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STUDY OF LYOPHILIC PROPERTIES OF PYROCARBON AS A POTENTIAL SORBENT FOR CLEANING WATER FROM OIL AND OIL PRODUCTS

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The lyophilic properties of pyrocarbon, obtained by pyrolysis of worn automobile tires, in relation to oil, gasoline, benzene, hexane, water, and water-oil and water-gasoline emulsions were studied. The research was carried out by the method of a lying drop on the surface formed by pyrocarbon particles of different dispersion, by determining the contact angle of wetting. The value of this angle was determined by analyzing images obtained photographically. It was established that organic substances and water have a significant contrast in terms of the wetting of pyrocarbon. Based on the determination of the contact angle, the work of adhesion in different systems was calculated depending on the temperature. Based on this, the conclusion was formulated that the selectivity of absorption of oil and oil products will increase with increasing temperature.

Key words: pyrocarbon; natural and wastewater treatment; lyophilic properties; contact angle; sorption; work of adhesion.

Introduction

Oil and oil products are among the most common pollutants of natural waters, especially surface waters. They enter reservoirs together with wastewater, surface washes, as a result of transport accidents, as well as directly during oil extraction [1]. The problem of pollution of natural water bodies as a result of Russia's aggression in the southern and eastern regions of Ukraine became particularly acute: the destruction of the infrastructure of communal enterprises, the destruction of military equipment, etc. Aromatic compounds contained in oil and oil products are characterized by high bioresistance, so they can accumulate in water and aquatic biota. This causes an extremely negative impact on natural water ecosystems, on the quality of water used in industry and public utilities. Aromatic compounds, for example, benzene and its homologues, have a negative effect on the immune system and cause cancer. Therefore, cleaning various waters from oil and oil products is becoming more and more important.

Practically the only methods of water purification from oil and oil products, which allow to

avoid secondary pollution, are adsorption methods. As sorbents, materials based on natural raw materials (sunflower husks [2], clay, perlite, kaolinite, clinoptilolite [3–5], activated carbon, cotton, etc.) and synthetic ones, such as polystyrene foam, are used. To increase the effectiveness of the sorbents, they are preliminarily hydrophobicized. In particular, the sorption capacity of hydrophobized sorbents based on polyurethane foam and polyimide is 90 and 30 times greater, respectively, compared to the initial sorbents [6]. These and other synthetic sorbents [7–11], in addition to high sorption capacity, have the ability to regenerate. This is important for their use as filter loads, but cleaning natural water bodies and soils with these sorbents is economically impractical.

The use of waste from other industries or products of utilization of such waste, which corresponds to modern technological ideas about the synthesis of chemical-technological systems, significantly reduces the cost of the water purification process. Such materials include, in particular, pyrocarbon, which is obtained during high-temperature processing of worn automobile tires. Previous studies have established

that they have a certain sorption capacity for oil and oil products [12].

The sorption capacity of solids in relation to liquids and the rate of sorption primarily depend on their lyophilicity. Capillary and other phenomena that occur during liquid absorption are derived from lyophilicity. Therefore, in order to evaluate the ability of solid bodies of a certain dispersion to absorb a specific liquid, and therefore their suitability for use in technologies for cleaning various environments from harmful liquid substances, it is necessary to determine the lyophilicity of solid particles in the corresponding systems.

The dominant characteristic of lyophilicity is the contact angle (θ), which depends on the surface tension of the phases. Depending on the value of θ , three types of wetting are distinguished [13]: complete wetting ($\theta \rightarrow 0^\circ$, the liquid spreads over the surface); wetting ($0^\circ < \theta < 90^\circ$), non-wetting ($90^\circ < \theta < 180^\circ$). Direct and indirect methods are used to determine the contact angle. Direct methods include the following: direct measurement of the edge angle for a drop of liquid on the surface of a solid body using an angular scale using optical systems (photographing the profile of the drop, projection on a screen, etc.) [14]. The error of measurement by these methods is within 0.1° . To determine the contact angle of viscous liquids, a plate with an applied drop of liquid is partially immersed in water. However, in the case of pyrocarbon, this method is not advisable to use due to its low density (no more than 0.8 g/cm^3), as well as the presence of air in the pores, which will be released from the pores in the water and affect the contact of the liquid with the solid surface. This method is generally unsuitable for determining the contact angle with the participation of dispersed particles because it is impossible to immerse and expose them in water. For the same reasons, the method based on determining the edge angle for a submerged plate, the angle of inclination of which is changed, as well as the method for determining the inflow and outflow angles, is also unsuitable. The mediated methods include Jung's and Wilhelmi's methods, by the height of liquid rising along the wall of a solid plate or in a capillary, etc. The disadvantage of Jung's method is that it is often impossible to determine the value of surface tension for contacting surfaces, in particular, for a liquid-solid system. Taking into account the advan-

tages and disadvantages of each of the methods, a direct method – photography was used to determine the contact angle.

The aim of the work was to study the lyophilic properties of pyrocarbon as a potential sorbent of oil and oil products.

Materials and research methods

Determination of the contact angle of wetting was carried out by a direct method – the lying drop method.

Pyrocarbon obtained by pyrolysis of worn tires of different dispersions was used for research: pieces with a size of 1–2 cm (a flat surface was obtained by grinding), as well as particles with a dispersion (mm) < 0.1 ; 0.1–0.25; 0.25–0.5; 0.5–1.0; 1.0–2.0. These pyrocarbon fractions were obtained by sieving crushed large pieces of pyrocarbon using a standard set of sieves. The different dispersibility of pyrocarbon particles is due to the features of its potential application in water purification processes, such as filter loading or for applying dispersed particles to the surface of a spilled oil product (on the surface of water or on a solid surface), as well as the fact that, as is known, the wettability of solid particles often significantly depends on their dispersion.

Crude oil from the Boryslav field, and 95-grade gasoline were used as fluids; benzene, and hexane as typical components of gasoline, tap water, as well as stable emulsions of oil and gasoline in water (these emulsions simulate wastewater generated in many technological processes). Stable emulsions were achieved by mixing water with organic substances under the influence of ultrasonic vibrations. For this, an ultrasonic disintegrator “Ultrasonic Disintegrator” UD-20 of the magnetostrictive type was used (radiation frequency – 20 kHz, radiation power – 11.2 W). The maximum content of organic liquids at which the emulsion was stable for at least 2 hours – 17 % (by organic phase).

Based on the values of the edge angle for the specified organic substances and water, it is possible to establish the so-called contrast (difference) of such a characteristic as wettability for different systems. This, in turn, will make it possible to predict the selectivity of the sorption of the studied solid materials with respect to organic substances and water, and therefore the expected effectiveness

of potential sorbents in the processes of cleaning various environments from oil and oil products.

Determination of the contact angle in the studied systems was carried out under isothermal conditions. First, liquids and solid materials, as well as the tips of the Variable Volume Pipette (varipipette) were kept separately in isothermal conditions. Only after that, drops of liquids with a volume of 0.2–0.3 cm³ were applied to the studied solid surfaces from a height (the distance between the surface and the pipette tip was 4–5 mm). To carry out research at temperatures of 20–40 °C, a TS-80 M-2 thermostat was used, and in the range of 5–15 °C – a thermostatic chamber made of polymethyl methacrylate, into which a heat carrier with a given temperature was fed (it was fed from a water ultra-thermostat UTU-4).

Images of drops on the surface of solid substances were obtained with the help of a digital camera in the mode of photo and video recording (cinema). Further, the photo images were processed to achieve maximum contrast between the liquid-solid and liquid-gas phase (air) phase interfaces. Using the method of tangents, the contact angle was determined for certain systems, analyzing at least three photographs for each of them.

Results and discussion

The behavior of organic substances on the surface of pyrocarbon of different fractions differ significantly. Drops of gasoline, benzene, and hexane spread over the surface very quickly after being applied to the pyrocarbon surface. The analysis of the behavior patterns of a drop of the indicated substances on a flat surface, as well as on the surface

of highly dispersed pyrocarbon (layer thickness 15 mm) showed that in the entire temperature range, the spreading of a drop with a volume of 0.25 cm³ takes place within 0.6–0.8 sec on the area about 1 cm² with the formation of an almost regular circle. After applying a drop, the diameter of the spreading zone decreases for 1.5–2.0 sec towards the center of the circle until it disappears altogether (Fig. 1).

This nature of the spread of the specified substances indicates that after applying a drop to the surface, it begins to be absorbed both by the layers of pyrocarbon (under its surface) and by its surface layer. It is obvious that these processes are due to the high dispersion of pyrocarbon and the affinity of non-polar liquids and pyrocarbon. Particles of smaller dispersion (0.1–2.0 mm) also quickly absorb the specified substances, but the nature of their spreading and absorption is difficult to assess due to the significant unevenness of the surface of the layer formed from them.

Since pyrocarbon is intended to clean from oil products not only hard surfaces but also water environments, the lyophilicity of pyrocarbon to water was determined. It was established that all pyrocarbon fractions are not wetted by water, the molecules of which are dipoles (Fig. 2); the value of the contact angle is equal to $133 \pm 2^\circ$.

In general, the obtained data indicate that gasoline, benzene, and hexane wet the pyrocarbon surface very well, regardless of the geometric dimensions of its particles. Since water does not wet pyrocarbon, pyrocarbon has a high selectivity for wetting by organic substances and water. Therefore, it is suitable for cleaning various aquatic environments from the specified organic substances.

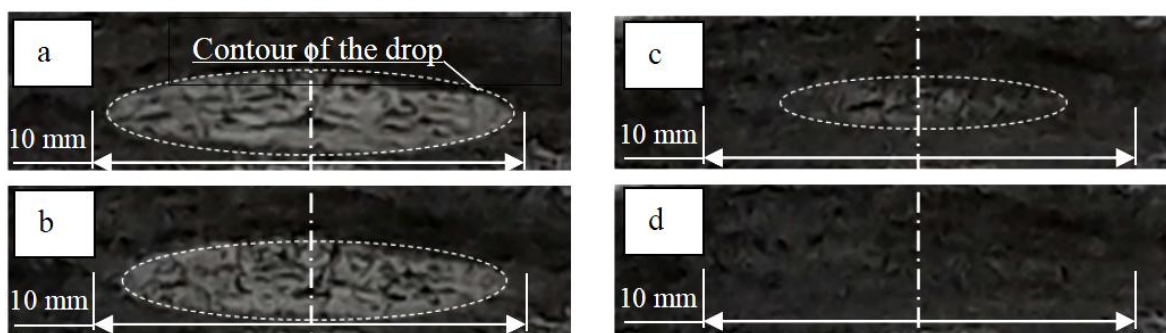


Fig. 1. Photo of the spreading and sorption of a drop of gasoline on the surface of pyrocarbon, time from the moment of application of the drop, sec: 1a – 0.4; 1b – 0.8; 1c – 1.6; 1d – 2.0

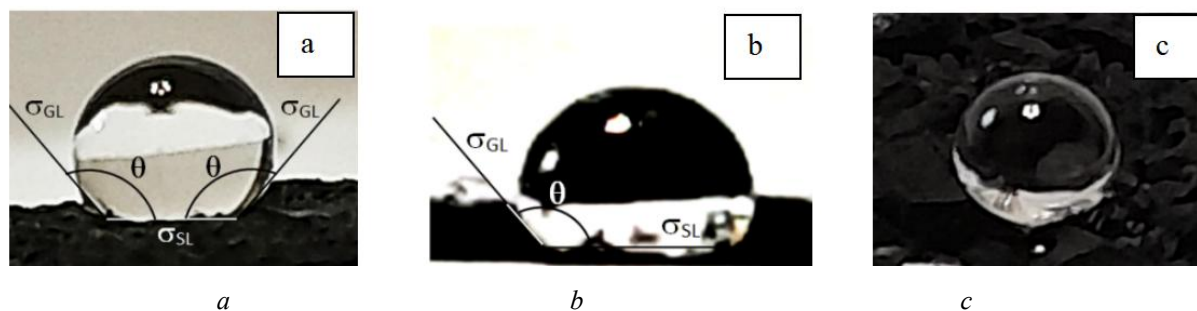


Fig. 2. Image of a drop of water on the surface of pyrocarbon at 20 °C:
a – flat continuous surface; *b* – surface formed by particles < 0.1 mm (image);
c – on particles with a dispersion of 1–2 mm;
 σ_{GL} is the surface tension at the “liquid – gas (air)” phase interface,
 σ_{SL} is the surface tension at the phase interface “liquid – solid (pyrocarbon)”

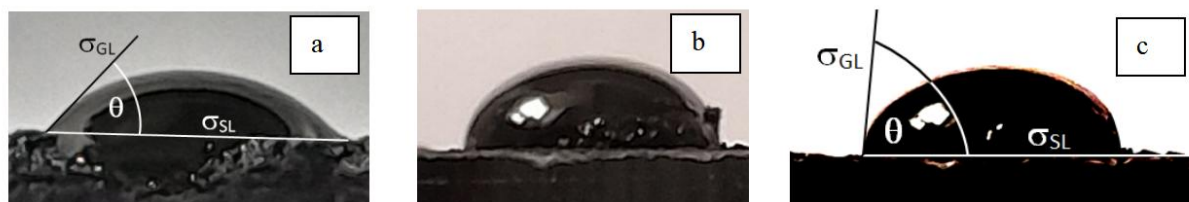


Fig. 3. Image of a drop of crude oil on the surface of pyrocarbon at 20 °C:
a – flat continuous surface; *b, c* – surface formed by particles < 0.1 mm
(*b* – original image; *c* – processed image)

The behavior of crude oil on the surface of pyrocarbon of different dispersions is significantly different. On a flat, continuous surface, oil wets pyrocarbon (Fig. 3, *a*); the average value of the contact angle at a temperature of 20 °C is 55°. The difference in wetting angle values (from 53 to 58°) is due to the uneven structure of the pyrocarbon surface. At the same time, oil wets the surface formed by highly dispersed particles (< 0.1 mm) much worse: the contact angle of wetting is about 86° (Fig. 3, *b, c*).

It was established that for pyrocarbon fractions <0.1; 0.1–0.25; 0.25–0.5; 0.5–1.0; 1.0–2.0 mm, the average value of the contact angle at a temperature of 20 °C is 86, 83, 80, 70, 63°. The decrease in the wetting angle with increasing pyrocarbon particle size can be explained by an increase in the flatness of the sample: the oil droplet is more in contact with surfaces with a larger flat surface area. The difference in the ability to wet the pyrocarbon surface with organic substances cannot be explained by the effect of surface tension. In

particular, the values of the surface tension of gasoline brand 95, benzene, hexane and oil are quite close ($\sigma_{LG} \cdot 10^3, J/m^2$): 27.5; 28.9; 18.4 and 28–29, respectively. This is probably due to a significant difference in the viscosity of these substances (for gasoline, benzene, hexane it is equal to 0.64; 0.74; 0.68 and 4.9 mm²/sec, respectively), while for oil it is almost 1–2 orders of magnitude higher – from 2 to more than 20.

Since the viscosity of liquids decreases with increasing temperature, this should naturally cause a decrease in the value of the contact angle, and therefore – an improvement in oil sorption. As a rule, the dependence of the contact angle on temperature for homogeneous surfaces is linear. But wettability is not a simple function of viscosity, the state of the solid surface plays a significant role. Therefore, the influence of temperature on the value of the contact angle of oil wetting was determined experimentally for pyrocarbon samples of different dispersion.

As expected, with increasing temperature, the value of the edge angle decreases, which will con-

tribute to the improvement of wetting of pyrocarbon particles with oil (Fig. 4, 5).

At the same time, a fairly clear dependence of the contact angle on the dispersion of pyrocarbon particles is observed. It is clear that the dispersion of 2–10 mm corresponds to a flat surface. Therefore, a further increase in its size will obviously not lead to a change in the wetting angle.

At temperatures above 30 °C, the contact angle of wetting of oil on a flat surface decreases sharply, as a result of which the wetting phenomenon transforms into full wetting, which is accompanied by the spreading of a drop of oil over the pyrocarbon surface. In other cases, with an increase in temperature up to ~30 °C, an almost linear decrease in the contact angle is observed. This generally corresponds to the dependence of the surface tension of liquids on temperature. However, after this temperature, there is some violation of the proportionality of the change of the edge angle with temperature, especially for pyrocarbon fractions of 0.5–1.0 and 1.0–2.0 mm.

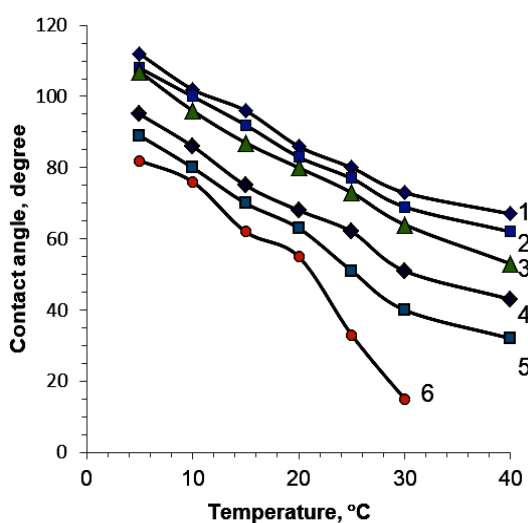


Fig. 4. Dependence of the value of the contact angle of pyrocarbon wetting with oil on temperature: pyrocarbon fraction, mm: 1 – <0.1; 2 – 0.1–0.25; 3 – 0.25–0.5; 4 – 0.5–1.0; 5 – 1.0–2.0; 6 – flat surface

Often oil or oil products form stable aqueous emulsions. Therefore, the wettability of pyrocarbon particles with aqueous emulsions of oil from the Boryslav field and gasoline grade 95 was further investigated. The aqueous emulsion of gasoline is

practically white, and the oil is light brown in color. The value of the contact angle for all types of emulsions is similar to that for water – about 135° (Fig. 6). This indicates that the water phase of the emulsion plays a predominant role in the interaction with the pyrocarbon surface.

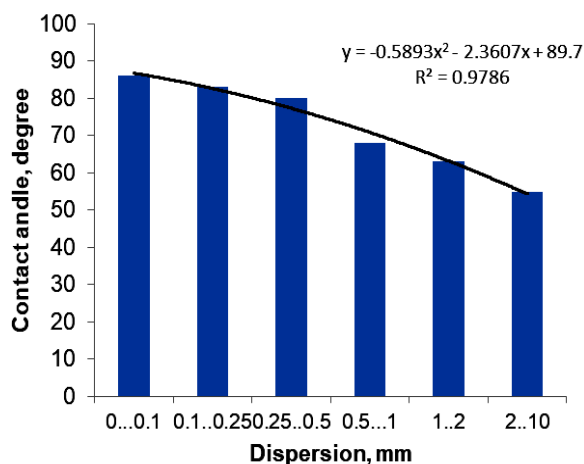


Fig. 5. Dependence of the contact angle of wetting on the dispersion of pyrocarbon (20 °C); dispersion of 2–10 mm corresponds to a flat surface

An increase in temperature has little effect on the value of the contact angle. Thus, in the temperature range of 5–40 °C, the value of the edge angle decreases from 142 to 130°. That is, emulsions in this temperature range remain hydrophobic. Therefore, it is not advisable to use pyrocarbon to clean water environments from persistent oil or gasoline emulsions. At temperatures above 60 °C, these emulsions begin to break down, as evidenced by the partial delamination of the water-organic phases. As the temperature increases, the system becomes more and more stratified. However, the value of the contact angle under these conditions changes slightly, since the organic phase in the drop partially separates – it moves up since its density is less than the density of water. And it is water that comes into contact with pyrocarbon. It can be predicted that during the movement of emulsions, which partially degrade at elevated temperature, sorption of petroleum products will occur through the pyrocarbon layer since the movement of the liquid phase is accompanied by its mixing and renewal of the surface near the solid particles. However, in real conditions, a targeted increase in the temperature of previously formed emulsions is not economically beneficial.

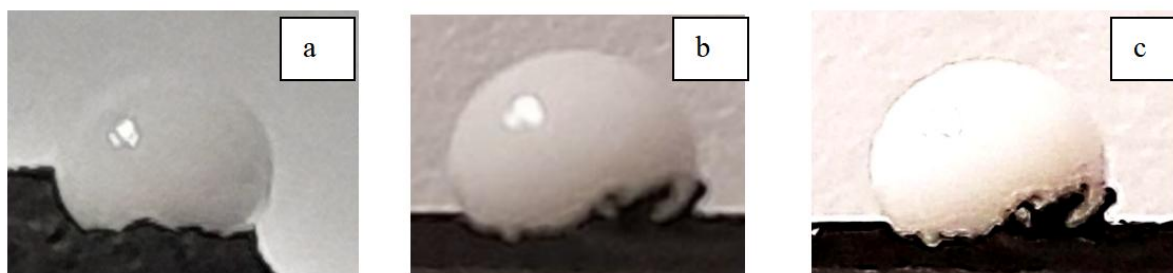


Fig. 6. Image of a drop of aqueous emulsion of crude oil on the surface of pyrocarbon at 20 °C: a – flat continuous surface; b, c – surface formed by particles < 0.1 mm (b – original image; c – processed image)

The value of the contact angle is determined by the intensity of the interaction of the liquid phase with the solid surface, that is, adhesion. The equilibrium work of adhesion (Wa) of a liquid on a solid surface is calculated using the Dupré – Young equation (1):

$$Wa = \sigma_{LG} (1 + \cos \theta), \quad (1)$$

where σ_{LG} is the value of the surface tension of the liquid at the liquid-gas interface, J/m²; θ is the value of contact angle, degree.

For the pyrocarbon-oil system, the equilibrium work of adhesion for pyrocarbon with dispersity <0.1; 0.1–0.25; 0.25–0.5; 0.5–1.0; 1.0–2.0 and for a flat surface at a temperature of 20 °C, respectively, is equal to ($Wa \cdot 10^3$, J/m²) 28.6; 32.0; 33.4; 38.2; 41.4 and 44.8. The work of oil adsorption on a flat pyrocarbon surface is almost 1.6 times greater than on a surface formed by particles with a dispersion of less than 0.1 mm. At the same time, the work of adhesion of water on the pyrocarbon surface at this temperature is equal to $21 \cdot 10^{-3}$ J/m². So, as was shown above, there are prerequisites for the selective sorption of oil and other organic substances (gasoline 95, benzene, hexane, etc.), whose surface tension values are similar to oil.

The increase in the efficiency of cleaning water from, for example, oil with an increase in the temperature of the environment is confirmed by the values of the equilibrium work of adhesion. An increase in temperature from 5 to 40 °C leads to an increase in the work of adhesion on a flat surface from $28.7 \cdot 10^{-3}$ to $56.0 \cdot 10^{-3}$ J/m² (grows almost twice), while for water from $21.9 \cdot 10^{-3}$ to $35 \cdot 10^{-3}$ J/m² (increases by 1.6 times). Therefore, it can be expected that the selectivity of sorption of oil and oil products from water environments will increase with an increase in its temperature.

Conclusions

Pyrocarbon of various dispersions is well wetted by such non-polar substances as oil, gasoline, benzene, hexane. Pyrocarbon particles with a relatively large flat surface area are best wetted. As the dispersion increases, the value of the contact angle increases. This indicates the high lyophilicity of pyrocarbon in relation to oil and oil products. Therefore, it is advisable to use it as a cheap sorbent for cleaning water from oil and oil products.

Water does not wet pyrocarbon regardless of its dispersion; it is hydrophobic. This, together with the ability of pyrocarbon to be wetted by the specified organic liquids, gives reason to expect that pyrocarbon will have a high selectivity for the absorption of oil and oil products from water environments.

Aqueous emulsions of oil and gasoline, like water, are hydrophobic – they do not wet pyrocarbon. An increase in temperature up to 40 °C practically does not affect the wetting of pyrocarbon with emulsions. Therefore, it is not advisable to use pyrocarbon for water purification from oil and oil product emulsions.

Based on the obtained results regarding the wettability of pyrocarbon with oil and other organic substances, the equilibrium work of adhesion was calculated, which confirms the selectivity of the sorption action of pyrocarbon with respect to oil and oil products from aqueous environments. This characteristic is strengthened with an increase in the temperature of the water environment.

References

1. O. Ya. Pylypchuk, T. I. Vysots'ka, T. V. Pichkur (2020). Znyzhennya vplyvu zaliznychnoho transportu na navkolyshnye seredovyshche: problema ochyshchennya gruntu vid naftoproduktiv. *Ekolohichni nauky*. 3(30), 113–118. doi.org/10.32846/2306-9716/2020.eco.3-30.19 (in Ukrainian).

2. L. V. Krychkovs'ka, Ye. A. Yelnahhar, V. L. Dubonosov (2019). Poshuky sorbentiv dlya elyuatsiyi naftoproduktiv z vody. *Visnyk Natsional'noho tekhnichnoho universytetu "KhPI". Seriya: Khimiya, khimichna tekhnolohiya ta ekolohiya*, 2, 47–52. DOI: 10.20998/2079-0821.2019.02.07 (in Ukrainian).
3. P. Qi, N. Lin, Y. Liu, J. Zhao (2013). Improvement of oil/water selectivity by stearic acid modified expanded perlite for oil spill cleanup. *J. Shanghai Jiaotong Univ.*, 18, 500–507. doi.org/10.1007/s12204-013-1426-x
4. D. Zadaka-Amir, N. Bleiman, Y. G. Mishael. (2013). Sepiolite as an effective natural porous adsorbent for surface oil-spill. *Microporous Mesoporous Mater.*, 169, 153–159. doi.org/10.1016/j.micromeso.2012.11.002
5. Zenovii Znak, Roman Mnykh, M. A. Pyrig, T. V. Zhuk (2022). Research of Oil Sorption by Natural Clinoptilolite. Chemistry, technology and application of substances, Vol. 5, No. 2: 58–64. <https://doi.org/10.23939/ctas2022.02.058>
6. E. Barry, A. U. Mane, J. A. Libera, J. W. Elam, S. B. Darling (2017). Advanced oil sorbents using sequential infiltration synthesis. *J. Mater. Chem. A*, 5, 2929–2935. doi.org/10.1039/C6TA09014A
7. S. Bayraktaroglu, S. Kizil, H. B. Sonmez (2021). A highly reusable polydimethylsiloxane sorbents for oil/organic solvent clean-up from water. *Journal of Environmental Chemical Engineering*, 9 (5), 106002. doi.org/10.1016/j.jece.2021.106002
8. J. Wang, H. Wang, G. Geng (2018). Highly efficient oil-in-water emulsion and oil layer/water mixture separation based on durably superhydrophobic sponge prepared via a facile route. *Mar. Pollut. Bull.* 127, 108–116. doi.org/10.1016/j.marpolbul.2017.11.060.
9. P. Narayanan, A. Ravirajan, A. Umasankaran, D. G. Prakash, P. S. Kumar (2018). Theoretical and experimental investigation on the removal of oil spill by selective sorbents. *J. Ind. Eng. Chem.*, 63, 1–11. doi.org/10.1016/j.jiec.2018.01.031
10. H. Zhu, S. Qiu, W. Jiang, D. Wu, C. Zhang (2011). Evaluation of Electrospun Polyvinyl Chloride/Polystyrene Fibers As Sorbent Materials for Oil Spill Cleanup. *Environ. Sci. Technol.*, 45, 4527–4531. doi.org/10.1021/es2002343
11. E. Piperopoulos, L. Calabrese, A. Khaskhoussi, E. Proverbio, C. Milone (2020). Thermo-Physical Characterization of Carbon Nanotube Composite Foam for Oil Recovery Applications. *Nanomaterials*, 10, 86. doi.org/10.3390/nano10010086
12. S. O. Hrynyshyn, Zenovii Znak, Ksenia Hrynyshyn, Volodymyr Skorokhoda (2023). Use of pyrocarbon obtained in the process of pyrolysis of rubber waste for absorption of oil and Petroleum products. *Chemistry, Technology and Application of Substances*. 6, 11, 27–31. <https://doi.org/10.23939/ctas2023.01.027>(in Ukrainian).
13. Daniel Bonn, Jens Eggers, Joseph Indekeu, Jacques Meunier, Etienne Rolley (2009). Wetting and spreading. *Rev. Mod. Phys.*, 81, 739–805. <https://doi.org/10.1103/RevModPhys.81.739>
14. Horielov V. O., Kisil R. I., Bodnar R. T., Stepaniuk Ya. V. (2004). Vyznachennia kraiovoho kuta zmochuvannia ridynamy poverkhon tverdykh til shliakhom vymyruvannia heometrychnykh rozmiriv lezhachoi krapli. *Metody ta prylady kontroliu yakosti*, No. 12, 38–41.

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ДОСЛІДЖЕННЯ ЛІОФІЛЬНИХ ВЛАСТИВОСТЕЙ ПІРОКАРБОНУ ЯК ПОТЕНЦІЙНОГО СОРБЕНТА ДЛЯ ОЧИЩЕННЯ ВОД ВІД НАФТИ І НАФТОПРОДУКТІВ

Досліджено ліофільні властивості пірокарбону, отриманого піролізом зношених автомобільних шин, щодо нафти, бензину, бензену, гексану, води та емульсій вода-нафта і вода-бензин. Дослідження виконували методом лежачої краплі на поверхні, утвореної частинками пірокарбону різної дисперсності, визначивши крайовий кут змочування. Значення цього кута визначали, аналізуючи зображення, отримані фотографічно. Встановлено, що органічним речовинам і воді притаманна значна контрастність щодо змочування пірокарбону. На основі визначення крайового кута змочування розраховано роботу адгезії у різних системах залежно від температури. На підставі цього сформульовано висновок, що селективність поглинання нафти і нафтопродуктів зростатиме зі збільшенням температури.

Ключові слова: пірокарбон; очищення природних і стічних вод; ліофільні властивості; крайовий кут змочування; сорбція; робота адгезії.