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STUDY OF ADSORPTION OF PHOSPHATE IONS FROM AQUEOUS SOLUTIONS

The object of research in this work is model aqueous solutions containing phosphate ions. Phosphorus is an essential nutrient for all life forms and determines the trophic state of freshwater ecosystems. The existing problem is that when excessive phosphorus enters water bodies, it causes their eutrophication, and, as a result, the accumulation of biotoxins, deterioration of water quality, death of aquatic organisms, etc. Phosphorus comes to surface water from domestic wastewater containing phosphates as components of synthetic detergents, photoreagents and water softeners. A significant contribution is made by the washout of phosphate fertilizers and pesticides from agricultural land, and runoff from livestock farms and industrial enterprises. Among the methods of wastewater treatment from phosphates, a special place is occupied by sorption. An analysis of modern scientific publications on this topic shows that the search for new effective sorbents obtained using resource-saving technologies is an important scientific and practical problem.

The work was aimed precisely at the search for such sorbents. Iron is known to have a high affinity for phosphate. Therefore, the paper proposes to use the sediments of groundwater iron removal stations as a sorbent. These sludges are produced in significant quantities and create significant environmental problems.

The sorption of iron-containing sorbent, which is a waste of iron removal stations with respect to phosphate ions, has been studied. It has been established that this sorbent is effective for extracting phosphate ions from water with an adsorption capacity of 72.67 mg/g. The sorption process is quite accurately described by the pseudo-second order sorption kinetic equation (determination coefficient $R^2=0.9737$). The rate constant of the sorption process was calculated to be $3.8\cdot10^{-4}$ g/mg $PO_4^{3-}\cdot min^{1/2}$. The use of the proposed sorbent will allow solving two environmental issues: replenishment of the list of cheap effective sorbents for removing phosphates and utilization of sludge from iron removal stations.

Keywords: *phosphates, wastewater treatment, surface water, eutrophication, sorbent, iron removal station sludge.*

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1. Introduction

Although phosphorus is an important nutrient, elevated concentrations of phosphate in water bodies can be harmful to aquatic life, human health, and the environment. An excess of phosphorus leads to the rapid growth of certain types of microalgae and disrupts the balance of aquatic ecosystems [1, 2]. Such processes are called eutrophication. As a result of eutrophication, the oxygen content decreases, fish die and the quality of water bodies as sources of water supply deteriorates. Phosphorus enters water bodies both naturally and as a result of anthropogenic activities. Natural processes include the processes of vital activity and decomposition of hydrobiont remains, erosion, weathering, and dissolution of rocks and minerals [3–5]. Anthropogenic pollution includes the inflow of domestic and industrial wastewater, the washout of phosphorus fertilizers and pesticides from agricultural land, runoff from livestock farms, etc. [6–8]. All this is of concern to the world community and requires the establishment of stringent requirements for the content of phosphates in waste and drinking water. Thus, in Western countries, the content of phosphates in wastewater should not exceed 1 mg/dm^3, and in water – 0.03 mg/dm^3 [9], and in Ukraine these values are 8 and 3.5 mg/dm^3, respectively [10]. Therefore, limiting the entry of phosphates into water bodies remains an urgent issue.

Phosphorus is found in natural and waste waters mainly in the form of phosphate ions, classified into orthophosphates, condensed phosphates (pyro-, meta-, and other polyphosphates), and organically bound phosphates [9]. To date, reagent, ion-exchange, biological and baromembrane methods of water purification are used to extract phosphates from water. But none of the methods allows to completely

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extract phosphates from wastewater [11]. From the point of view of technology and resource saving, it is rational to remove phosphates with the help of sorbents, because adsorption technologies make it possible to remove even trace concentrations of contaminants. In modern water treatment, a wide variety of sorption materials are used. One of the main disadvantages of many sorbents is their lack of availability and high cost. Therefore, the search for and creation of new, cheaper, but effective sorption materials is an urgent task.

Of great practical interest is the use of waste as a raw material for the production of sorbents, which are formed in large volumes during the purification of natural waters from iron. Every year, about 4 thousand tons of iron oxide sludge that need to be disposed of is accumulated at facilities for the treatment of wash water from iron removal stations [12]. About a third of the mass in the waste is iron-containing minerals, including oxides, hydroxides, and salts of ferrous and ferric iron. It is clear that iron compounds, especially in the nanosized state, are used in agriculture, medicine, and in the production of sorption materials [13]. Therefore, research on the use of iron-containing wastes from groundwater deironing stations as sorption materials is promising. The disposal of such sludge by depositing cannot be considered a rational solution, since this creates a secondary environmental problem. A lot of sediment is formed, and more and more areas are required that need to be reclaimed. The dry sludge is characterized by increased sawing and, if the recycling technology (overdrying) is not followed, there is a risk of air pollution and contamination of large areas with powder. That is, the use of iron sludge to remove phosphates from wastewater will help solve two environmental issues: replenishment of the list of cheap sorbents and disposal of sludge from iron removal stations.

So, *the object of research* is model aqueous solutions containing phosphate ions. *The aim of the research* is to find an effective and cheap sorbent for wastewater treatment of phosphates.

2. Research methodology

When carrying out adsorption studies, let's use model solutions of monosubstituted potassium phosphate (KH_2PO_4) in distilled water, which were prepared by dissolving a calculated sample of a solid salt of analytical grade. The deposit of deferrization of underground waters is a dense water-saturated mass of brown color. The precipitate was dried in an oven at a temperature of 50 °C for 12 hours to obtain a fine powder. Dry sludge composition, %: Fe – 26.56; CaO – 21.3; Al_2O_3 – 0.51; SiO_2 – 10.25.

Sorption of phosphate ions was studied under static conditions at room temperature. A sorbent weighing 0.1 g was weighed in a box, a 100 cm^3 solution containing PO_4^{3-}·100 mg/dm^3 and a sorbent were added to a conical flask, and the flask was placed in an ELPAN Water bath shaker 357 (Poland) with a rotation frequency of 150 rpm. At certain intervals, the sorbent was separated on a «blue tape» filter and the content of phosphates was determined by the well-known method on a ULAB 101 spectrophotometer (China) by the color of molybdic blue with reduction with ascorbic acid [14].

The mass of sorbed PO_4^{3-} ions was calculated by the formula:

$$a=\frac{(C_0-C)\cdot V}{m_s},$$

where C_0 – the initial concentration of PO_4^{3-}, mg/dm^3; C – PO_4^{3-} concentration at the time of sampling τ, mg/dm^3; V – the volume of the solution, dm^3; m_s – the weight of the sorbent sample, g.

3. Research results and discussion

The integral kinetic curve of the sorption of phosphate ions from model solutions, plotted from the experimental data, is shown in Fig. 1.

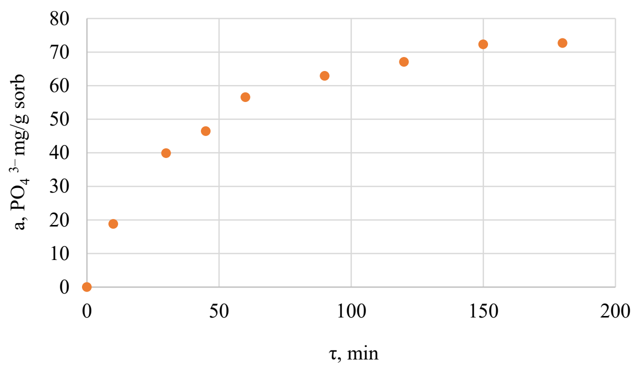

Fig. 1. Kinetic curve of adsorption of phosphate ions

From the dependence obtained, it is possible to see that the time to reach sorption equilibrium does not exceed 150 min. The sorbent is active and quickly reaches its maximum sorption capacity. The equilibrium capacity of the sorbent is 72.67 mg PO_4^{3-}/g, which is quite significant compared to the known proposed sorbents [13].

It is known that the theoretical processing of kinetic curves using kinetic models allows one to draw conclusions about the mechanism of sorption [15].

Usually, pseudo-first and pseudo-second order kinetic models are used to describe the sorption process [15]. The pseudo-first order model or Lagergren's equation is widely used to describe adsorption from solution. The dependence plot in linear coordinates of this equation turned out to be non-linear. Therefore, a pseudo-second order equation was used to describe the adsorption kinetics. The integrated form of the pseudo-second order rate equation is:

$$\frac{\tau}{a}=\frac{1}{k_2 a_e^2}+\frac{\tau}{a_e},$$

where k_2 – the pseudo-second order adsorption rate constant, g/(mg·min$^{1/2}$).

To describe the adsorption kinetics, a graph was plotted in the coordinates $\tau/a=f(\tau)$. The graph is shown in Fig. 2. The linearity of the dependence $\tau/a=f(\tau)$ confirms that the sorption process has the second order of sorption, i. e. the sorption process is limited by the chemical reaction on the surface of the sorbent. This conclusion correlates with the data given in the literature [13].

A limitation of this study is the use of model one-component solutions. It would be expedient to study the effect of various factors on the efficiency of phosphate sorption. Such as pH, initial concentration, sorbent dose, etc.

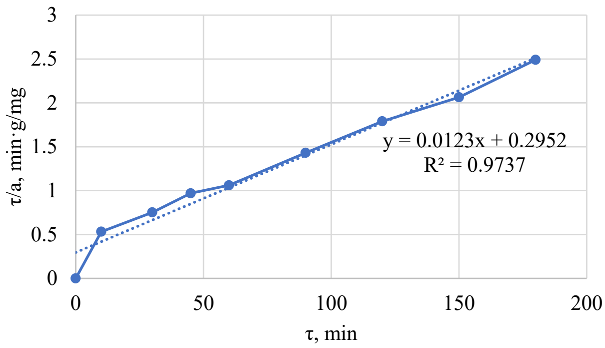

Fig. 2. Kinetic curve of adsorption of phosphate ions in the coordinates of the pseudo-second order equation

In addition, the use of a finely dispersed powdered sorbent causes significant difficulties in application. Therefore, a promising direction for the development of this study should be considered in the search for methods for the formation of iron sludge. It is known that it is desirable to use granular granular adsorbents.

4. Conclusions

The sorption properties of iron-containing sorbent, which is a waste of iron removal stations with respect to phosphate ions, have been tested. It has been established that this sorbent is effective for extracting phosphate ions from water with an adsorption capacity of 72.67 mg/g.

The sorption process is quite accurately described by the pseudo-second order sorption kinetic equation (determination coefficient R^2=0.9737). The rate constant of the sorption process was calculated to be $3.8 \cdot 10^{-4}$ g/mg $PO_4^{3-} \cdot min^{1/2}$.

Conflict of interests

The authors declare that there is no conflict of interest regarding this study, including financial, personal nature, authorship or other nature that could affect the research and its results presented in this article.

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