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**PHOSPHATES PURIFICATION
OF WASTE WATER BY NATURAL MATERIALS
AND INDUSTRIAL WASTES (COMPARATIVE STUDY)**

The management phosphates in freshwater has significant importance to regulate eutrophication. Phosphate excess leads to highly undesirable changes in ecosystems structure. The increasing of water body trophicity can result in water quality deterioration.

This paper presents the testing results of reactive materials used for phosphorus removal from wastewater at sewage treatment plant. Twelve materials of different origin available in Belarus were tested as potential reactive materials for phosphates removal. They are natural materials, industrial by-products and manufactured sorbents.

Based on chemical composition the available and inexpensive materials rich in Al, Fe, Mg and Ca were selected. Relationship between purification degree of phosphates and specific material consumption (mg/mg PO_4^{3-}) was investigated to choose potential reactive materials for phosphorus. Four materials (water conditioning sludge (WCS), dead-catalyst of petroleum hydrocarbon cracking (DCC), electric arc furnace slug (EAF-slug), dolomite burnt at 700°C) have been chosen for detailed sorption tests. WCS, DCC, EAF-slug and burnt dolomite have the apparent sorption capacities of: 13.6; 21.2; 35.3; 70.8 $\text{mg PO}_4^{3-}/\text{g}$ respectively. Results have shown that the raw natural materials (chalk, clay, dolomite and tripoli powder) and wastewater electric coagulation treatment sludge are of low efficiency.

Results for experiments with synthetic solutions of phosphates are in correlation with results for actual wastewaters.

Key words: eutrophication, phosphates, wastewater treatment, industrial wastes.

Introduction. Over the past few decades, considerable attention is paid to the reduction of phosphorus compounds entering the water bodies. It is important to control the process of anthropogenic eutrophication, as phosphorus plays a key role in increasing the number of organisms of lower trophic levels of aquatic ecosystems – bacteria, algae, and others. [1]. Excessive emission of phosphorus compounds into the ecosystem results in their higher trophic status with regard to natural. In this case, the established system of food relations is disturbed and there appears a new one and primary bioproduction (trophicity) and biogenic migration increases. Trophic growth leads to the water bloom during the growing season, which adversely affects the quality of the water body and it becomes unsuitable for most varieties of water management [2].

Phosphorus emission into water bodies is due to the discharge of sewage and runoff from urban and agricultural areas [3]. The regulation of phosphorus amount can be done by a balanced use of fertilizers and wastewater treatment from phosphorus to secure the safe ecosystem level.

The most widely used methods for wastewater purification from phosphorus are biological removal with the help of phosphorus accumulating organisms, chemical precipitation of phosphorus compounds in the form of low soluble compounds and sorption using materials with high potential for the removal of phosphates.

The first two methods are most appropriate to use in the sewage treatment facilities in terms of population equivalent (PE) of more than 10,000.

In Belarus the allowable concentrations of total phosphorus are set depending on the weight of organic substances coming with sewage and amount to 4.5 and 2.0 mg/dm^3 for treatment plants, whose PE is within 10,001–100,000 and more than 100,001, respectively. Total phosphorus is not standardized for wastewater treatment plants with a PE indicator less than 10,001 [4]. However, the uncontrolled discharge of P-containing wastewater from small water treatment facilities within the catchment of water bodies can lead to exceeding the maximum permissible concentration of phosphates (MPC – 0.066 mgP/dm^3).

For small sewage treatment facilities the use of reagent or biological treatment is limited by high capital and operating costs, the complexity of implementation and management. Therefore, research in this area is focused on the search of inexpensive available filtration materials and assessment of their ability to remove phosphates from wastewater. A wide range of materials including rocks, production waste and manufactured sorbents has been studied [5], which are classified according to the origin and the sorption capacity [6]. In accordance with the origin the sorbents are divided into natural materials, industrial by-products, and manufactured products. By sorption capacity ($\text{PO}_4^{3-}/\text{g}$), they are classified into materials with very low (less than 0.3), low (0.3–1.5), medium (1.5–3.1), high (3.1–30.6) and very high (more than 30.6) capacity for phosphates [6].

Such natural materials as granular bentonite clay [7], aragonite, clinoptilolite, montmorillonite, shell limestone [8], dolomite [9] and wollastonite [10] are known to be used to clean wastewater from phosphate. Investigations of the following industrial wastes – blast furnace slag [11], industrial sorbents – Polonite[®] [12], Filtra P[®] [13], Filtralite P[®] have been carried out [14].

The aim of this work was to evaluate the possibility of using materials based on natural raw materials and waste for wastewater purification from phosphates.

Main part. Materials and sorbents with a high content of compounds of Al, Fe, Ca and Mg available in Belarus have been chosen as an object of our research. We used three groups of materials – natural raw materials, production waste and manufactured sorbents. They are represented by low-melting clay, tripoli, dolomite, chalk, dead cracking catalyst, the EAF slag, precipitation of treatment plant of industrial enterprises and industrial sorbent Polonite[®]. The oxide composition of the materials used are listed in Table 1.

Fusible clay is a mountain rock containing one or more groups of aluminosilicate minerals. The rocks composed of more than 50% of particles (hereinafter wt %) with the size up to 0.01 mm belong to clays. We have used clay from deposit “Lukoml-1” (Vitebsk region) which belongs to hydro-mica-kaolinite group with high iron content [15].

Tripoli from deposit “Stalnoye” Mogilev region is a rock, the peculiarity of which is the zeolite content to 30% [16].

Chalk – monomineral of biogenic origin, the main its component is CaCO₃. We used the chalk from deposits of Volkovysk (Grodno region) [17].

Dolomite from deposit Ruba (Vitebsk region) was also used. The weight ratio of CaO:MgO = 1.46. Bulk weight of dolomite is 2,000–2,800 kg/m³ [17].

Dead catalyst of petroleum hydrocarbon cracking (DCC) – waste of the fourth class of danger [18], which is produced at JSC “Mozyr Oil Refinery”. DCC is a fine gray powder. DCC is formed at periodic replacement of cracking catalyst (lot-1) and destruction of the catalyst particles, caught in the electrostatic precipitator (lot-2). The particle size of the lot-1 is 10–100 μm, for lot-2 – 5–20 μm. The active component of DCC is a zeolite, the content of which is up to 40% [19].

Electric arc furnace slag (EAF-slag) of “Byelorussian Steel Works” (BMZ) is a by-product of steel production, which refers to the waste of the fourth class of danger [18].

Water conditioning sludge is waste of the fourth class of danger [18] produced by the Minsk CHP-3 in reagent water softening.

Precipitation of electrocoagulation wastewater treatment of “Belcard”, JSC “Grodnotorgmash” and RUE “Mogilev Metallurgical Works” (MMW) is a waste resulting from wastewater treatment of galvanic production [19], which belongs to the third class of danger [18].

Polonite[®] is industrial sorbent obtainable by calcining at 900°C and subsequent crushing lime mineral – opoka [12, 21].

Phosphate solutions were prepared using monosubstituted potassium phosphate and 0.01 M KCl. The pH value was adjusted to 7.0 ± 0.5 with solutions of 0.01 M KOH and HCl.

Determination of the influence of specific material consumption on the degree of purification from the phosphate was carried out on the phosphate solutions with concentration of 100 mg PO₄³⁻/dm³. A weighed portion of finely particulate material (particle size less than 0.25 mm) and dried to moisture content not more than 1%, are dosed into the solution and kept with occasional agitation for two hours. The sorbent is then separated on a paper filter “white” ribbon. The residual content of phosphate was determined in the filtrate.

When using dolomite samples obtained by thermal treatment for one hour at temperatures ranging from 200 to 700°C with a step of 100°C, a sample material was dosed into phosphate solution with concentration of 100 mg PO₄³⁻/dm³ and kept for one hour at a constant stirring. Then sample was filtered and the residual phosphate content and the pH value were determined in the filtrate.

The capacity for phosphate was determined to characterize the material efficiency. We consider capacity as the amount of phosphate removed from the solution per unit mass of material. The material capacity for phosphates was investigated in closed opaque polyethylene containers. Test material was dosed into solutions with different concentrations of phosphate in the range of 1–300 mg PO₄³⁻/dm³. Samples were kept at 20 ± 0.5°C under constant agitation for two days. The spent sorbent was separated by filtration. The residual phosphate content was determined in the filtrate. Experimental data were approximated with the help of using a Langmuir equation [6]:

$$A = A_{\infty} \frac{K_L \cdot C_{\text{eq}}}{1 + K_L \cdot C_{\text{eq}}}, \quad (1)$$

where in A , A_{∞} – phosphate capacitance value and the maximum capacity for phosphate respectively, mg PO₄³⁻/g; K_L – the equilibrium constant; C_{eq} – equilibrium concentration of phosphate in the solution mg PO₄³⁻/dm³.

Table 1

The average oxide composition of the materials by wt %

Oxides	Clay [15]	Tripoli [16]	Chalk [17]	Dolomite*	Dolomite thermo-processed at 700°C*	DCC [19]	EAF "BMZ"*	Sludge "CHP-3"*	Precipitations of "Belcard" [20]	Precipitation "Grodnortorgmash" [20]	Precipitation "MMZ" [20]	Polomite® [12]
CaO	4.3	21.0	54.3	30.0	37.3	–	53.3	69.7	5.0	3.9	0.7	25.1
FeO	7.5	1.7	0.1	0.4	1.5	–	8.0	16.2	47.6	30.4	77.0	2.7
Al ₂ O ₃	13.2	7.6	0.6	0.3	1.8	51.4	5.5	–	0.5	4.8	0.7	5.3
MgO	2.5	2.5	0.6	21.0	27.1	–	2.6	8.4	–	0.4	0.5	0.8
SiO ₂	65.1	64.6	1.2	1.7	5.7	45.3	20.2	5.7	2.7	–	6.4	60.1
Cr ₂ O ₃	–	–	–	–	–	–	–	–	15.1	5.9	2.7	–
MnO	–	–	–	–	–	–	3.0	–	–	–	5.9	–
SO ₃	–	0.1	–	–	–	–	1.7	–	1.9	0.8	0.2	–
K ₂ O	0.8	1.3	0.2	0.7	1.0	–	–	–	–	0.2	–	1.0
Na ₂ O	1.2	1.0	0.1	1.0	1.5	0.9	–	–	–	5.1	–	0.2
TiO ₂	0.3	0.2	–	–	–	–	–	–	0.4	0.6	–	0.3
ZnO	–	–	–	–	–	–	2.5	–	4.8	4.8	–	–
P ₂ O ₅	–	–	–	–	–	–	–	–	3.2	30.6	–	1.0
La ₂ O ₃	–	–	–	–	–	2.1	–	–	–	–	–	–
CO ₂	5.1	–	42.9	44.9	24.1	–	3.2	–	18.8	12.5	5.9	–

* Elemental analysis was performed on the scanning electron microscope JSM-5610 LV system EDX chemical analyses JED-2201.

Value A mg PO₄³⁻/g of material was defined by the formula (2):

$$A = \frac{(C_{in} - C_{res}) \cdot V}{m}, \quad (2)$$

where C_{in} , C_{res} – initial and residual concentration of phosphate in solution, mg PO₄³⁻/dm³; V – volume of the sample dm³; m – mass of sample material, g.

The distribution coefficient of phosphate was determined by the formula (3):

$$K_d = \frac{A_{max}}{C_{eq}}, \quad (3)$$

where A_{max} – the maximum capacity of phosphates mg PO₄³⁻/g; C_{eq} – equilibrium concentration of phosphates, mg PO₄³⁻/dm³.

Phosphate concentration and pH were determined by the photometric method [22] and potentiometric method [23] respectively.

For a preliminary assessment of the effectiveness of the use of selected materials, we made experiments to determine the effect of specific consumption of materials on the degree of purification of the phosphate solution with a concentration of

100 mg PO₄³⁻/dm³. Experimental results are presented in Fig. 1.

Of all the materials tested, the lowest degree of phosphates removal in the experimental conditions is achieved by using untreated natural raw materials (Fig. 1, a).

Phosphate removal in this case probably is based on physical sorption by material surface. The maximum purification efficiency of the phosphate does not exceed 15%. In the order of decreasing purification degree in the specific consumption of 200 mg of material/mg PO₄³⁻ the natural raw material is in the following sequence chalk, fusible clay, tripoli and dolomite.

It is known that heat treatment of natural materials leads to an increase in their sorption capacity with respect to phosphates [21]. To investigate the influence of heat treatment conditions on the degree of purification of the phosphate among tested rocks dolomite was chosen because its thermal activation requires less energy expenditure [23]. In addition, this raw material is available on the cost characteristics.

The results of dolomite application subjected to heat treatment to remove phosphates are shown in Fig. 2.

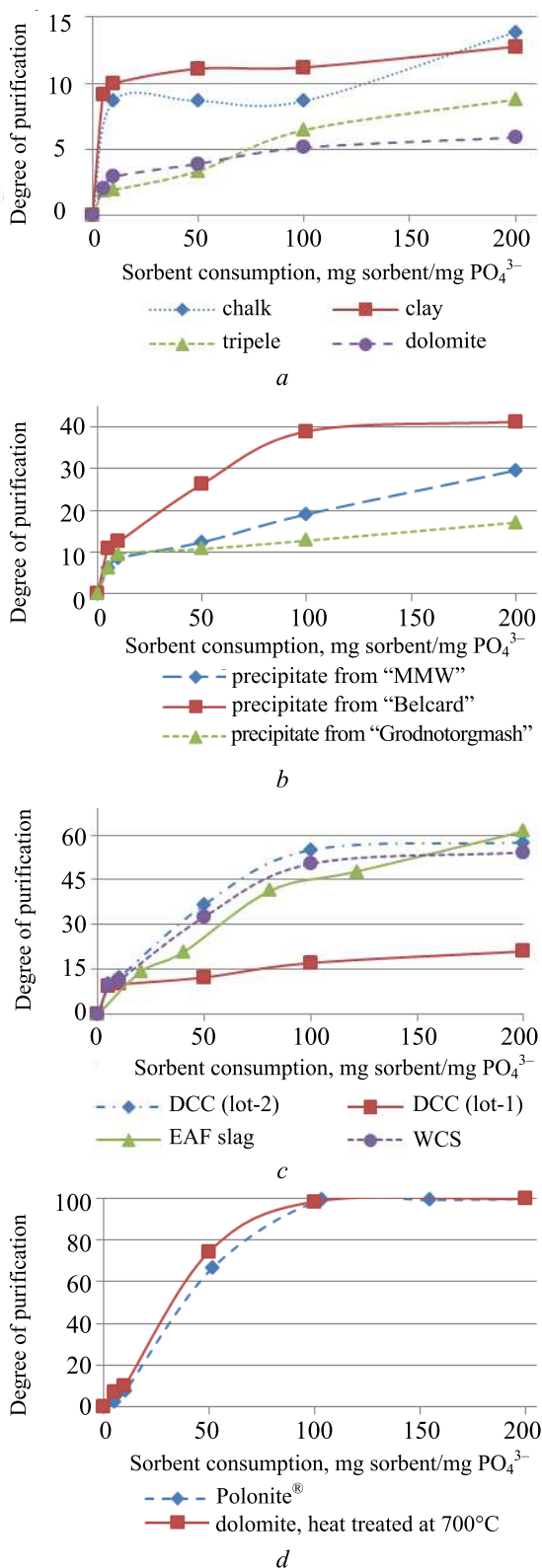


Fig. 1. The dependence of the degree of purification of phosphate on material consumption: *a* – natural raw materials; *b* – precipitation of electrocoagulation wastewater treatment; *c* – waste production and water conditioning; *d* – Polonite® and dolomite, heat treated at 700°C

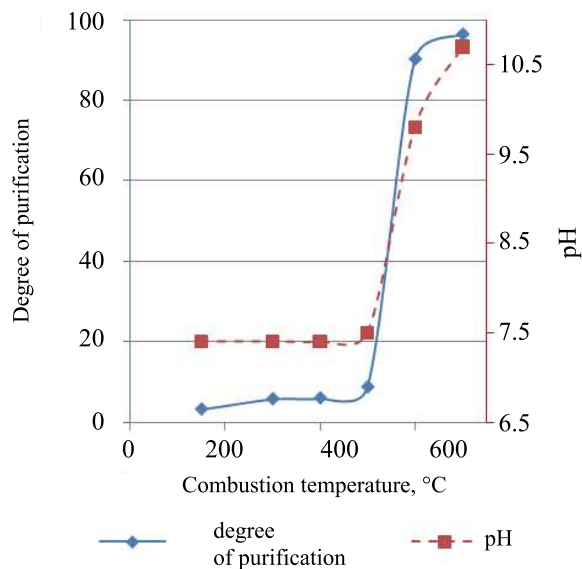


Fig. 2. The effect of dolomite heat treatment on the ability to remove phosphates

Fig. 2 shows that with increasing heat treatment temperature from 500°C to 700°C there is an increase in the degree of purification from 5.6% to 96.4% and a growth of pH value from 7.3 to 10.3. This is because at a temperature of 650°C there happens a decomposition of magnesium carbonate [24], resulting in formation of magnesium oxide which binds phosphates on the surface of calcined dolomite. Obviously, it means that in this case the phosphate removal process is based on the formation of the low soluble magnesium phosphate.

More effective removal of phosphates occurred with the use of precipitation of electrocoagulation wastewater treatment (Fig. 1, *b*). The maximum degree of purification for the precipitation of JSC “Belcard”, JSC “MMZ” and JSC “Grodnotorgmash” respectively equals to 17%, 30% and 42%.

Fig. 1 shows the results of phosphates removal with the help of waste generated in steel production, oil refining, and water conditioning. It has been found that these materials with a maximum specific consumption of 200 mg of material/mg PO₄³⁻ have similar values of purification efficiency. The efficiency of phosphates removal with their help is in the range of 54.2– 61.3%. An exception is the samples of DCC-1, their purification efficiency was only 21%. Thus, we can conclude that the disperse composition of particles affects the degree of purification when using DCC.

The best results in the phosphate removal are achieved by using a manufactured sorbent Polonite® and dolomite thermally treated at 700°C (Fig. 1, *d*). The use of these materials at specific consumption of 100 mg of material/mg PO₄³⁻ removes not less than 98.5% of the initial amount of phosphates.

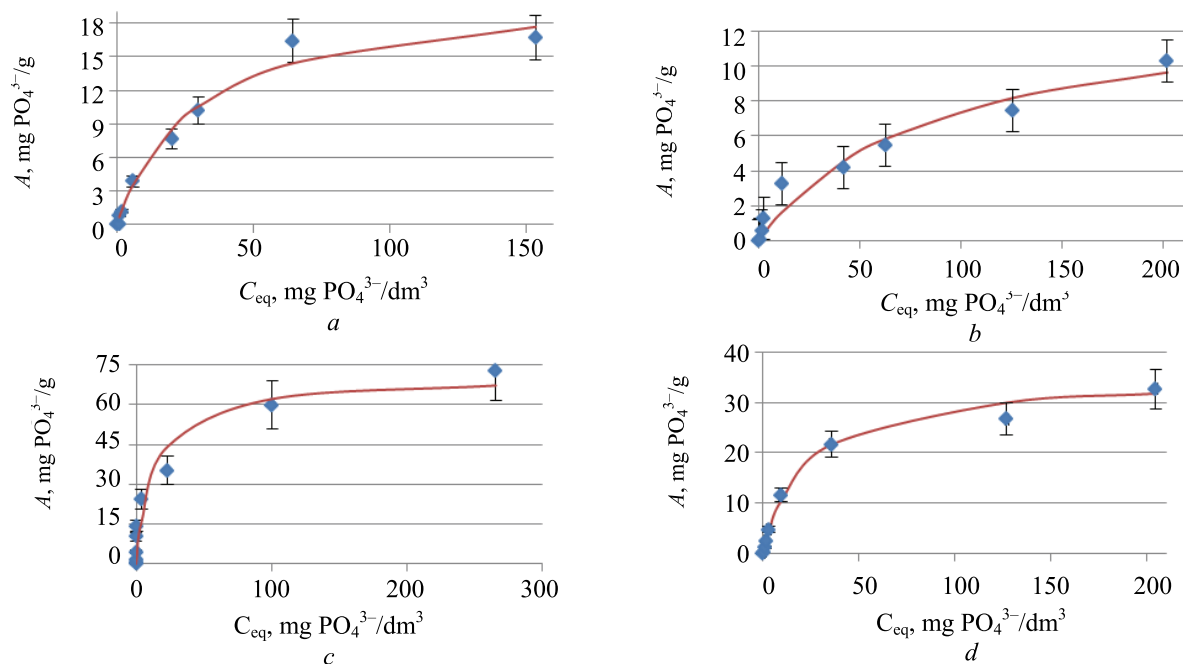


Fig. 3. Dependence of the materials capacity on phosphates on its equilibrium concentration in the solution:
a – DCC (lot-2); *b* – WCS;
c – dolomite, heat treated at 700°C; *d* – EAF-slag

Further growth in the specific consumption leads to the increase in the purity degree up to 99.8%. The presence of free calcium and magnesium oxides in the compositions of Polonite[®] and heat treated dolomite helps suggest that there is one and the same mechanism for phosphate removal, i. e. chemical bonding in sparingly soluble calcium and magnesium phosphates, respectively.

It is known that the ultimate sorption capacity and the distribution ratio are the most important parameters characterizing the efficiency of sorption materials and being used to determine the optimum conditions of the process [25]. In this paper, these indicators were used for comparison of the materials for the ability to remove phosphates from solutions.

For further study we selected materials, the use of which provided the greatest degree of purification: heat treated at 700°C dolomite, WCS, EAF-slag and DCC (lot-2).

Evaluation of the ability to remove phosphates was performed by determining the maximum capacity of phosphate material, which was estimated on the basis of sorption isotherms shown in Fig. 3.

Constants of Langmuir equations used for the approximation of the experimental data and the distribution coefficients of phosphates are shown in Table 2. For comparison, the Table shows the maximum capacity of phosphates for Polonite[®] [21].

The data presented in Fig. 3 and Table 2, are well described by the Langmuir equation, which confirms the chemical nature of the processes that underlie the removal of phosphates [6].

Table 2

Parameters of studied materials

Material	A_{\max} , mg/g	K_L , dm ³ /mg	R^2	K_d , g/g
WCS	13.6	0.012	0.961	51.1
DCC (lot-2)	21.2	0.033	0.982	109.2
EAF-slag	35.3	0.045	0.990	159.8
Dolomite, heat treated at 700°C	70.8	0.072	0.946	273.3
Polonite [®]	119	–	–	–

According to [5, 12, 26], the basic ways of phosphate removal using test materials are interaction of phosphates with ions of Al, Fe, Ca, Mg; ion exchange; interaction with hydroxides of Mg and Ca and aluminosilicates fixation. On the basis of the composition data of the tested materials it can be assumed that for a thermally processed dolomite, WCS and EAF-slag the main method of phosphates removal is the formation of calcium and magnesium phosphates. The main method for phosphate removal for DCC is ion exchange and fixation by aluminosilicates.

The investigated materials have lower sorption capacity than the manufactured sorbent. However, according to the classification mentioned above, the heat-treated dolomite and EAF-slag refer to materials with very high phosphate sorption capacity but DCC and WCS have high phosphate sorption capacity.

The results of materials tests obtained from solutions of phosphates were used to determine the doses in the purification of sludge water of Minsk treatment plant. The concentration of phosphate in the sludge water was in the range of 60–350 mg PO₄³⁻/dm³. Application of the heat-treated dolomite, EAF-slag, DCC and at a

rate of consumption of 13.6 kg/m³ can achieve purity degree of 95, 74 and 51% respectively. After the use of these materials for the removal of phosphates from waste water they may find use as soil ameliorants.

Conclusion. The laboratory research of heat treated at 700°C dolomite, WCS, EAF-slag and DCC (lot-2) lead to the conclusion of their possible use for the purification of waste water and cleaning runoff from farmland. They also can be used as filter medium and substratum for biogeochemical barriers, filtration fields, hydrobotanical sites etc.

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