INTRODUCTION

While fulfilling its purpose in nature, the aquatic environment is at the same time a direct functional element of the economic mechanisms of the infrastructure of urban housing and communal services, agriculture, forestry and fisheries, transport, industry, etc. Water supply plays a special role in meeting the needs of normal living of the population. The intensification of water management and anthropogenic impact on the water basin everywhere violated the natural conditions of the formation of the aquatic environment, i.e. – the groundwater horizons and surface water basins. The data on the poisoning and pollution of aquifers, surface runoff, year basins and water areas of the seas clearly indicate the severity of the problem. The water quality affects the condition of different recipients (wildlife, vegetation, soils, agriculture, forestry and fisheries, transport, industrial production, housing and communal services, etc.) and above all the health of the population.

The dramatic increase of the surface and groundwater exploitation in the second half of the 20th and the beginning of the 21st century, the mass phenomena of the small rivers degradation, the decrease of their water content, pollution and eutrophication of reservoirs, require comprehensive measures to improve the status of water bodies. The most widely measures used for surface and groundwater treatment are adsorption (Sakalova et al., 2019; Zelenko et al., 2019), biological (Malovanyy et al., 2018; Malovanyy et al., 2019), and reagents (Tulaydan et al., 2017) technologies. The biodegradation of biomass with the collection of biogas that is a valuable energy source is often used to treat biological contamination and to dispose of waste activated sludge after biological contamination (Malovanyy et al., 2016; Nykyforov et al., 2016).

There is also an increase in the groundwater phosphate contamination due to the non-standard use of mineral fertilizers in agriculture and the use by households of large quantities of the household phosphate-containing chemicals that enter the surface water bodies of sewage.

ABSTRACT

The article states that the receipt of insufficiently treated wastewater into water bodies is largely caused by the use of outdated water treatment technologies, the deterioration of the technological equipment, late adjustment of the technological regime, and effective methods of removing phosphates from water in decentralized water supply. In this regard, it is necessary to implement comprehensive measures to prevent and reduce the deterioration of water quality, to develop the effective methods of removing the phosphorus-containing substances from wastewater, to conduct constant monitoring (through automated observation posts) of surface water quality with timely management decisions. The adsorption properties of granular composite materials based on glauconite were investigated. The composite granular glauconite materials with sunflower husk adsorbent have been found to be most effective. The efficiency of wastewater treatment was 78%.

Keywords: enriched glauconite, activated carbon, sunflower husk adsorbent, phosphate ions
The flow of insufficiently treated wastewater into the water bodies is largely caused by the use of outdated water treatment technologies, the deterioration of technological equipment, and late adjustment of the technological regime. It should be noted that there are practically no effective methods of removing phosphates from water in decentralized water supply.

In this regard, it is necessary to implement comprehensive measures to prevent and reduce the deterioration of water quality, develop effective methods of removing the phosphorus-containing substances from wastewater, conduct constant monitoring (through automated observation posts) of the surface water quality with timely management decisions.

The main sources of drinking water supply in Ukraine are surface water and groundwater. Most river basins and reservoirs, which mainly serve the population’s water needs, cannot be considered environmentally safe, because they do not always meet the drinking water requirements due to the increased content of pollutants. High level of technogenic loading on reservoirs and use of outdated technologies of drinking water preparation, use in the technology of preparation of drinking water of chlorine, inefficient coagulants, absence of adsorption filters, lead to the flow of significant amount of inorganic and organic pollutants into the drinking water – constituting a real threat to the health of the nation (Bezdenezhnych, et al. 2017).

The Poltava region is located in the Dnieper River catchment area. The main sources of water resources of the region are the rivers Sula, Psel, Vorskla, Oril and their tributaries, as well as the Kremenchug and Dneprodzerzhinsk reservoirs on the Dnieper River. There are 69 small reservoirs, 583 lakes in the region. In the south and southwest, the region is adjacent to two large reservoirs: Kremenchug and Dneprodzerzhinsk, with a total volume of 13520 and 2450.9 million m$^3$ of water, respectively.

The natural resources of groundwater are one of the main sources of economic and drinking water supply in the settlements of the Poltava region. Groundwater is deposited in the form of several aquifers that differ in their reserves and chemical characteristics (Recruitment…, 2017).

The mass of pollutants dumped into the surface water bodies of the Poltava region in 2017 amounted to 33.46 thousand tonnes (per inhabitant of the region 29.84 kg) (Regional…, 2017), including phosphates of 0.178 thousand tonnes.

All cities, towns and about 30% of the villages in the region are provided with centralized water supply. 54% of water is abstracted from the underground drinking water sources and 46% from surface water intakes (Gorishni, Plavny and Kremenchuk) (Environmental…, 2018). In the cities of Kremenchuk and GorishniPlavny, the supply of high-quality drinking water to consumers is more difficult in the summer. Deterioration of the quality of surface water bodies is associated with the discharge of wastewater containing a large number of pollutants, including the phosphorus compounds.

**MATERIALS AND METHODS**

A large number of water treatment methods have several disadvantages and do not provide the required efficiency of water purification from phosphorus compounds. For the biological removal of phosphorus, the systems with activated sludge and molecular oxygen are used as the oxidizing agent. The processes of nitrification and dephosphation seem to contradict each other under normal biological treatment conditions. Under the aerobic conditions of aerotanks, phosphorus compounds are absorbed by the activated sludge organisms, but the ability of the phosphorus-absorbing bacteria to release phosphorus under the aerotubes and secondary sedimentation conditions increases the content of phosphates in the treated waters (Pavlinova et al., 2015).

In the course of biological wastewater treatment, the concentration of phosphorus in the wastewater is reduced, however, the content of phosphorus in the wastewater after the biological treatment exceeds the MPC value for phosphorus for the discharge of treated wastewater in surface water 2–5 times. The method of biological dephosphation is not possible to implement without the construction of additional structures, which will be cleaned. It is also difficult to distribute the silt flows (Apostoluk et al. 2012).

The coagulation purification methods are characterized by high consumption of scarce and expensive coagulants, the production of which is associated not only with significant material costs but also with the environmental problems. At the treatment plants, there is an urgent need for the construction of reagent farms and their equipped with special technological equipment, which
The presence of a negative uncompensated charge in the structural cell of glauconite resulting from the substitution of tetravalent silicon with trivalent aluminum or divalent magnesium in the crystal lattice of the mineral; the presence on the side faces of crystals of the glauconite OH-groups attached to the silicon atoms, a hydrogen cation, which may react under certain conditions.

Molecular adsorption of glauconite is the penetration of electrolyte solutions into the free cavities of the crystalline structure present in this mineral, with simultaneous and equivalent adsorption of cations and anions from the electrolyte solutions (Shmandij et al., 2012).

The fine-grained glauconite from the Bystritsk deposit of Khmelnitsky region was selected for the research. The concentration of pure glauconite in the breed is 70%, dust – 4% (Vezenci et al., 2011).

The surface morphology was studied on a TESCAN MIRA II LMU electron microscope according to the equipment manufacturer’s technique. The essence of the method is to scan the surface of the sample with a focused electron beam, which allows obtaining an image of the object surface with high spatial resolution (up to several nanometers) (Belyaev et al., 2011).

Adsorbents in the form of granular materials are used for water purification. Granular adsorbents have high mechanical and chemical resistance, greater moisture-holding capacity and have better adsorption rates than non-granular materials. There are a lot of technological methods of granulating materials, however, only some of them are suitable for natural aluminosilicates having the power form. The most widely used are the methods of running-in and molding (extrusion). Granulation was performed by our extrusion method. This method is based on pushing the starting material through a die with further drying. Prior to the granulation process, homogenization of the granular mass was carried out. For the formation of granules of the desired length at the outlet of the granulator, a cutting device was installed. Drying of the granules was carried out at a temperature of not more than 700–800°C. The method is highly productive and quite economical (Bezdyenyezhnih et al., 2016).

As a filler, it is proposed to use a sunflower husk adsorbent that has high adsorption properties and is a waste of agricultural products.
Table 1. Specific surface area and porosity of glauconite

| Diameter pore diameter, % | Micropore volume, cm³/g | Specific surface area, m²/h |
|---------------------------|--------------------------|-----------------------------|
| 15–50 nm                  | 0.042                    | 46.7                        |
| 50–100 nm                 | 34                       |                             |
| >100 nm                   | 22                       |                             |
|                           |                           | 44                          |

Table 2. Results of glauconitic sand repulsion (1 kg output sample)

| No. | The name of the peptide solution | Content of clay fractions, % | Balance fractions content after peptization process, % |
|-----|---------------------------------|-----------------------------|-------------------------------------------------------|
| 1.  | Water (20°C)                    | 3.3                         | 96.7                                                  |
| 2.  | Water (70°C)                    | 3.9                         | 96.1                                                  |
| 3.  | H₂O+10 mg NaOH                  | 4.2                         | 95.8                                                  |
| 4.  | H₂O+10 mg NaCl                  | 3.8                         | 96.2                                                  |
| 5.  | H₂O+10 mg NHCO₃                 | 4.6                         | 95.4                                                  |
| 6.  | H₂O+10 mg KMnO₄                 | 6.3                         | 93.7                                                  |
| 7.  | H₂O+10 mg H₂O₂                  | 7.5                         | 92.5                                                  |
| 8.  | H₂O+10 mg Na₂O(SiO₂)            | 3.2                         | 96.8                                                  |

As can be seen from Figure 1, the investigated sample of glauconite has a developed surface relief. At high magnification (20000–50000 times) it is possible to distinguish the presence of a considerable number of plate microstructures in the form of petals, with sizes <0.5–1.0 microns, which indicates a high porosity of the surface of the samples, such microstructures are the active centers at which the processes occur molecular and ionic adsorption.

The specific surface of the adsorbent is determined by the size of the particles forming the adsorbent, the system of their mutual stacking in the grain and the porosity of the grain. Table 1 shows the results of the studies.

Enrichment of glauconite was carried out by with the desulphurization method, which allows the removal of light clay fractions of <0.05 mm in size. The removal of pre-dried glauconite sand was carried out in a special container for repellent. Different solutions-peptizers are used to intensify the process (Kormosh et al., 2011). Table 2 presents the results of the ablation of glauconitic raw materials with different solutions-peptizers.

Fig. 1. Electron microscopic images of the surface of a sample of natural glauconite: a) magnification 20,000 times, b) magnification 50000 times
RESULTS AND DISCUSSION

The results obtained allow us to draw the following:

• the preferred peptizers are the solutions of strong oxidizers – KMnO₄, which allows increasing the yield of the clay fraction by more than twice, compared to water;
• the optimal yield of the enriched clay fraction using peptizers is 6.2–7.5% of the total weight of the sample.

In order to study the adsorption properties under static conditions of the experiment, the following types of granular materials were developed:

• enriched glauconite;
• a mixture of enriched glauconite with activated carbon in a ratio of 1: 1;
• a mixture of enriched glauconite with adsorbent from sunflower husk in a ratio of 1: 1.

During the granulation process, two stages of processing were carried out: homogenization and formation.

At the homogenization stage, the semi-finished product is mixed with water. The water content was selected experimentally and amounts to 28–30 wt.%, which allows achieving the optimum consistency of the granular mass required for the formation of granules; less water leads to its uneven distribution in the mixture, and as a consequence, incomplete granulation, and more to the formation of a liquid mass that is not granular. For complete homogenization, the semi-finished product is mixed with water for at least 15 minutes.

At the stage of forming, the processed mass is given the necessary shape and size. Formation is carried out by extrusion using a FS-004 laboratory screw feeder with a capacity of up to 50 kg/h. The molding technology is to push the treated mass through a die with 1.0 mm diameter holes. In order to secure the form of the granules, they are dried at 200°C for 1 h to dryness with constant stirring and then subjected to thermal activation. As a result of firing, the granules become stronger and denser, which increases their durability during operation. A sample of the adsorption material obtained is presented in Figure 2.

Obtaining granular materials makes it possible to increase the bulk weight, which has a positive effect on the adsorption capacity. The surfaces of the modified adsorption materials were studied on a REM 106-B scanning electron microscope. The results are shown in Figure 3.

The analysis of Figure 3 showed the presence of a looser structure of the composite granules of glauconite with the adsorbent of sunflower husk. Figure 3(a) shows the pores and defects of the structure that cause the physical adsorption of pollutants from wastewater.

In order to improve the adsorption properties of filter fillings used for the modification of their chemical reagents. This treatment leads to an increase in the distance between the lamellar in structure, leaching of cations, the increase in the specific surface, which in turn leads to higher adsorption capacity.

It is known that the use of acid modification can effectively affect the structure of aluminosilicates and create defects in the crystal lattice of the adsorptively active minerals. In addition, the acid structure of the mineral undergoes significant changes. Treatment of aluminosilicate mineral with acids leads to the displacement of alkali and alkaline earth metals, aluminum and iron and their replacement by hydrogen cations, which results in an increase in the specific surface area up to 2 times compared with the inactive form. Modification, unlike activation, does not alter the structure of the source mineral, and is usually carried out with salts or organic substances (Shmandiy et al., 2018).

The authors studied the possibility of chemical modification of granular adsorption materials based on glauconite with 8% CaCl₂ solution with mixed acid-salt treatment. For this purpose, the samples of granular materials were placed daily

Fig. 2. A sample of a granular mixture of enriched glauconite with a sunflower husk adsorbent
in the modifier solutions. The modification was performed at a ratio of components 1:40. With this modification of glauconite, there is, firstly, acid activation of the sorbent, which complicates its surface and creates more pores; and secondly, $\text{Ca}^{2+}$ cations are involved in ion exchange, providing additional activity to the sorbent.

The analysis of the operation of wastewater treatment plants in the Poltava region revealed that the efficiency of wastewater treatment from phosphorus compounds is low, wastewater treatment plants remove only 30% of phosphates (Derzhagentstvo..., 2018). Filtration through natural adsorbents is one of the simplest and cheapest ways to treat wastewater. The mechanism of phosphate removal is the chemical deposition of soluble compounds, mainly calcium orthophosphate, which are formed by the interaction of phosphate anions with calcium cations. The obtained granules were tested under static conditions for the ability to bind the phosphate ions from prepared model effluents. To 100 cm$^3$ of model solutions, 2 g of granular materials were added, namely: mixtures of glauconite with adsorbent from sunflower husk and glauconite with activated carbon. The adsorption process was carried out under static conditions for 40 min. (time to reach adsorption equilibrium) with constant stirring on a magnetic stirrer. For comparison, a similar adsorption process with granular glauconite was performed. The hydrogen index (pH) for all solutions during the experiments was in the range of 6–7. The determination of phosphates in the test water was performed on a KFK-2MP photocolorimeter.

![Fig. 3. Electron microscopic images of the surface of composite adsorbents: a) glauconite with sunflower husk adsorbent; b) Glauconite with activated carbon](image)

![Fig. 4. Efficiency of sewage treatment when using different adsorption materials](image)
The initial and final concentrations determined the efficiency (E) of wastewater treatment:

\[ E = \frac{C_{\text{init}} - C_{\text{final}}}{C_{\text{init}}} \cdot 100\% \]  

(1)

where: \( C_{\text{init}} \) and \( C_{\text{final}} \) – the initial and final concentration of the solution, mg/dm³

The results of determining the efficiency of wastewater treatment when using different adsorption materials are shown in Figure 4.

When comparing the results obtained, it is evident that the composition of the granular materials of glauconite with the adsorbent from sunflower husk have the best adsorption rates, the effluent treatment is 78%. It should be noted that the widespread use of activated carbon is limited by its high cost, so it is promising to use the wastes of agro-industrial complex to obtain efficient and inexpensive adsorbents.

CONCLUSIONS

The scientific novelty is the improvement of the method of obtaining composite adsorbents on the basis of glauconite and studying their adsorption properties to minimize the ecological danger of water bodies, namely the purification of wastewater from the phosphate ions.

On the basis of the conducted research the following conclusions were formulated:

- determined that the pore diameter distribution was: 15–50 nm – 34%; 50–100 nm – 22%; > 100 nm – 44%;
- the surface characteristics of the sample of natural glauconite were established: specific surface area – 46.7 m²/g; micropore volume – 0.042 cm³/g; obtained adsorbent from sunflower husk;
- it was found that the preferred peptizers are solutions of strong oxidants – KMnO₄ and they allow increasing the yield of the clay fraction by more than 2 times. The yield of the enriched clay fraction is 6.2–7.5%;
- the adsorbent from the sunflower husk was obtained and the physicochemical parameters of which were determined: humidity – 1.5%; bulk weight – 0.66 g/cm³;particle size distribution – 0.03–0.1 mm;dispersion – 10 nm; pore size – 0.5–50 nm;
- to improve the chemical modification, proposed mixed acid-salt treatment using 8% CaCl₂ solution;

- the adsorbing properties of granular composite materials based on glauconite were investigated. Composite granular glauconite materials with sunflower husk adsorbent were found to be most effective. The efficiency of wastewater treatment was 78%.

Thus, the conducted studies allow obtaining an effective adsorbent for wastewater treatment. The combination reduces the cost of the adsorbent, improves the adsorption properties and allows the disposal of vegetable waste.

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