularities of extraction process of tarry substances of manufacturing sewage of an ammonium sulphate with use of sodium and calcium bentonites, an absorbite and peat, and definition of a specific surface area of the specified adsorbents.

Materials and Methods. The phenolic sewage was used for experiments, which are got from a balancing tank of PJSC “EVRAZ Dneprodzerzhynskii KHZ” (Kamianske). Such substances were applied as adsorbents: AG-5 absorbite, valley peat, and also natural sodium and calcium bentonite clays. Let's notice that oils and tars of coke-chemical manufacturing represent mix of one- and polycyclic aromatic and heterogeneous ring compounds. Despite it, it is almost impossible to standardize the integral indicator defining the maintenance of such multicomponent mixture in sewage as it will depend both on component structure, and on method of determination. In this work the content of tarry substances was determined by a gravimetric method [6].

The experiment consisted in the following. Each of four tests of phenolic waste water with initial concentration of tarry substances of 100, 200, 500 and 1000 of mg/dm^3 was subjected to pressure flotation with addition of both modifications bentonite clay, absorbite and peat. The volume of each separate test was 400 cm^3 . Researches were conducted on laboratory floatation unit in conditions as close as possible to manufacturing: flotation time – 20 min., temperature of waste water – 323 K, intensity of air delivery – $0.15\text{ dm}^3/h$. The dose of each adsorbent constituted 200 mg/dm^3 . After

flotation time finished the tests from high layers of liquid have been selected to determine the residual concentration of tarry substances. Results of the experiment are presented in Table 1.

Table 1

Results of the sewage adsorption disposal of ammonium sulphate manufacturing

Initial concentration of tarry substances, mg/dm ³	Residual concentration of tarry substances, mg/dm ³			
	Na bentonite	Ca bentonite	absorbite	peat
100	10	25	11	42
200	36	105	41	125
500	255	400	310	419
1000	750	900	800	918

As it seen in Table 1, effectiveness of the adsorption cleaning is low, especially if to compare it to results of the previous experiments [4, 7]. However, at the heart of a research there was a determination of the true specific surface area of each of adsorbents under the identical conditions of conducting distortionless process caused by addition of any foreign substances (coagulums, flocculants). Low effectiveness of cleaning has a talk by lack of flocculant addition (in a case with bentonite clay) or a poor dose of reagent (for absorbite and peat). In further reasonings made an assumption that process discussed above is well described by the theory of monomolecular adsorption of Langmuir on the phase boundary "solution – adsorbent". The experimental data allowed calculating the limit value of adsorption (capacity of the adsorption monomolecular layer), a constant of the adsorption equilibrium, and, above all, a specific surface area of each adsorbent. Calculations carried out by method of construction and linearization of adsorption isotherms of Langmuir.

Adsorption of tarry substances on the phase boundary "solution – adsorbent" in this case is described by the equation of Langmuir adsorption isotherm [8]:

$$A = \frac{A_{\infty} b C}{1 + b C}, \quad (1)$$

where A_{∞} – limit value of adsorption, mol/g;

b – constant of the adsorption equilibrium;

C – residual concentration of tarry substances (equilibrium concentration), mol/dm³.

Having determined the size of adsorption (A) at various equilibrium concentrations (C), it is possible to calculate the limiting adsorption (A_{∞}) and the specific surface area of an adsorbent (S_m). The size of adsorption A (mol/h) is determined by the equation [8]:

$$A = \frac{(C_0 - C)V}{m}, \quad (2)$$

where V – volume of waste water, dm³;

m – adsorbent mass, g;

C_0 – output concentration of tarry substances, mol/dm³;

C – residual concentration of tarry substances (equilibrium concentration), mol/dm³.

The values calculated using formula (2) for each adsorbent are presented in Table 2, and at their values the classical (in coordinates $A - C$) and linearized (in coordinates $C/A - C$) adsorption isotherms are constructed (Fig. 2 and 3 respectively).

Adsorption isotherms, represented in Fig. 2, have the similar form and, according to Gils classification [2], can be carried to the most common class L2 (Langmuir's class). The isotherms of this class are bent on an axis of concentration. At achievement of some particular concentration of absorbate in adsorbent substance the formed curves are almost parallel to axes of concentration of sorbate (reach saturation state). Isotherms of this kind are obtained when studying adsorption of solutions of the surface-active substances (SAS), dyes and compounds which molecules are in solution in the form of associates. In spite of the fact that components of a disperse phase of tarry substances which are not

relating to one of the listed types of compounds, the reference form of adsorption isotherms can be explained with the fact that SAS molecules have rather large area. Also the possibility of polymerization of molecules among themselves and with components of phenolic sewage is not excluded.

Table 2

Input data for construction of classical and linearized isotherms of Lengmyur

Adsorbent	Residual concentration of tarry substances C , mol/dm ³	Reduction of tarry substances concentration $C_0 - C$, mol/dm ³	Adsorption value A , mol/g	C/A , g/dm ³
Na bentonite	0.000070	0.000634	0.001268	0.055556
	0.000254	0.001155	0.002310	0.109756
	0.001796	0.001725	0.003451	0.520408
	0.005282	0.001761	0.003521	1.500000
Ca bentonite	0.000176	0.000528	0.001056	0.166667
	0.000739	0.000669	0.001338	0.552632
	0.002817	0.000704	0.001408	2.000000
	0.006338	0.000704	0.001408	4.500000
Absorbite	0.000077	0.000627	0.001254	0.061798
	0.000289	0.001120	0.002239	0.128931
	0.002183	0.001338	0.002676	0.815789
	0.005634	0.001408	0.002817	2.000000
Peat	0.000296	0.000408	0.000817	0.362069
	0.000880	0.000528	0.001056	0.833333
	0.002951	0.000570	0.001141	2.586420
	0.006465	0.000577	0.001155	5.597561

Essential similarity of a form of the isotherms represented in Fig. 3 to a classical look allowed to obtain almost rectilinear segments by linearization of the experimental data in coordinates $C/A - C$. The limiting value of adsorption is calculated using the equation [8]:

$$A_{\infty} = \frac{\Delta C}{\Delta(C/A)} \quad (3)$$

Length of a segment x which cuts off the plot constructed according to the experimental data at axis of ordinates is equal:

$$x = \frac{1}{A_{\infty} b}. \quad (4)$$

From here, the constant of the adsorption equilibrium b is found using the equation:

$$b = \frac{1}{A_{\infty} x}. \quad (5)$$

Knowing the size of the threshold adsorption (monolayer capacity) and the area which is occupied by adsorbate molecules in the dense bed on an adsorbent surface, a specific surface area of an adsorbent is found using the equation [8]:

$$S_m = A_{\infty} N_A \omega_m, \quad (6)$$

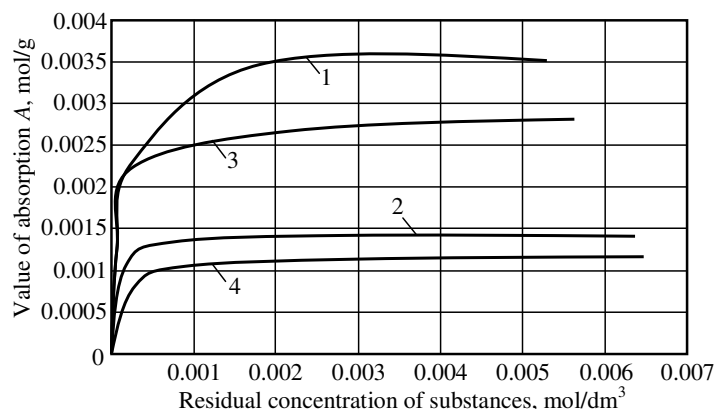


Fig. 2. Adsorption isotherms of tarry substances on a surface of sorbents: 1 – Na bentonite; 2 – Ca bentonite; 3 – absorbite; 4 – peat

where S_m – specific surface area of an adsorbent, m^2/g ;

N_A – Avogadro number, $6,022 \cdot 10^{23} \text{ mol}^{-1}$;

ω_m – area of an adsorbate molecule, nm^2 .

The values calculated by formulas (3)...(6) are presented in table 3.

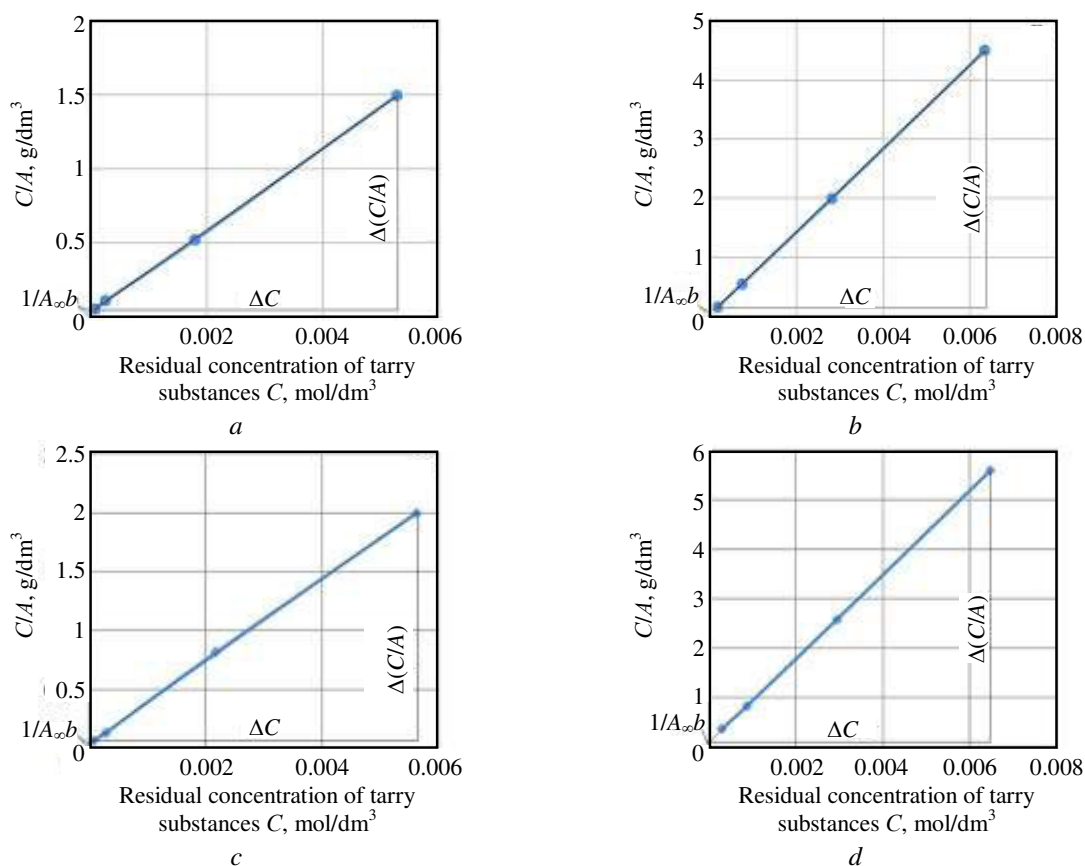


Fig. 3. Linearized adsorption isotherms of tarry substances on a surface of sorbents: sodium bentonite (a); calcium bentonite (b); absorbite (c); peat (d)

Table 3

Characteristics of adsorbents for manufacturing sewage disposal an ammonium sulphate from tarry substances

Item	Na bentonite	Ca bentonite	Absorbite	Peat
Threshold value of adsorption, mmol/g	3,61	1,42	2,87	1,18
Constant of the adsorption equilibrium	4989	4219	5645	2344
Specific surface area of an adsorbent, m^2/g	1847	728	1467	603

Results. The constant of the adsorption equilibrium is equal to the relation of constants of adsorption and a desorption and characterizes interaction energy of an adsorbent with an adsorbate: the stronger this interaction expressed, the larger value of a constant. As we see, there is intensive interaction of an adsorbent with an adsorbate, especially in case of bentonite clay and absorbite, that will promote efficient process behavior of adsorption of tarry substances. Let's notice that high values of a specific surface area of natural bentonite of both types are comparable to values of this index of an acid absorbite or zeolites. It can be explained with the fact that the area of an adsorbate molecule (in this work – the average area of the main SAS of a tarry phase of phenolic waters accepted to be equal to 85 nm^2) is 2...5 times exceeded the area of a molecule of spreading adsorbates – N_2 (16 nm^2), C_2H_4 (23 nm^2),

C₆H₆ (40 nm²), CCl₄ (39 nm²) [9]. Anyway, bentonite clay of both types shows high adsorption properties in relation to tarry substances of phenolic sewage of ammonium sulphate manufacturing.

With relation to purification indicators of natural alkaline bentonite clay, we recommend to use it as reagent for the process intensification of extraction of tarry substances from ammonium sulphate manufacturing sewage at flotation. Higher rates of cleaning will be reached at combined use of bentonite clay and cationic flocculant.

Conclusions. The specific surface area of adsorbents during the tarry substances sorption from the phenolic manufacturing sewage is determined for the first time, (m²/g): sodium bentonite clay – 1847; AG-5 absorbite – 1467; calcium bentonite clay – 728; valley peat – 603. It is constructed adsorption isotherms of tarry substances for the specified sorbents. Based on the theory of monolayer adsorption of Langmuir, the main indexes of adsorbents are defined: the threshold value of adsorption A_{∞} , constant of the adsorption equilibrium b , specific surface area of an adsorbent S_m . The most efficient sorbent – natural sodium bentonite, is recommended for the manufacturing implementation at the coke-chemical enterprises of Ukraine.

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