

The study of the effectiveness of coagulants and white sludge in the process of dephosphotation of municipal wastewater

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Abstract. The results of the test coagulation of clarified wastewater of urban sewage facilities are presented in this work. A dose of aluminum and iron-containing coagulants in terms of metal oxide (Me_2O_3) was used as a parameter for comparison of the efficiency of reagent removal of phosphorus from wastewater. It was shown that the uses of any of the selected coagulants make it possible to bring the degree of purification of municipal effluents to the requirements of fishery co-op permissible exposure limit at the stage of simultaneous subsidence, while the best efficiency results are obtained for an aluminum oxychloride coagulant.

1 Introduction

The main sewage receivers of water and sewage utilities (WSU) of the Russian Federation (Vodokanalov) are internal reservoirs and small watercourses. One of the results noted that decreasing the buffer capacity of internal reservoirs is because of their eutrophication, due to the excess supply of biogenic elements - nitrogen and phosphorus with industrial and municipal effluents [1]. Phosphorus is still considered as a key biogenic element that controls the process of lakes eutrophication, although the N-P control paradigm gradually replaces the phosphorus paradigm [2].

The majority construction of sewage treatment plant (STP) in the Russian Federation with a capacity of 20-50 thousand m^3 per day took place in the 70s of the last century. During this period, the main purpose of municipal effluent cleaning was to remove organic compounds and suspended substances. Removal of some biogenic elements occurred simultaneously - as a result of the microbiological activity of a wide spectrum of action and co-precipitation with suspended substances during settling in primary and secondary settling tanks. The limited capabilities of existing facilities for the treatment of municipal

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wastewater from biogenic elements using outdated technologies are represented in Table 1. It should be emphasized that these technologies continue to be applied to the Russian sewage treatment facilities in the present days [3].

As can be seen from data in Table 1, the best indicators of total phosphorus removal were achieved using chemical-mechanical wastewater treatment with chemical reagents.

Table 1. Cleaning performance indicators [4].

Technical process	Treatment efficiency			
	BOD ₅	Total suspended solids	Total nitrogen	Total dissolved phosphorus
Primary treatment	30	60	15	15
Mechanicochemical purification	55-70	80-90	25-30	75-90
Customary biological treatment	90	90	30	30

There are several traditional technological schemes for the reagent removal of phosphorus are used at wastewater treatment facilities in the Russian Federation: pre-deposition (addition of reagent before primary settling), simultaneous deposition (addition of reagent to the channel of clarified aeration tank water), post-deposition (addition of reagent after secondary settling tanks). A simultaneous deposition is the simplest technique requiring medium doses of coagulants [5]. Since 2019, the Russian Federation was provided large scale technical re-equipment of water and sewage facilities with sewage treatment facilities with a capacity of more than 20 thousand m³ per day based on the best achievements [6].

This paper presents the results of coagulation test of clarified wastewater of sewage treatment facility JSC «Apatityvodokanal» (Apatity city, Murmansk Oblast) by test coagulation method. Solutions of iron (III) sulfate, aluminum sulfate, aluminum-silicate coagulant (ASC), oxysulfate, and aluminum oxychloride were traditionally used in water purification processes as coagulants [11-22].

Additionally, as a sorbent of phosphate ion it was tested white mud (WM), obtained by neutralizing aluminate solutions of alumina production [7]. Initially, white mud was used as a sorbent to remove fluorine from wastewater [8]. In the subsequent the scope of the WM application was significantly expanded and, on its basis, methods for the production of a sorbent for the purification of industrial effluents from lead and cadmium [9] compounds and a method for purifying wastewater from phosphorus compounds were developed [10]. The latter circumstance determined its selection as an object of comparison when assessing the efficiency of the process of dephosphorization of wastewater by the tested coagulants.

2 Experimental

Working solutions of iron (III) sulfate and aluminum sulfate were prepared by dissolving in water Fe₂(SO₄)₃·9H₂O (qualification “pure”, GOST 9485-74) and Al₂(SO₄)₃·18H₂O (qualification “pure”, GOST 3758-75) respectively.

For the production of aluminum-silicate coagulant, it was used nepheline concentrate (NC) produced by OJSC «Apatit» (Kirovsk city, Murmansk Oblast), which is released during the processing of apatite-nepheline ore at concentration plants. The mineral nepheline, the amount of which in the composition of the NC is 80÷85%, has several unique properties, such as the constancy of the chemical composition and the ability to decompose with almost all, even diluted, inorganic (and some organic) acids.

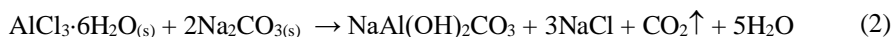
Decomposition of the nepheline concentrate was carried out by 12.5% H₂SO₄ at a rate of 85% stoichiometry per $\Sigma([Al_2O_3]_{acid-soluble}, [Na_2O], [K_2O])$, where $[Al_2O_3]_{acid-soluble}$, $[Na_2O]$, $[K_2O]$ – is the content of acid-soluble Al₂O₃, Na₂O, K₂O in NC, respectively, for 15 minutes. According to the reaction (1), the final products of the interaction of nepheline

with acid were salts of aluminum, alkaline elements and weakly dissociated orthosilicic acid H_4SiO_4 .



At the end of the decomposition process, the resulting pulp was filtered to separate the insoluble residue, the solution was analyzed for its Al_2O_3 content, after which it was diluted to an operating concentration of 10 g/l (by Al_2O_3).

Aluminum oxysulfate and oxychloride were prepared by dissolving active aluminum hydroxide in sulfuric or hydrochloric acid, which in turn was obtained by thoroughly mixing crystalline aluminum chloride ($AlCl_3 \cdot 6H_2O$) and anhydrous sodium carbonate (Na_2CO_3) (both "chemically pure"), taken with 10% excess of the stoichiometrically necessary amount to form aluminum and sodium bicarbonate by reaction (2):



The reagents mixing process was carried out in a laboratory mixer-grinder "WARING" at room temperature, during which intensive CO_2 release was observed, indicating the progress of the process, and the formation of a bulk-increasing dry friable mass. The completion of the reaction was indicated by the cessation of CO_2 isolation. The resulting product was leached with water at 50 °C for 15 minutes at a ratio of L:S = 5:1, after which the precipitate was separated from the solution on a suction filter and washed on a filter to $pH \approx 7$. During leaching and washing, the precipitate $NaAl(OH)_2CO_3$ was hydrolyzed by reaction (3): to form active aluminum hydroxide in the form of pseudobemite.



The obtained aluminum hydroxide was dissolved in a calculated amount of sulfuric or hydrochloric acid, the solutions were analyzed for the content of Al_2O_3 , Cl^- , or SO_4^{2-} , and then diluted to an working concentration of Al_2O_3 (10 g/l).

In Table 2 there are shown the characteristics of the working solutions of coagulants.

Table 2. Characteristics of working solutions of coagulants.

Designation	Characteristic								
	Fe_2O_3 , g/l	Al_2O_3 , g/l	SiO_2 , g/l	Na_2O , g/l	K_2O , g/l	SO_4^{2-} , g/l	Cl^- , g/l	pH	ρ , g/cm ³
Ferric sulphate (SF)	10	-	-	-	-	18	-	2.04	1.023
Aluminium sulphate (SA)	-	10	-	-	-	28	-	1.04	1.037
ASC (ASC)	0.8-0.9	10	13-14	4.5-5.5	2-2.5	38-41	-	3.06	1.063
Aluminium oxysulphate (OSA) $Al(OH)_{0.6}(SO_4)_{1.2}$	-	10	-	0.55		25.6	-	3.91	1.027
Aluminium oxychloride (OXA) $Al(OH)_{2.25}Cl_{0.75}$	-	10	-	0.84	-	-	8.5	4.26	1.013

White mud produced by the Bogoslovsk aluminum plant was provided for testing by LLC "Sorbent-K" (Yekaterinburg city). The product contained a sulphate form of a sodalite group aluminosilicate with a weight fraction of up to 90% - iron hydrogen garnet with weight fraction up to 15% and finely dispersed aluminum hydroxide with weight fraction up to 5%. The chemical composition of WM is given in Table 3.

A sample of wastewater provided by JSC "Apatityvodokanal" with a phosphorus content of 1.8 mg/l (based on total P) was used as the object of investigation of coagulants and WM sorbent.

Table 3. Chemical composition of white sludge produced by the Bogoslovsk aluminum plant [10].

Designation of ingredient	Mass fraction, %
Alumina	25-35
Silica	20-25
Ferrous oxide	3-10
Calcium oxide	3-10
Sodium oxide	15-20
Sulfur oxide	3-6
Potassium oxide	0.5-2.0
Free alkali	not more than 0.02
Moisture content	not more than 15

To carry out the test coagulation, wastewater was poured into the glasses, after which a calculated amount of coagulant solutions with a concentration of 10 mg Al₂O₃/liter was introduced into it with vigorous stirring. In all tests, the pH of the purified water was adjusted to 8 before coagulation, which was ensured by its correction and control on an automatic potentiometric titrator ATII-02 0.1 M with a solution of Na₂CO₃.

The consumption of coagulants varied from 10 to 50 mg Al₂O₃/liter of wastewater. After the introduction of the coagulant, the mixture was stirred for 2 minutes, and then stirrer was turned off, aluminum hydroxide flakes were settling out. The settling process was carried out for 60 minutes, after which the clarified part of the solutions was decanted, filtered, and analyzed for the residual phosphorus content in it. In the process of settling, the sedimentation rate of coagulation flocs and the final pH of the purified water were also determined.

Wastewater was purified from phosphorus using the WM sorbent at a flow rate of 0.5 to 5 g/l of wastewater and a contact time of 4 and 7 hours. At the end of the sorption process, the pulp was settled, the clarified part of the solutions was drained by decantation, filtered and analyzed for its residual phosphorus content, and the final pH of the purified water was determined.

The residual phosphorus concentration was determined by inductively coupled plasma atomic emission spectrometry on Optima 8300.

3 Results and discussion

The experiment results are shown in Figures 1-5. The same efficiency of all types of coagulants was shown in Figure 1, fundamentally that was explained the different mechanisms of the purification process. Thus, if, in the case of cleaning water from suspended particles and metal ions, for example, Cu²⁺ or Co²⁺, they are sorbed on the surface of the resulting aluminum hydroxide flakes, followed by their co-precipitation and removal, then when water is purified from phosphorus, it is removed due to the formation of insoluble aluminum phosphate by the reaction (4).



It was also indicated by the fact that an increase in concentration coagulant of more than 10 mg Al₂O₃/liter for ASC, OSA, and OXA, and 20 mg Al₂O₃/liter for iron and aluminum sulphates does not lead to a decrease in the degree of purification, which may be due to the low but sufficient solubility of the AlPO₄, which does not allow the water to be completely purified from phosphorus. However, it should be pointed out that the water to be purified had a low initial phosphorus content (≈1.8 mg/l) during tests. At its increasing, it will be required additional studies to adjust coagulant flow to achieve an acceptable degree of purification.

The different results were observed when using the WM sorbent to remove phosphorus from water (figure 2). The nature of the linear dependencies were indicated the mechanism of phosphate ion sorption on the surface of WM particles, which, in turn, linearly depends on the amount of sorbent introduced into the water being purified. At the same time, considering the small difference between the residual phosphorus concentration and the sorption time at the same sorbent consumption, it can be assumed that the sorption process proceeds at a high rate and to increase the degree of purification it is more effective to increase the sorbent consumption than to increase the sorption time. However, it will lead to an increase in the amount of mud and, respectively, to an increase in the cost of its separation from water and disposal.

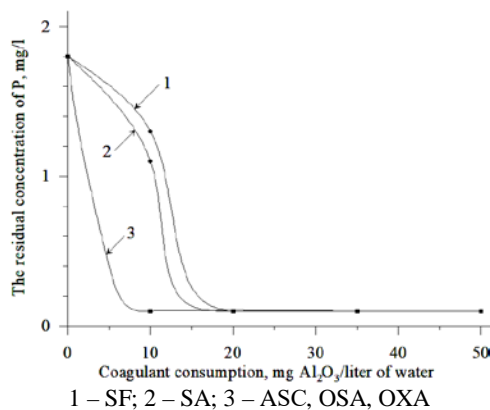


Fig. 1. Influence of the consumption of coagulants on the residual concentration of phosphorus

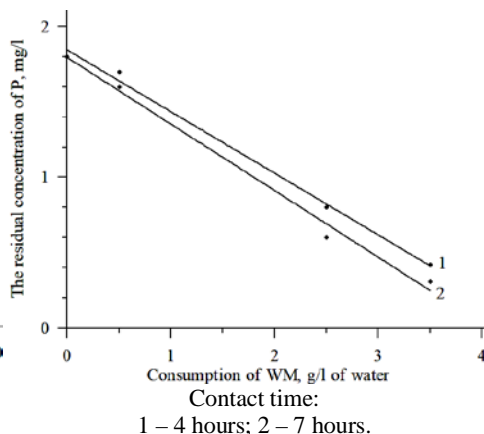


Fig. 2. Influence of WM consumption and contact time on the residual phosphorus concentration

The dependences of the residual concentration of phosphorus (C_P , mg/l) on the WM consumption (G , g/l of water) are satisfactorily described by the following equations:

- for a contact time of 4 hours: $C_P = 1.845 - 0.409 \cdot G$;
- for a contact time of 7 hours: $C_P = 1.796 - 0.442 \cdot G$.

The results data on the influence of the flow rate and the type of coagulants on the final pH value of purified water was shown in figure 3. As expected, when using aluminum oxychloride, the lower value pH of purified water was observed, which has the highest basicity than other coagulants.

The dependences of the final pH value on the flow rate of concentration of coagulants (G , g Al_2O_3 /liter of water) were satisfactorily described by the following equations:

- for iron (III) sulfate: $pH = 8.030 - 0.019 \cdot G$;
- for aluminum sulfate: $pH = 8.021 - 0.031 \cdot G$;
- for aluminosilicate coagulant: $pH = 8.075 - 0.050 \cdot G$;
- for aluminum oxysulfate: $pH = 8.010 - 0.023 \cdot G$;
- for aluminum oxychloride: $pH = 8.010 - 0.013 \cdot G$.

White mud has the opposite influence due to its nature, it has alkaline properties, consequently, the pH of the purified water rises during its use (figure 4). Although, in this case, the effect of the WM consumption is more significant than the effect of the time of its contact with water, which indicates a high rate of desorption of OH⁻ ions from its surface into the water volume, as a result of which the acid-base equilibrium is achieved relatively quickly.

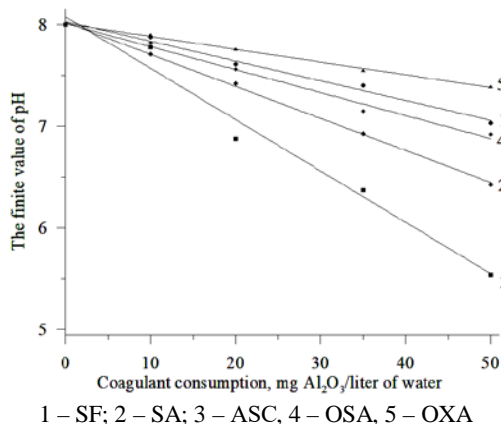


Fig. 3. Influence of the consumption of coagulants on the final pH value of water

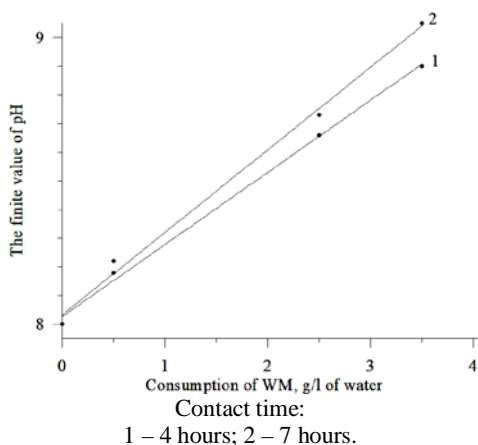


Fig. 4. Influence of WM consumption and contact time on the final pH value of water

The dependences of the final pH value on the WM flow rate (G , g/l of water) were satisfactorily described by the following equations:

- for a contact time of 4 hours: $\text{pH} = 8.026 + 0.252 \cdot G$;

- for a contact time of 7 hours: $\text{pH} = 8.032 + 0.288 \cdot G$.

Research data on the effect of the consumption of coagulants on the sedimentation rate of coagulation flakes were shown in figure 5. As shown in figure, at low flow rates (less than 10 mg Al₂O₃/liter of purified water for aluminum oxychlorides and oxysulfates and less than 20 mg Al₂O₃/liter of purified water for aluminum iron sulfates), the deposition rate is low, which can be explained by the small amount of formed hydroxide particles, which significantly complicates the process of their aggregation, which contributes to the deposition of particles. With increasing of the coagulants consumption the amount of formed particles increases. This facilitates their aggregation with the formation of large agglomerates, the deposition rate of which is significantly higher. Further increase in the consumption of coagulants (more than 30 mg Al₂O₃/liter of purified water for aluminum oxychlorides and oxysulfates and more than 40 mg Al₂O₃/liter of purified water for iron and aluminum sulfates) leads to the formation of an excessively large amount of large agglomerates (flakes) of particles, which, in its turn, interferes with the process of their deposition due to its constraint, reducing the rate of deposition of particles.

Moreover, it should be noted that the maximum deposition rate for aluminum oxychloride and oxysulfate is achieved at their consumption of ≈ 30 mg Al₂O₃/liter of water being purified, while for iron and aluminum sulfates, the maximum deposition rate requires an increase in their consumption to 40 mg Al₂O₃/liter of purified water. This proves that the use of oxychloride and aluminum oxysulfate produces larger and accordingly heavier coagulation flakes whose deposition rate is higher.

The intermediate value was occupied by aluminosilicate coagulant because it contains both aluminum sulfate and dissolved silica (SiO₂), which plays the role of a flocculant and contributes to the formation of large coagulation flakes. This is probably explained by the fact that the maximum deposition rate of coagulation flakes is achieved at a lower coagulant flow rate (≈ 30 mg Al₂O₃/liter) than iron and aluminum sulphates, while increasing their deposition rate.

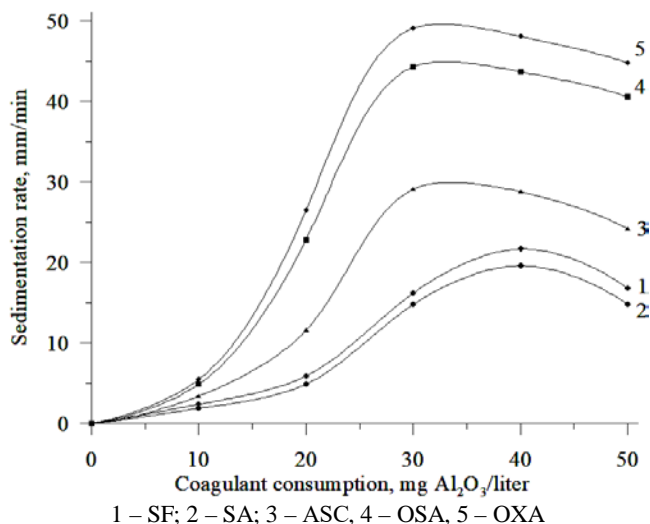


Fig. 5. Influence of the consumption of coagulants on the sedimentation rate of coagulation flakes

4 Conclusions

The process of dephosphotation of municipal wastewater was carried out. It was found that all aluminum and iron-containing coagulants are suitable for purifying wastewater from phosphorus. In this case, the best results in terms of efficiency (degree of purification, final pH value of purified water, rate of precipitation of coagulation flakes) were obtained for a coagulant based on aluminum oxychloride.

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