

PREPARATION OF A MODIFIED PEAT ADSORBENT USING
MICROWAVE RADIATION FOR WASTEWATER TREATMENT

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Abstract. The biogeochemical processes of modifying peat adsorbents and their treatment of wastewater from oil products and heavy metal ions, as well as the use of the adsorbent for cleaning oil spills in natural water bodies, were investigated. The modified peat adsorbents were obtained via thermal destruction by exposure to microwave radiation. The kinetics of peat modification at different microwave radiation powers, as well as changes in the fractional composition of peat during the modification process, were investigated. The dependence of the modified adsorbent's adsorption capacity on pH was determined. The use of modified peat adsorbents allows to reduce peat deposits in the Poltava region, which pose a potential danger to the environment, as well as to increase the level of environmental safety by minimizing wastewater pollution from oil products and heavy metal ions.

Keywords: peat adsorbent, thermal destruction, microwave radiation, treatment, wastewater, oil products, heavy metals, biogeochemical processes.

1. Introduction

Recently, the pollution of water bodies caused by oil and refined products has become alarming. An urgent task is to create effective purification methods of water from oil products and the elimination of oil pollution. Among the known effective methods, the adsorption method of wastewater treatment should be highlighted, which is widely available and economically feasible. The adsorption method allows for the removal of a wide range of man-made and natural pollutants. The spent adsorbent does not need to be regenerated; it can be disposed of or incinerated together with the removed pollutants. Waste materials and substances hazardous to the environment are often used in the manufacture of adsorbents, and their use contributes to

environmental safety.¹⁻³ Materials that adsorb oil hydrocarbons must have high oil capacity, buoyancy, low water absorption, and a porous surface. Peat has these properties, and its deposits in the Poltava region are significant.⁴

Effective adsorption materials should be easy to extract and recycle, non-toxic, cheap, and accessible.^{5,6} These requirements are met by adsorbents obtained by modifying natural materials to improve their adsorption properties. One of the natural materials for creating adsorbents is peat, which is widely used in its unmodified form for purifying various liquid media.^{7,8} Peat is a renewable natural bioresource that is formed as a result of the natural death and incomplete decay of marsh plants under the influence of biological processes under high humidity and a lack of oxygen.

Highly porous carbon adsorbent from peat is traditionally produced in recuperative furnaces by thermal treatment, which changes the structure of peat as a result of organic substances thermal destruction.⁹ This method is characterized by significant energy consumption, a long process time, high temperatures (400°C), and a high probability of peat ignition.

An alternative way for peat modification is to perform thermal destruction by exposing peat to microwave (ultra-high frequency - UHF) radiation, which allows to obtain a highly porous hydrophobic material. From an environmental standpoint, the most promising method is the extraction of organic components by microwave pyrolysis, as the microwave heating process does not introduce any pollutants into the processed material or the environment. Another advantage of microwave radiation is that electromagnetic waves penetrate to a considerable depth of the material being processed and, when absorbed, create a volumetric distribution of heat sources, ensuring efficient heating of

materials with low thermal conductivity. When using a traditional thermal pyrolysis scheme, the thermal conductivity of materials significantly affects the rate of heat input to the reaction zone. Since the temperature of the materials in the entire reactor volume can be controlled by changing the power of the microwave generator, an additional advantage of microwave pyrolysis is the ability to quickly control the rate of pyrolytic reactions and the composition of the products at the reactor outlet.

Based on the above analysis, we state the relevance, environmental, and economic feasibility of using microwave radiation in the process of peat modification to obtain a highly porous hydrophobic adsorbent for wastewater treatment.

The scientific novelty of the work is the scientific substantiation of the adsorbent production from peat by exposing it to microwave radiation, ensuring effective wastewater treatment from oil products and heavy metal ions.

The work aims to study the processes of modifying peat adsorbents and their application for the purification of wastewater from oil products and heavy metal ions, as well as for cleaning oil spills in natural water bodies.

2. Experimental

We used moss peat with a particle size of less than 5.0 mm and a moisture content of 20–25%. The peat was divided into fractions, and the fractional composition was determined by the sieve method. The main physical and chemical properties of peat were determined according to the standard methods.¹⁰

To clean the water surface from the motor oil, we used 2 dm³ of water, 100 cm³ of Mobil Ultra motor oil, and 300 g of peat modified by thermal destruction under the influence of microwave radiation.

The peat was modified by thermal destruction under the influence of microwave radiation, which allows obtaining a highly porous hydrophobic material, but more energy efficiently. During the modification, peat was poured into a quartz crucible, a closed bowl with peat was placed in a microwave oven (a household microwave oven of the Pluto type was used in the study), the microwave power was set, and the required time was maintained. The closed bowl with the modified peat was cooled in a desiccator to room temperature. The degree of peat modification was determined gravimetrically and calculated as the ratio of mass change to the initial mass, expressed as a percentage. The moisture absorption of peat was determined by measuring the mass of moisture absorbed by peat placed in an exciter with a solution of concentrated sulfuric acid, providing a constant humidity of $95 \pm 2\%$.

Peat moisture absorption (W, wt.%) was calculated as the ratio of moisture mass to the initial peat mass, expressed as a percentage. The oil capacity of peat (KH, g/g) was determined by the gravimetric method by saturating it under static conditions with oil products with a viscosity of 50 cSt at 20°C and calculating the ratio of the mass of consumed oil products to the initial mass of peat. The adsorption capacity of peat for methylene blue (MB) and iodine was measured using standard methods.

The organic mass of peat is a complex mixture of various high molecular weight compounds: humic substances (50%), hemicellulose (30–40%), fibre, and lignin (5–10%). The solution to the problem of integrated peat use should be based on the use of all its valuable components and properties. The chemical composition of peat determines its adsorption capacity to absorb various substances from gases and liquids. Peat is primarily a natural ion exchanger. The main source of inorganic compounds entering peat is the water migration of mineral components supplied by flood and groundwater, as well as air and biogenic migration. The chemical elements of the inorganic part of peat are found in the form of ions, salts, or complex compounds in five forms:

- 1) inorganic peat minerals;
- 2) inorganic components of peat water;
- 3) ion-exchange heteropolar organo-mineral complexes;
- 4) complex heteropolar organo-mineral compounds;
- 5) adsorption complexes of organic substances with the mineral part of peat.

The inorganic components of peat water occur in ionic, molecular, and colloidal forms, as well as in the form of organic-mineral complexes. The inorganic part of peat water is represented mainly by cations (mainly Ca²⁺, Mg²⁺, Fe³⁺, Al³⁺, K⁺, Na⁺) and anions (HCO₃⁻, NO₃⁻, Cl⁻, SO₄²⁻) of chemical elements. The content of cations in peat water (especially Ca²⁺) affects the acidity of the medium and determines the concentration of dissolved organic compounds.

Ion-exchange heteropolar organo-mineral complexes are formed when functional groups of organic acids react with strong base cations (Ca²⁺, Mg²⁺, K⁺, Na⁺) due to ion-exchange reactions of active groups of humic substances with peat water cations. Complex heteropolar organo-mineral compounds are formed when ionic and covalent or ionic and coordination bonds between cations and molecules of peat organic matter are combined. Among organo-mineral compounds, the most important are intrinsically complex compounds – chelates (cyclic structures closed by coordination bonds of terminal atoms and formed due to the equilibrium reaction between metal ions and an organic molecule, when more than one bond is established between the components).

Pectin substances, which are a complex chemical complex of pentoses, hexoses, and uronic acids, are quite common in plants. Their main role is to glue the membranes and give them strength and elasticity during plant growth.

Lignin substances, also known as hemicelluloses, are carbohydrate polymers that can be easily hydrolyzed by mineral acids or alkalis. They are formed by carbohydrates with five or six carbon atoms in the backbone, which are respectively called pentosans with the general formula $(C_5H_8O_4)_n$ and hexosans $(C_6H_{10}O_5)_n$, where n is the polymerization degree. The composition of hemicelluloses also includes uronic acids, the share of which in the dry weight of peat is 2–5%. The content of hemicelluloses in peat-forming plants is 11–43%, and the polymerization degree varies from 100 to 30,000.

It is believed that peat carbohydrates can be a raw material for chemical and biochemical processing. Peat hydrolyzates differ little from wood hydrolyzates and can be used to produce alcohols, phenols, and feedstuffs (yeast, protein preparations, fats, vitamins, etc.).

Peat is primarily a natural ion exchanger; the practical use of peat is due to its ecological safety, availability, and low cost. The main physical and chemical parameters of peat are: humidity, acidity, ash content, calorific value, degree of decomposition, moisture capacity, porosity, structure, thermal conductivity, bulk density, and chemical composition. The use of peat as an adsorbent is primarily determined by its microstructure and dispersion, porosity, and a fairly large specific surface area. The adsorption properties of peat are associated with the presence in the structure of such covalently bound functional groups as amine, amide, alcohol, aldehyde, carboxyl, ketone, phenolic, quinone, peptide, and methoxyl functional groups. Also, the adsorption properties of peat are caused by the presence of polymolecular associates, which are characterized by a certain organization at the macro level, in particular, humic acids and lignin.¹¹

To determine the adsorption capacity of the adsorbent, oil (10 g) was poured onto the surface of the water in a beaker. After that, the adsorbent was scattered in small portions over the surface of the oil-contaminated water, periodically stirring the contents of the glass until the oil was completely absorbed by the adsorbent. The amount of adsorbent consumed was determined by weighing, on the basis of which the adsorbent absorption capacity was calculated. To eliminate the influence of the adsorbent structure on the adsorption capacity, it was subjected to fine grinding to a fraction size of <0.25 mm.

To test the effectiveness of the peat modified by drying, the process of cleaning the surface of water from engine oil was investigated. Drying the peat makes the adsorbent as hydrophobic as possible, so more peat is on

the surface. After collecting the adsorbent and filtering the water, it was found that engine oil residues were present in concentrations below the permissible limits.

Thus, the use of the developed adsorbent contributes to the improvement of the state of ecological danger of the technogenic type,¹ which is formed by environmental pollution. We came to this conclusion by comparing the actual concentrations of harmful substances with the corresponding background indicators (typical for areas where the habitat of the flora and fauna species characteristic of it is preserved in a slightly changed form) of the Kremenchuk socio-economic zone.

3. Results and Discussion

To optimize the peat modification process, we studied the effect of microwave power (Fig. 1) and treatment time on the degree of peat modification (Fig. 2), which was estimated by the decrease in peat weight during the modification process.

The kinetics of modification at different microwave radiation powers (Fig. 1) showed an increase in the modification rate (the decrease in peat weight) with increasing microwave radiation power. The maximum yield of modified peat was found to be 60–62 wt.%, *i.e.*, the peat weight decreased by 38–40 wt.%.

The analysis of peat modification kinetic curves showed that the initial modification rate increases linearly with the increase of microwave power in the studied range (Table 1).

Table 1. Effect of microwave radiation power on the initial rate (V_{initial}) of peat modification

Power, W	V_{initial} , %/min
60	0.4
270	1.9
440	3.1
495	3.5
600	4.3

Fig. 2 shows that the increase in the microwave power, *i.e.*, the amount of energy absorbed by the peat, leads to a higher degree of peat modification at the same modification time.

The analysis of the change in the fractional composition of peat during the modification process (Table 2) allows us to state that the dispersion of peat particles decreases, and the share of particles with a size of less than 1.0 mm in the modified peat is about 80 wt.% against 60 wt.% in the original peat.

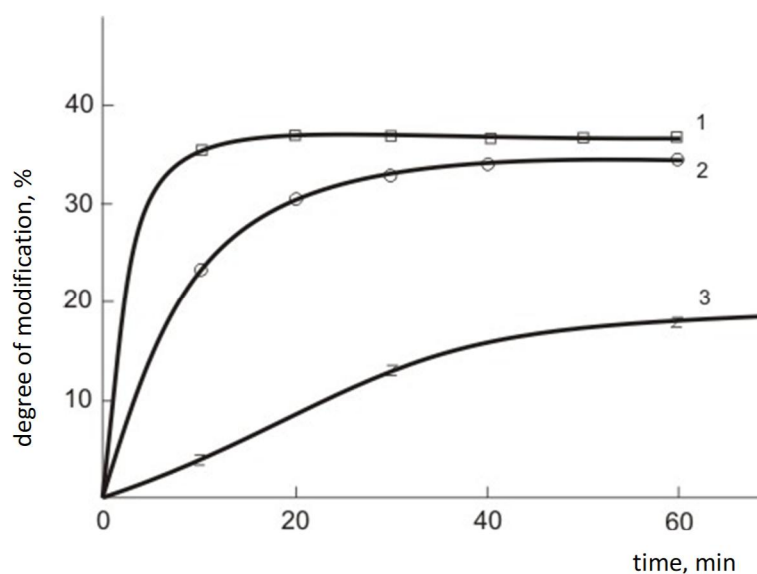


Fig. 1. Kinetics of peat modification at different microwave radiation powers: 495 W (1); 270 W (2); 60 W (3)

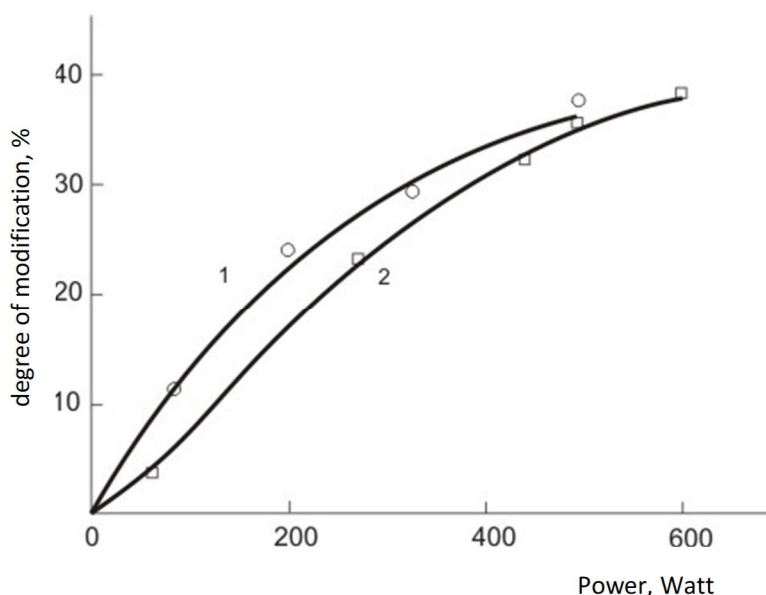


Fig. 2. Degree of peat modification vs. microwave radiation power. Modification time: 10 min (1) and 60 min (2)

Table 2. Changes in peat fractional composition during the modification process

Fraction size, mm	Share of the fraction, wt. %	
	initial	modified
less than 0.5	37.0±0.5	53.3±0.5
0.5 - 1.0	24.6±0.5	26.7±0.5
1.0 - 1.4	12.9±0.4	8.3±0.4
1.4 - 3.0	16.7±0.2	9.5±0.2
more than 3.0	8.8±0.2	2.2±0.2

We investigated the effect of microwave power and modification time on the ability of peat to absorb moisture. Fig. 3 shows the typical dependencies of changes in peat moisture absorption during the modification process. The effect of microwave radiation on peat is manifested in a decrease in the maximum moisture absorption of modified peat compared to the original (unmodified) peat by 2 times (from 20-22% to 10-12%), *i.e.*, the hydrophobicity of peat increases during the modification process.

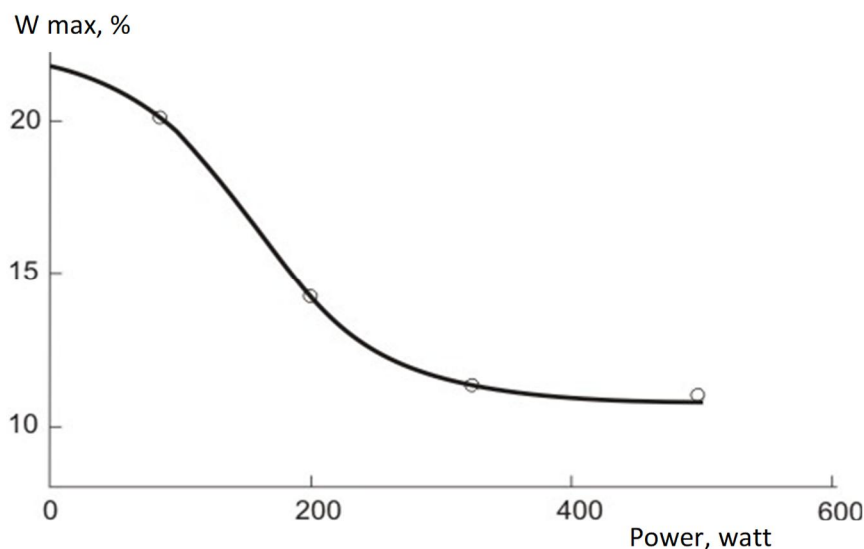


Fig. 3. Moisture absorption vs. microwave power. The modification time is 60 min

Thus, from a technological point of view, the optimal microwave power is at least 400 W, which ensures the achievement of the maximum degree of modification within 15-20 minutes.

As a result of peat treatment with microwave radiation, thermal destruction of organic compounds occurs, which is accompanied by the release of volatile products, due to which a porous structure is formed in peat, and the composition and properties of the surface change.

The study of adsorption properties under static conditions allows to determine the maximum adsorption capacity of a material. This capacity depends on its total specific surface area (taking into account the pore surface) and its surface nature, including its hydrophilic-lipophilic balance, as well as on the content of surface groups capable of forming surface compounds and complexes involving adsorbate molecules. In this regard, the adsorption of adsorbates such as methylene blue (MB) and iodine on the same adsorbent proceeds differently.

MB and iodine molecules are known to be adsorbed mainly on the surface of meso- and micropores, namely on the surface of pores larger than 1.5 and 1.0 nm, respectively. The difference in the adsorption of MB and iodine on a solid surface occurs due to their acid-base nature. MB is preferentially adsorbed on negatively charged surface active centres and positive ones, while iodine is preferentially adsorbed on uncharged (hydrophobic) surface areas due to dispersion (hydrophobic) interactions. At the same time, it is partially adsorbed on positively charged centers because in aqueous solutions, molecular iodine is in equilibrium with ionic forms (iodide and iodate, which are formed during the decomposition of hypoiodic acid).

Thus, the study of the influence of the conditions and parameters of peat modification under the influence of microwave radiation on its adsorption properties allows us to expand our understanding of the change in the composition and properties of the peat surface during the modification process.

We have studied samples of modified peat obtained at different microwave dose rates and the same modification time, and samples obtained at different modification times and the same microwave dose rate.

Fig. 4 and Fig. 5 show the effect of microwave radiation power in the range of up to 600 W and the impact of modification time, respectively, on the adsorption activity of peat both for iodine and MB. The adsorption capacity for iodine increases by 1.2–1.4 times, and for MB this value decreases by more than 2 times with an increase in both microwave radiation power and the duration of its impact on peat.

Based on the experimental data, it can be concluded that the content of charged sites on the peat surface decreases during the modification process due to the thermal destruction of functional organic compounds, resulting in the hydrophobic nature of the peat surface.

To confirm the assumption of an increase in the hydrophobic properties of peat during modification, the effect of microwave radiation power on the ability of peat to adsorb such hydrophobic organic substances as oil and oil products was studied, and this dependence was compared with the dependence of the degree of modification (Fig. 6).

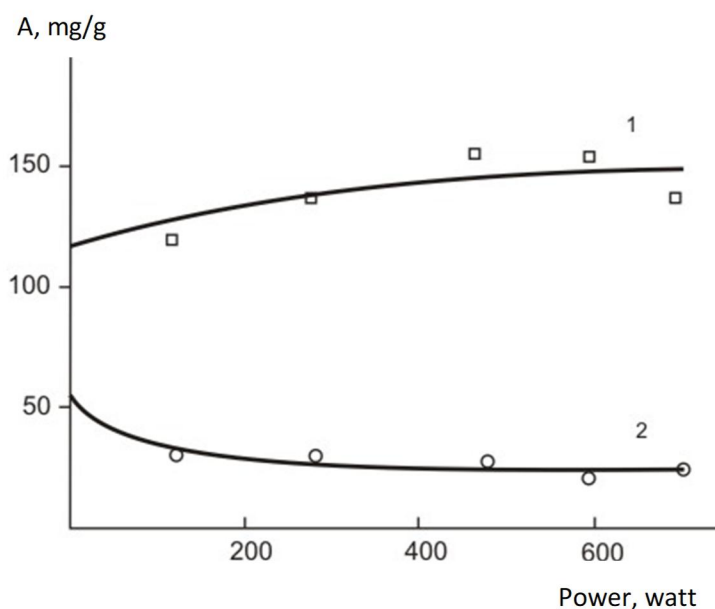


Fig. 4. Adsorption activity of iodine and MB vs. power of microwave radiation. The modification time is 60 min

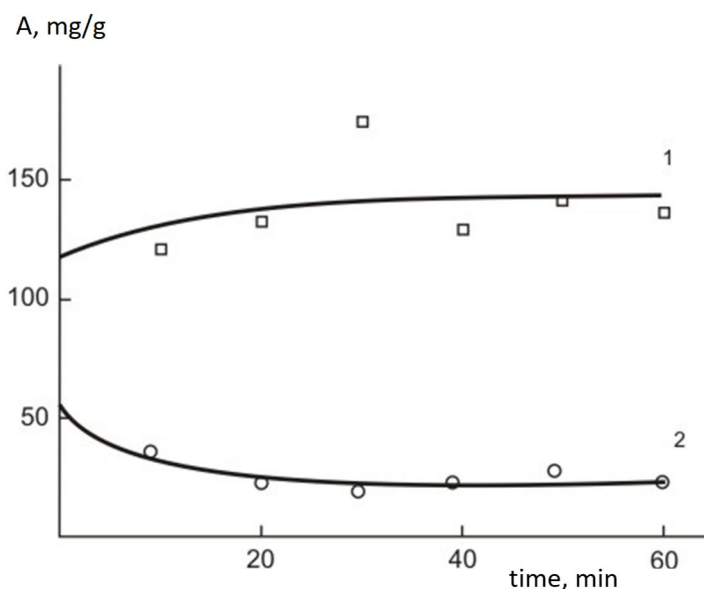


Fig. 5. Kinetics of the dependence of the adsorption activity of iodine and MB at a microwave power of 495 W

Fig. 6 shows that the dependencies of the modification degree and the oil capacity factor correlate quite well with each other. However, the ability of peat to adsorb oil products increases faster than the thermal destruction of organic compounds in peat, which is probably due to the peculiarities of the porous structure formation during the modification process.

Thus, an effective hydrophobic adsorbent was obtained as a result of optimizing the conditions and parameters of peat thermal destruction under the influence of microwave radiation.

The most common surface water pollutants are petroleum products,¹² biological contaminants,¹³ ammonium ions,^{14,15} and heavy metals.¹⁶

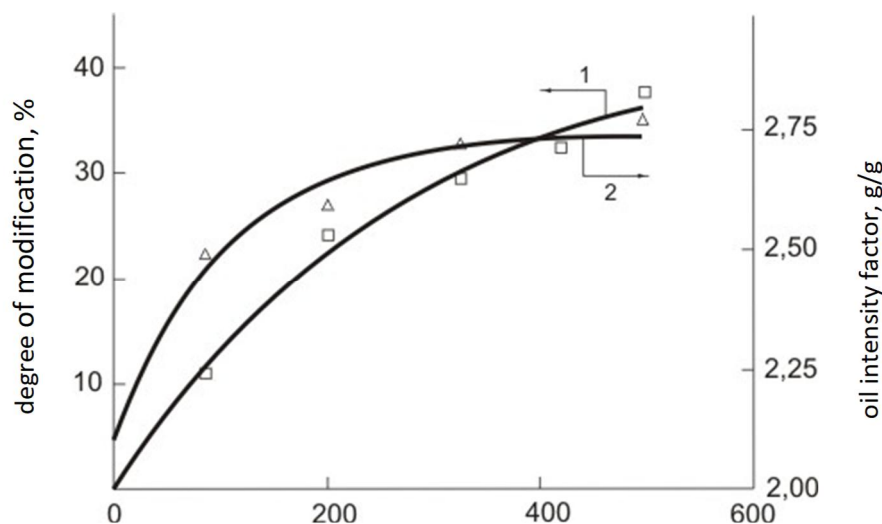


Fig. 6. Degree of peat modification and the oil capacity coefficient vs. microwave radiation power. The modification time is 60 min

When studying the process of wastewater treatment with modified peat adsorbent, it was found that the degree of absorption depends on the pH and the time of contact of the wastewater with the adsorbent. The highest adsorption efficiency is observed at pH=5. Moreover, both a decrease and an increase in pH lead to a slight decrease in the degree of absorption of oil products.¹⁷ Increasing the hydrophobic

properties of peat in the process of microwave modification significantly affects the absorption of oil products and also depends on pH (Fig. 7) due to the thermal destruction of functional organic compounds, namely hemicelluloses.

Based on the data obtained, we can state that the modification of the adsorbent significantly affects the absorption of oil products.

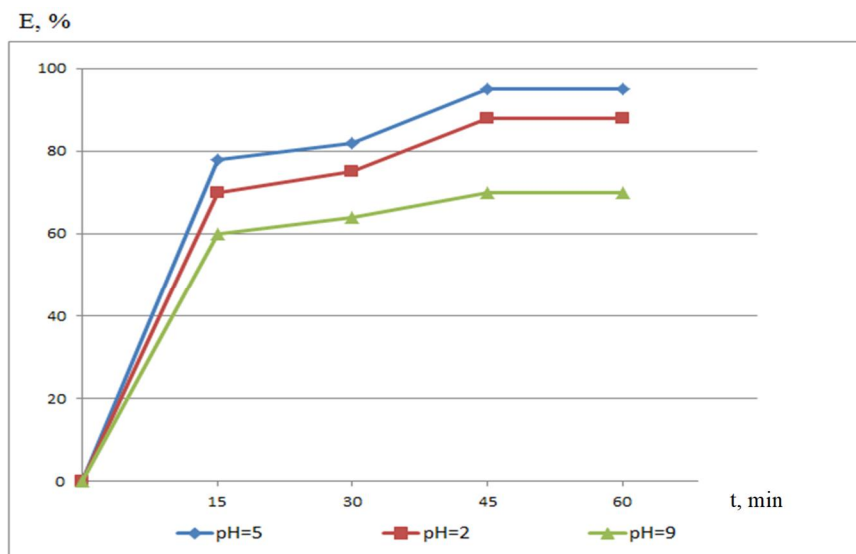


Fig. 7. Efficiency of adsorption of oil products E by modified peat as a function of time t of phase contact at different pH

Spent adsorbents do not harm the environment, since oil and its products absorbed by the adsorbent are completely retained by them. This allows safe disposal of used adsorbents, and the cleaning of environmental objects occurs naturally. So, it is an environmentally friendly

complete process. The adsorbent is quickly distributed on the water surface, and in contact with oil, it acts as a barrier that limits the pollution zones and, by irreversibly absorbing oil, prevents the spread of the pollutant both in breadth and depth. The process guarantees the collection of

spent adsorbent by physical methods; the simplicity and versatility of methods of utilizing spent adsorbent are due to the use of natural, low-ash raw materials.

Based on the above analysis, we propose environmentally friendly and low-cost ways to dispose of used adsorbents:

- a) incineration at power plants to generate heat and electricity;
- b) use in the production of road surfaces;
- c) use in the manufacture of waterproof surfaces;
- d) landfilling at a landfill;
- e) disposal at household waste landfills (with preliminary separation of oil products).

Predicting the directions of our further research, we state that it would be advisable to use magnetically sensitive adsorbents, which, after wastewater treatment from pollutants, could be easily separated from the treated medium by magnetic separation.^{18,19} Remediation and restoration of disturbed soils is also a promising area for the use of sorbents produced from natural minerals.²⁰⁻²³

4. Conclusions

1. Modified peat adsorbents were obtained *via* the method of thermal destruction by exposure to microwave radiation.

2. It was found that when the power of microwave radiation varies in the range from 0 to 600 W and the duration of its exposure from 0 to 60 min, the absorption capacity for iodine increases by 1.2 to 1.4 times, and for MB decreases by more than 2 times with an increase in both the power of microwave radiation and the duration of its exposure.

3. When studying the process of wastewater treatment with a modified peat adsorbent, it was found that the degree of absorption depends on pH and the time of contact of wastewater with the adsorbent. The highest adsorption efficiency is observed at pH=5 after 45 minutes.

4. The use of the adsorbent for cleaning up oil spills in natural reservoirs is substantiated.

The practical use of peat is due to its environmental safety, availability, and cheapness, and will reduce peat deposits that pose a potential hazard to the environment, as well as minimize the level of wastewater pollution from oil products and heavy metal ions.

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ОТРИМАННЯ МОДИФІКОВАНОГО ТОРФ'ЯНОГО АДСОРБЕНТУ ІЗ ЗАСТОСУВАННЯМ МІКРОХВИЛЬОВОГО ВИПРОМІНЮВАННЯ ДЛЯ ОЧИЩЕННЯ СТІЧНИХ ВОД

Анотація. Досліджено біогеохімічні процеси модифікації адсорбентів із торфу й очищення ними стічних вод від нафтопродуктів та іонів важких металів, а також використання адсорбенту для очищення розливів нафтопродуктів на природних водоймах. Отримано модифіковані адсорбенти з торфу методами термодеструкції через вплив мікрохвильового (НВЧ) випромінювання. Досліджено кінетику модифікування торфу за різних потужностей мікрохвильового випромінювання, а також зміни фракційного складу торфу в процесі модифікування. Визначено залежність адсорбційної здатності модифікованого адсорбенту від рН. Використання модифікованих торф'яних адсорбентів дозволяє зменшити поклади торфу на Полтавщині, які становлять потенційну небезпеку для навколишнього середовища, а також підвищити рівень екологічної безпеки через мінімізацію забруднення стічних вод від нафтопродуктів та іонів важких металів.

Ключові слова: торф'яний адсорбент, термодеструкція, мікрохвильове випромінювання, очищення, стічні води, нафтопродукти, важкі метали, біогеохімічні процеси.