The object of the study was polymeric alumino-silicon coagulants modified with the monomeric form of orthosilicate acid. The methods and precursors for obtaining stable solutions of composite alumino-silicon coagulants, as well as the effectiveness of coagulation treatment of a surface source of drinking water, were considered. The samples were obtained in two ways:

1) partial hydrolysis of medium-basic aluminum polyhydroxychloride together with sodium silicate solution (PolyAKKg);

2) mixing highly basic aluminum polyhydroxychloride together with a ready solution of orthosilicic acid with a high (above 50 %) monomer content (PolyAKKz).

In the course of research, the problem of the short shelf life of composite alumino-silicon coagulants was solved, which had prevented their industrial implementation in drinking water preparation processes.

It was established that the resulting composite coagulants had the following parameters: Al_2O_3, 8.075–8.725 %; SiO_2, 0.058–0.725 %; Al/Si ratio, 20–250; basicity, 41.4–80.7 %. The effectiveness of the obtained composite coagulant and commercial coagulant was tested under laboratory conditions at a surface source of drinking water by reducing turbidity and by the concentration of residual aluminum in the water after coagulation. The results showed that composite coagulants of the PolyAKKz type with the addition of orthosilicic acid with a high monomer content (above 50 %) obtained using methanesulfonic acid hydrolysis as a precursor have higher solution stability compared to other precursors or coagulants of the PolyAKKg type.

The study results could be used to design new composite coagulants for the preparation of drinking water from surface sources with high turbidity

Keywords: aluminum hydroxychloride, composite coagulants, orthosilicic acid, aluminosilicic coagulants, water purification

UDC 542.9
DOI: 10.15587/1729-4061.2023.282696

INFLUENCE OF THE MONOMER FORM OF ORTHOSILICIC ACID ON THE STABILITY OF POLYALUMOSILICON COAGULANTS AND THEIR EFFICIENCY IN THE TREATMENT OF DRINKING WATER

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Received date 06.04.2023
Accepted date 16.06.2023
Published date 30.06.2023

***How to Cite:** Mandryka, A., Pasenko, O., Vereschak, V., Osokin, Y. (2023). Influence of the monomer form of orthosilicic acid on the stability of polyalumosilicon coagulants and their efficiency in the treatment of drinking water. Eastern-European Journal of Enterprise Technologies, 3 (10 (123)), 6–14. doi: https://doi.org/10.15587/1729-4061.2023.282696*

1. Introduction

Coagulation is the most common process of water purification in the processes of preparation of both drinking and wastewater or technological water. One of the biggest factors affecting the coagulation process is the parameters of the water to be treated [1]. Coagulation treatment of water at low temperature (below 5 °C), low turbidity (less than 2 NTU), and high coloration (above 40 points) is quite a difficult task. This is due to the fact that low temperature and low turbidity suppress the hydrolysis of metals in water, and a high content of dissolved organic substances, especially humic compounds, can lead to the formation of soluble salts with aluminum or iron [1]. It should also be noted that at the moment, one of the most effective coagulants for treating surface water during a flood is polymeric highly basic aluminum hydroxychloride. However, the increased pollution of drinking water sources in the world, as well as the obsolescence of existing treatment facilities, leads to the need to use increased doses of aluminum coagulants to remove organic substances. This leads either to exceeding the maximum permissible concentration of aluminum (above 0.2 mg/dm^3) or to exceeding the concentration of trihalomethanes (above 50 μg/dm^3) [2]. This problem can be solved by the design of stable and highly effective alumino-silicon coagulants, which can be used in comparatively smaller quantities than existing analogs while maintaining the same coagulation efficiency. Therefore, scientific research into this area is relevant.

2. Literature review and problem statement

It is known from the literature [3] that the use of highly basic aluminum hydroxychlorides leads to the formation of floccules of smaller sizes and with a slower rate of thickening than when using medium and low basic aluminum hydroxychlorides or aluminum sulfate. This leads to an increased load on sedimentation tanks of drinking water treatment facilities. Polymeric organic flocculants based on acrylic acid are used to accelerate the processes of sedimentation and thickening of floccules [4]. However, the mass use of such flocculants leads to their accumulation in rivers [5] and other water sources, where they enter together with washing waters from settling tanks and filters. Due to their low capacity for biodegradation [6] (ESPR-D-14), this causes risks of accumulation of potentially carcinogenic substance in drinking water to high levels. Also, the use of polymer organic flocculants often leads to the so-called "clogging" of filters, which most often occurs precisely during the flood period during the coagulation purification of slightly turbid waters with a low temperature. At the same time, the use of low- and medium-basic coagulants for the treatment of water at low temperature (below 5 °C) is impossible due to the incomplete hydrolysis of this class of coagulants and the increased content of residual aluminum in the water after treatment, which negatively affects the quality of drinking water [5, 7].

Previously, this problem was not solved because it was not necessary to use increased doses of coagulant and the problem of accumulation of polyacrylamide residues in surface water sources [8] was not so acute.

A possible solution to the described problems may be the use of composite alumino-silicon coagulants using orthosilicic acid as an inorganic flocculant, which is capable of environmentally safe decomposition [9]. As a precursor for obtaining such coagulants, it is proposed to use highly basic aluminum polyhydroxychlorides, as the most effective for water purification at low temperatures [10].

Aluminum salts and soluble compounds of silicon (sodium silicate, metasilicic acid, mixtures of orthosilicic acid, silicate gel) can be mixed or obtained in different ways. Thus, it is known about the production of aluminum-silicon coagulant by means of sulfate-acid leaching of nepheline ores [11], during the simultaneous hydrolysis of $AlCl_3$ and sodium silicate in an aqueous solution, or when mixing previously obtained polymeric orthosilicic acid [12]. However, the cited works did not analyze the influence of the form of orthosilicic acid on the stability of the resulting coagulant and its effectiveness.

However, in [11] it is reported that when obtaining composite coagulants with the help of leaching of natural or synthetic aluminosilicate material, cloudy, unstable solutions are formed. Such solutions can be used for several hours or must be dried to a dry state, which requires significant energy consumption. In work [12], the modification of highly basic aluminum polyhydroxychlorides with orthosilicic acid leads to unstable solutions that are prone to cloudiness and gel formation; the influence of the form of orthosilicic acid on the stability of the composite coagulant is not considered in the work. It should also be noted that the use of increased doses of coagulants based on aluminum hydroxychloride poses a risk to human life [13].

The above data show that the influence of the form of orthosilicic acid in the precursor before mixing or after co-hydrolysis or leaching on the stability of the obtained coagulants was not studied in previous studies, nor was the influence of the acid agent used for the hydrolysis of sodium metasilicate on the stability and efficiency of the resulting composite coagulant.

This allows us to state that it is appropriate to conduct a study to synthesize new composite coagulants based on aluminum hydroxychloride and orthosilicate acid and the influence of its monomeric form on the stability of the obtained coagulants and their effectiveness.

3. The aim and objectives of the study

The purpose of this work is to study the influence of an aqueous solution of orthosilicic acid with a high monomer content (above 50 %), as well as some acid precursors for the hydrolysis of sodium metasilicate, on the stability and effectiveness of the polymeric aluminosilicate coagulant. This will make it possible to design new composite coagulants based on aluminum hydroxychloride and the monomeric form of orthosilicate acid with greater stability and coagulation efficiency.

To accomplish the aim, the following tasks have been set:

– to investigate the stability of a series of samples of alumino-silicon coagulant with different Al/Si ratio, basicity, and production method;

– to conduct an analysis of water after treatment to determine the effectiveness of removing turbidity from water and residual aluminum at different water temperatures;

– to analyze the sediment after coagulation to confirm co-precipitation of orthosilicic acid together with aluminum hydroxide during hydrolysis.

4. The study materials and methods

4. 1. Preparation of polymeric aluminum-silicon coagulant

The objects of the research are polymeric alumino-silicon coagulants modified with the monomeric form of orthosilicate acid.

From the literature data, it is known about 2 main methods of obtaining composite alumino-silicon coagulants; this is the mixing of ready-made precursors (ready-made orthosilicic acid and hydroxychloride or aluminum sulfate) and the use of hydroxychloride or aluminum sulfate as an acid precursor for the hydrolysis of sodium metasilicate to obtain orthosilicic acid or its oligomers directly in solution coagulant [12, 14, 15]. The method of acid leaching of ore alumino-silicon raw materials leads to obtaining metastable mixtures with an undefined structure and variable chemical composition and therefore cannot be used to obtain liquid stable coagulants for drinking water treatment.

Therefore, two main methods of obtaining polymeric alumino-silicon coagulant (PolyAKK) were used:

– method 1. A concentrated solution of liquid glass manufactured by Zaporizhsklofluus (Ukraine) with a silicon content of 23 % by SiO_2, a silicate module of 2.9, was dissolved in prepared water in a volume of 500 ml, calculated to obtain a concentration of orthosilicic acid of 2, 5, 10 g/dm^3. After that, 500 g of aluminum polyhydroxychloride "Alyumofloc-10" manufactured by "Khimefekt" LLC (Ukraine) of medium basicity (41.4 %) was added. The addition took place with intensive stirring to prevent hydrolysis. After that, the mixture was kept with stirring for 2–3 hours and at a temperature of 45–50 °C;

– method 2. Previously, solutions of orthosilicic acid (2, 5, 10, 20 g/dm^3 of orthosilicic acid) were obtained using some acids (chloric, sulfate, orthophosphoric, methanesulfonic acid) [16]. Then, stabilized orthosilicic acid with a high monomer content (above 50 %) was mixed with highly basic aluminum polyhydroxychloride of the brand "Alyumofloc-Cl" produced by "Khimefect" LLC in a ratio of 1:1 by weight.

The samples obtained by the above methods had the following parameters: Al_2O_3 – 7.5–9.5 %, SiO_2 – 0.05–0.55 %, Al/Si ratio 20–250, basicity 41.4–80.7 %.

4. 2. Laboratory coagulation

Laboratory coagulation tests were performed using Flocculator 2000 (Sweden). As a sample for coagulation treatment, water from the Kamensky reservoir was used in the period March–April 2023, during the flood period, with the following parameters: Turbidity – 9 NTU, aluminum – 0.04 mg/dm^3, temperature 2–4 °C. To maintain the temperature, the samples were stored in a refrigerator at 2 °C.

Doses of different coagulants (initial and modified) in terms of Al_2O_3 were added to 500 ml of water while stirring. The sample was stirred at 140–150 rpm during the addition of coagulant for 2 min, then at 40 rpm in the process of coagulation and thickening of floccules. The sample was settled for 15 min. After that, a sample of clarified water was taken to measure turbidity and residual aluminum. Turbidity was measured on a Drawell DU-8200 spectrophotometer (China), according to standard samples, residual aluminum in water after coagulation by reaction with ferroin according to DSTU 7525:2014 and GB 5749-2006 [17, 18].

5. Results of studying the stability and efficiency of composite alumino-silicon coagulants

5. 1. Stability of coagulants

As is known [14, 15], most composite alumino-silicon coagulants are unstable mixtures with a storage time in the liquid state from several hours to 2–3 months. The main problem with the storage of such coagulants is the polymerization of orthosilicic acid, which leads to turbidity and gel formation. Such products cannot be used in industrial production, as unpredictable stability can lead to failure of dosing equipment and deterioration of water treatment quality. In work [19] it was shown that the monomeric form of orthosilicic acid is prone to the formation of complex compounds with aluminum hydroxychloride. Therefore, in the current work, the stability of coagulants obtained by methods 1 and 2 using orthosilicic acid with the maximum monomer content was investigated (Fig. 1).

Fig. 1 shows the storage period of the obtained samples of composite coagulants until the moment of gelatinization or the formation of sediment, which makes its industrial use impossible. The green color indicates the storage time of the sample during which the solution was transparent, without the formation of sediment or changes in viscosity. Orange shows the moment when the sample becomes cloudy, without the formation of sediment or gelatinization, at which the coagulant can still be used in the preparation of drinking water.

Table 1 and Fig. 1 demonstrate that the coagulants obtained by technique No. 2, when using orthosilicic acid (obtained using methanesulfonic acid), have extremely high stability in a wide range of Al/Si ratios. Coagulants obtained by technique No. 2 can be stored without changes for 9 months, which exceeds the standard requirements for commercial products (6 months). The use of coagulants obtained by technique No. 2 with orthosilicic acid (obtained using sulfuric or orthophosphoric acid) leads to unstable products. The introduction of sulfate or orthophosphate anions into highly basic aluminum hydroxychlorides leads to their destruction and gel formation.

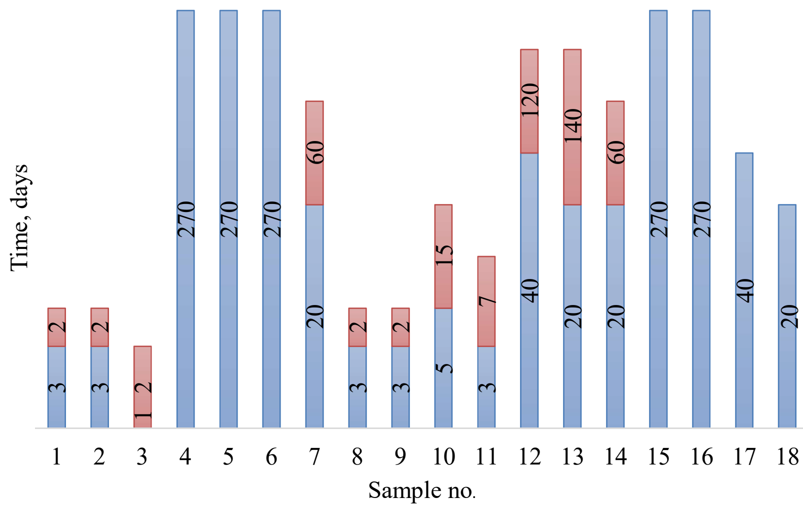

Fig. 1. Study of stability of composite coagulants

Table 1

Composition and technique of obtaining samples of composite aluminum-silicon coagulants

No.	Basicity, %	Production technique	Al/Si	Concentration Al_2O_3, %	Concentration SiO_2, %
1	41.4	1	250	8.075	0.058
2	41.4	1	100	8.075	0.148
3	41.4	1	20	8.075	0.725
4	80.7	$2(CH_3SO_3^-)$	250	8.725	0.063
5	80.7	$2(CH_3SO_3^-)$	100	8.725	0.153
6	80.7	$2(CH_3SO_3^-)$	50	8.725	0.312
7	80.7	$2(CH_3SO_3^-)$	20	8.725	0.781
8	80.7	$2(HPO_4^{2-})$	250	8.725	0.063
9	80.7	$2(HPO_4^{2-})$	50	8.725	0.312
10	80.7	$2(SO_4^{2-})$	250	8.725	0.063
11	80.7	$2(SO_4^{2-})$	50	8.725	0.312
12	41.4	$2(CH_3SO_3^-)$	250	8.075	0.058
13	41.4	$2(CH_3SO_3^-)$	100	8.075	0.148
14	41.4	$2(CH_3SO_3^-)$	20	8.075	0.725
15	80.7	«Pure» coagulant	n/a	17.45	0
16	80.7			8.725	
17	41.4			16.15	
18	41.4			8.075	

The coagulant obtained using technique No. 1 using liquid glass and medium basic aluminum hydroxychloride also turned out to be unstable. However, the coagulant of medium-basic aluminum hydroxychloride, obtained by technique 2 using orthosilicic acid (obtained with methanesulfonic acid), turned out to be sufficiently stable for commercial use.

5. 2. Coagulation efficacy

After examining the samples of coagulants for stability, those samples that showed stability of 40 days or more were selected. Later, these samples were examined for coagulation properties. Freshly obtained analogs of coagulant samples No. 4–7 and 12–14 inclusive, as well as freshly obtained samples of Alumofloc-Cl and Alumofloc-10, were kept for 14 days (approximate time from production to use). And after that, laboratory tests were conducted on the effectiveness of removing turbidity and residual aluminum in water. Water for the tests was used from the Kamensky reservoir during the flood of 2023. Water parameters are as follows: turbidity – 9 NTU, residual aluminum – 0.04 mg/dm^3, pH – 7.2. Laboratory coagulation was performed for two temperatures of 2 °C and 20 °C, simulating cold water during the flood. And also, when water quality deteriorates in the summer period as a result of flowering. The results are shown in Fig. 2–5, as well as the corresponding approximation coefficients and the value of the approximation reliability in Tables 2–6, which were described by a polynomial of the 4th power according to the formula: $y=a_3{\cdot}x^4-a_2{\cdot}x^3+a_1{\cdot}x^2-b{\cdot}x+c$. The charts described by the equation of the straight line together with the approximation coefficients are shown in Fig. 2, 6, 7. As can be seen, alumino-silicon coagulants in general more effectively remove turbidity from water at the same doses of Al_2O_3. Medium base composite coagulants more effectively remove turbidity at all temperatures. However, when they are used, there is a very rapid exceedance of MPC for residual aluminum in drinking water. That is why their use is not recommended at a water temperature below +6–+8 °C. In the case of coagulation in water with a temperature of 20 °C, medium-base composite coagulants show better turbidity removal efficiency compared to high-base coagulants. And at the same time, they do not cause exceeding the MPC for aluminum due to complete hydrolysis in water with a temperature of 20 °C and above. It can also be seen that the effectiveness of turbidity removal to the requirements of DSanPiN 2.2.4–171–10 [7] occurs at lower effective doses for composite coagulants than for conventional aluminum hydroxychlorides. Fig. 5–8 show the change in the concentration of residual aluminum depending on dosage. It is shown that composite coagulants, in comparison with ordinary hydroxychlorides, coagulate more completely, which leads to a decrease in residual aluminum. This is due to the fact that during the coagulation of polymer coagulants with a higher molecular weight, heavier floccules with a developed surface are formed on which non-hydrolyzed cations of the coagulant are sorbed. When aluminum hydroxychloride is modified with solutions of orthosilicic acid with a high monomer content, an adduct with an even higher molecular weight is formed, as well as a tendency to form aluminosilicates during hydrolysis in water.

The concentration of residual aluminum is also affected by the basicity of the coagulant (propensity to hydrolysis), as well as the temperature conditions of use.

Table 2

Approximation coefficients and value of reliable approximation for Fig. 3

Sample	a_3	a_2	a_1	b	c	R^2
Al-Cl	0.0007	0.0264	0.3876	2.5955	9.0761	0.9990
No. 12	0.0005	0.0235	0.3858	2.7812	9.0712	0.9992
No. 13	0.0006	0.0267	0.4249	2.9635	9.0589	0.9993
No. 14	0.0007	0.0313	0.4772	3.1650	9.0728	0.9993

Table 3

Approximation coefficients and value of reliable approximation for Fig. 4

Sample	a_3	a_2	a_1	b	c	R^2
Al-Cl	0.0016	0.0550	0.6489	3.4356	8.7778	0.9928
No. 4	0.0017	0.0562	0.6686	3.5606	8.7820	0.9935
No. 5	0.0019	0.0646	0.7505	3.8077	8.7057	0.9879
No. 6	0.0020	0.0680	0.7961	4.0181	8.6955	0.9873
No. 7	0.0022	0.0745	0.8584	4.2156	8.6749	0.9856

Fig. 10 shows the hydraulic particle size in coagulated water depending on the type of coagulant at a dose of 15 mg/dm^3 for Al_2O_3. The hydraulic coarseness was studied for a temperature of +2 °C, as the most difficult temperature for coagulation.

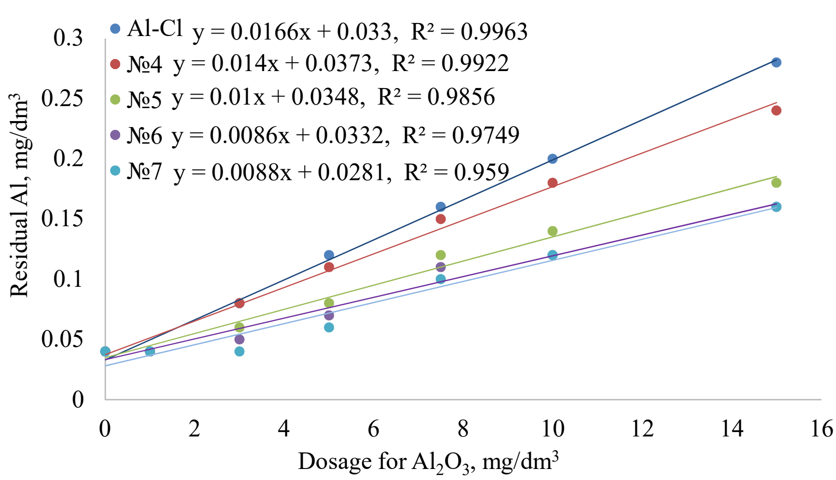

Fig. 2. Comparative coagulation of Alumofloc Cl (Al–Cl) and composite alumino-silicon coagulants No. 4–7 for removing turbidity from a surface water source (the Kamensky reservoir, flood period) at a temperature of 2 °C

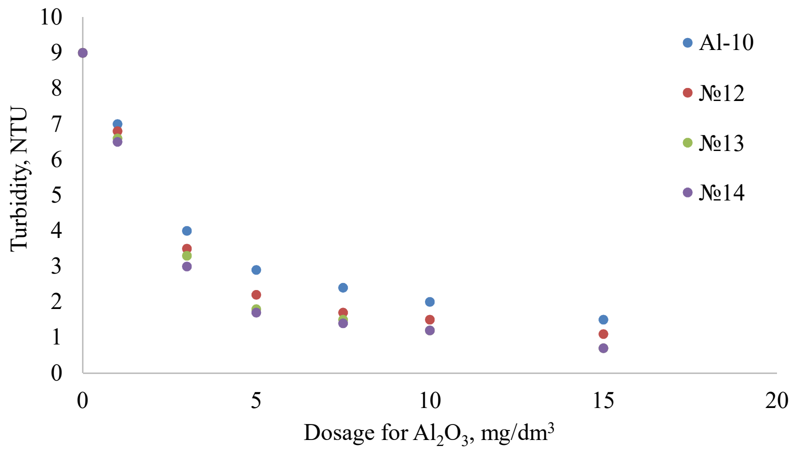

Fig. 3. Comparative coagulation of Alumofloc-10 (Al–10) and composite alumino-silicon coagulants No. 12–14 for removing turbidity from a surface water source (the Kamensky reservoir, flood period) at a temperature of 2 °C

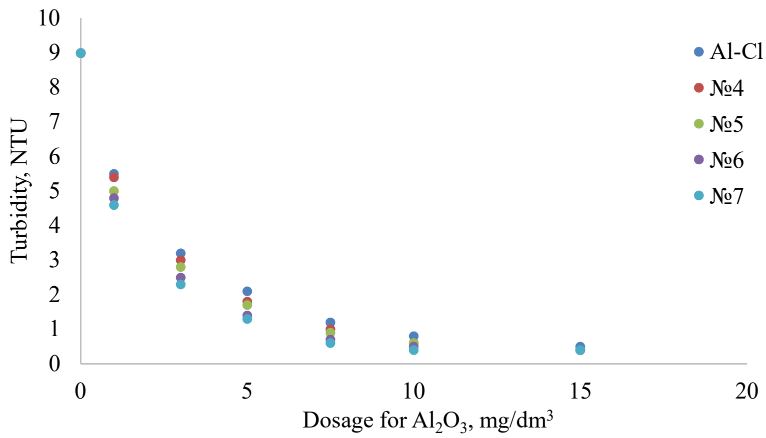

Fig. 4. Comparative coagulation of Alumofloc Cl (Al–Cl) and composite alumino-silicon coagulants No. 4–7 for removing turbidity from a surface water source (Kamensky reservoir, flood period) at a temperature of 20 °C

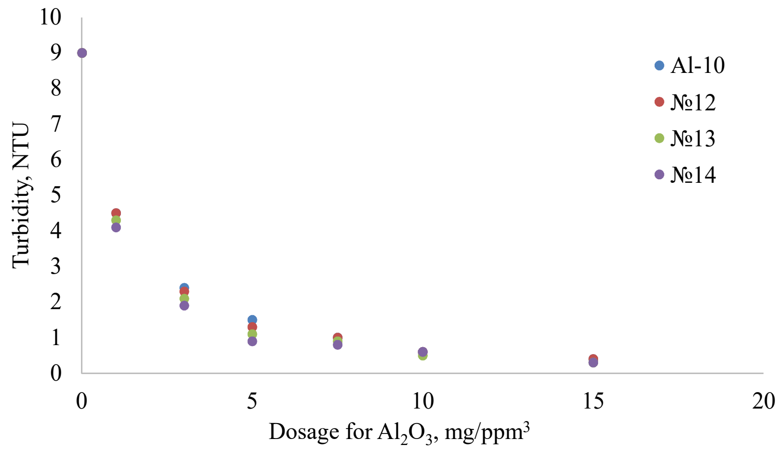

Fig. 5. Comparative coagulation of Alumofloc-10 (Al–10) and composite alumino-silicon coagulants No. 12–14 for removing turbidity from a surface water source (Kamensky Reservoir, flood period) at a temperature of 20 °C

Table 4

Approximation coefficients and value of reliable approximation for Fig. 5

Sample	a_3	a_2	a_1	b	c	R^2
Al-10	0.0025	0.0831	0.9298	4.3410	8.6654	0.9840
No. 12	0.0025	0.0826	0.9353	4.4064	8.6884	0.9862
No. 13	0.0026	0.0876	0.9880	4.5977	8.6708	0.9848
No. 14	0.0026	0.0885	1.0128	4.7329	8.6414	0.9820

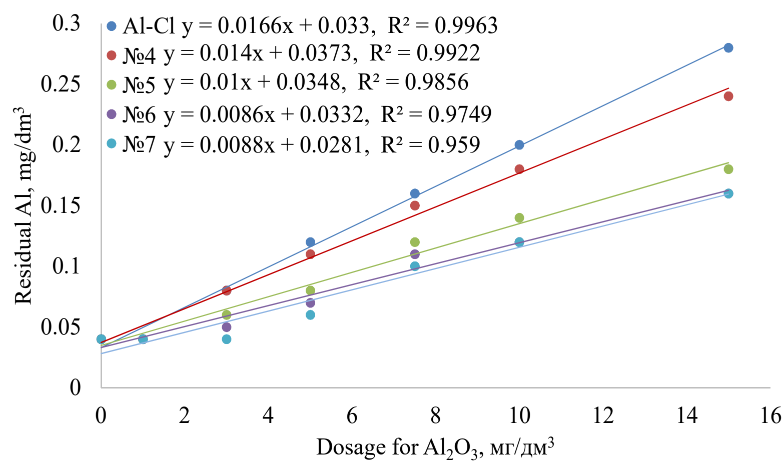

Fig. 6. The content of residual aluminum depending on the type and dosage of coagulants: Alumofloc Cl (Al–Cl) and composite alumino-silicon coagulants No. 4–7 at a temperature of 2 °C

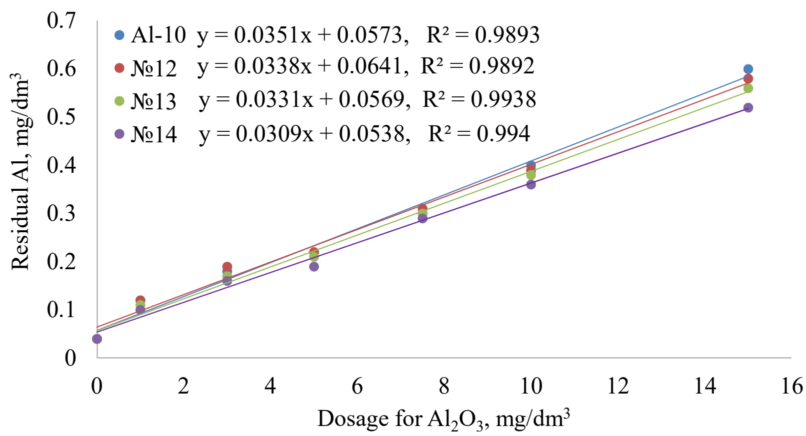

Fig. 7. The content of residual aluminum depending on the type and dosage of coagulants: Alumoflok-10 (Al-10) and composite alumino-silicon coagulants No. 12–14 at a temperature of 2 °C

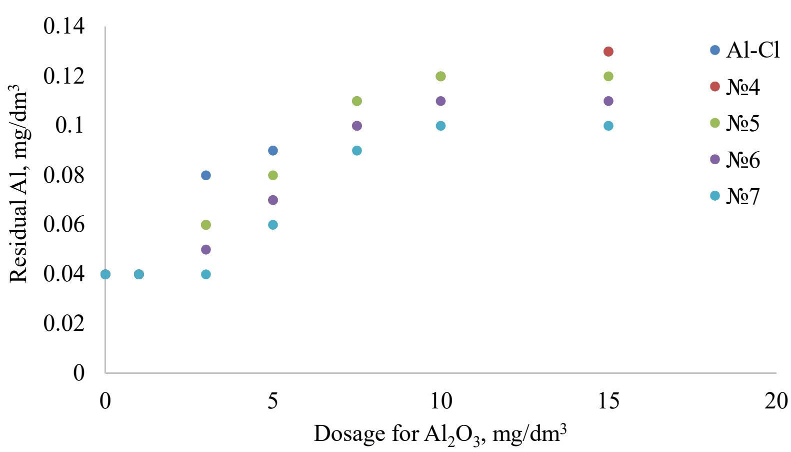

Fig. 8. The content of residual aluminum depending on the type and dosage of coagulants: Alumofloc Cl (Al–Cl) and composite alumino-silicon coagulants No. 4–7 at a temperature of 20 °C

Table 5

Approximation coefficients and the value of reliable approximation for Fig. 8

Sample	a_3	a_2	a_1	b	c	R^2
Al-Cl	$5 \cdot 10^{-6}$	0.0001	0.0005	0.0116	0.0362	0.9809
No. 4	$-8 \cdot 10^{-7}$	$4 \cdot 10^{-5}$	0.0010	0.0031	0.0389	0.9948
No. 5	10^{-5}	0.0004	0.0039	0.0023	0.0397	0.9982
No. 6	10^{-5}	0.0004	0.0044	0.0066	0.0410	0.9977
No. 7	10^{-5}	0.0004	0.0048	0.0109	0.0422	0.9914

Table 6

Approximation coefficients and the value of reliable approximation for Fig. 9

Sample	a_3	a_2	a_1	b	c	R^2
Al-10	$9·10^{-6}$	0.0003	0.0033	0.0016	0.0387	0.9965
No. 12	$-8·10^{-6}$	0.0002	0.0013	0.0144	0.0358	0.9872
No. 13	$8·10^{-7}$	0.0003	0.0036	0.0024	0.0399	0.9976
No. 14	$2·10^{-5}$	0.0005	0.0056	0.0097	0.0418	0.9937

Sample tests of composite coagulants and conventional hydroxychlorides in water at 20 °C showed a deviation of 5 %, which is an acceptable error when measuring hydraulic coarseness or calculating treatment facilities. It demonstrates that with a decrease in the Al/Si ratio in the composite coagulant, the hydraulic particle size increases due to the higher molecular weight of the adduct, as well as less hydrated flocs. That has a positive effect on the density of floccules, the speed of their deposition, and the operation of treatment facilities.

5. 3. Sediment analysis after coagulation

To understand the behavior of the adduct between aluminum hydroxychloride and orthosilicic acid monomer, analyzes of sediments after coagulation of natural water were carried out. Before analysis, the sediment was dried to constant weight at 102–105 °C. The sediments were X-ray amorphous, which is characteristic of the sediments obtained during hydrolysis and without calcination. Elemental analysis was performed by energy dispersive X-ray spectroscopy on a Bruker EDX device. The results of the analysis are given in Table 7.

Table 7

Elemental analysis of sediments after coagulation with different types of coagulants at a dose of 15 mg/l for Al_2O_3

E, %	Coagulant								
	Alumoflok-Cl	No. 4	No. 5	No. 6	No. 7	Al–10	No. 12	No. 13	No. 14
O	64.46	60.26	60.42	59.79	59.36	62.83	61.2	60.84	60.55
Mg	0.44	0.67	0.74	0.68	0.72	0.51	0.72	0.7	0.64
Al	31.15	32.13	32.08	32.24	32.34	32.15	32.31	32.41	32.38
Si	0.15	0.78	1.24	1.64	1.72	0.16	0.32	0.82	1.62
S	2.4	2.7	2.9	2.94	2.94	2.27	2.81	2.27	2.32
Cl	0.55	1.45	0.4	0.58	0.8	0.88	0.92	1.02	0.87
Ca	0.5	1.14	1.28	1.1	1.07	0.65	0.91	1.16	1.07
Fe	0.35	0.87	0.94	1.03	1.05	0.55	0.81	0.78	0.55
Al/Si in sediment	215	43	27	20	19	208	105	41	21
Al/Si yield	0	250	100	50	20	0	250	100	20

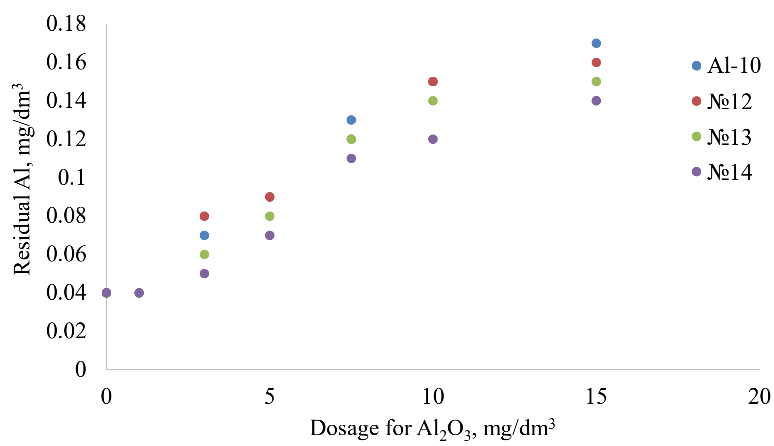

Fig. 9. Residual aluminum content depending on the type and dosage of coagulants: Alumoflok 10 (Al–10) and composite alumino-silicon coagulants No. 4–7 at a temperature of 20 °C

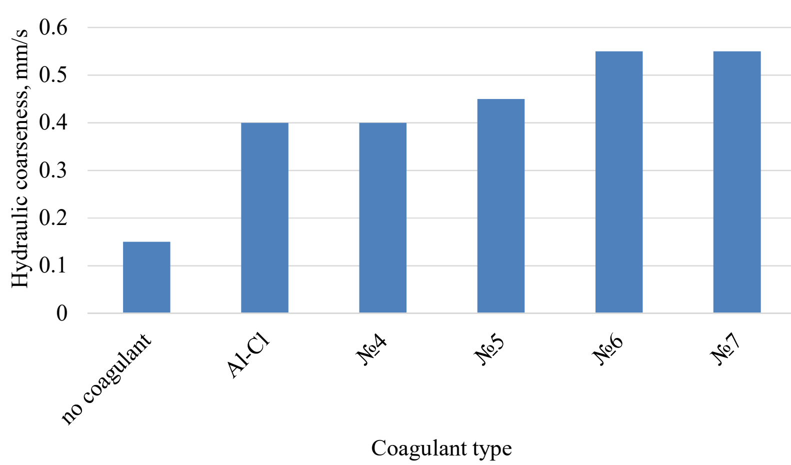

Fig. 10. Hydraulic particle size depending on the type of coagulant at a dose of 15 mg/l for Al_2O_3

As can be seen from the results of the analysis, even when pure aluminum hydroxychlorides are used in the coagulation process, complexes with soluble compounds of silicon in water and the formation of aluminosilicates in the sediment are formed. At the same time, samples of composite alumino-silicon coagulants were significantly enriched in silicon during the coagulation process, which indicates a better removal of not only turbidity but also soluble organic and inorganic impurities in water.

6. Discussion of results of investigating the stability and efficiency of composite aluminum-silicon coagulants

During the research, a series of samples of composite coagulants were obtained by two techniques, as well as using different acid precursors in the process of obtaining orthosilicic acid. The composition of the samples and the technique of obtaining them are indicated in Table 1. After that, a comparative study of the stability of the obtained samples and "pure" coagulants without modification was carried out under conditions of storage at 20 °C. The results of the stability study are shown in Fig. 1.

It was found that samples obtained by technique 2 have better stability in all ranges of Al/Si ratios and at different relative basicities of the original coagulant. Thus, for samples 12–14, the shelf life without sediment formation or gelatinization of the sediment was higher than that of the "pure" coagulant with the same Al_2O_3 concentration. This can be explained by the fact that during the preparation of composite coagulants by technique 2, polyhydroxychloride is mixed with orthosilicic acid, which was previously obtained under optimal conditions for the maximum yield of orthosilicic acid monomer [9]. And probably there was an interaction between aluminum polyhydroxychloride and orthosilicic acid monomer, which is thermodynamically advantageous [20]. The formed adduct has the same or higher stability than the original coagulants at comparable Al_2O_3 concentrations. It is thanks to this that a longer shelf life of composite coagulants samples is achieved, in contrast to existing methods. In such methods, acid leaching of alumino-silicon raw materials occurs with the uncontrolled production of orthosilicic acid in polymer form with a very short shelf life of several days [6]. Or mixing with previously obtained samples of orthosilicic acid using suboptimal, from the point of view of monomer yield, acid precursors for the hydrolysis of sodium silicate [7]. This way leads to obtaining samples with a shorter shelf life than obtained in the current study.

Samples of composite coagulants with a shelf life in a liquid state, without the formation of a sediment or gelatinization, performed better in laboratory tests for the purification of natural water from turbidity, as well as the content of residual aluminum at water temperatures of 2 and 20 °C. This can be explained by the fact that the molecular weight of aluminum hydroxychloride increases due to the formation of an adduct between aluminum polyhydroxychloride and orthosilicic acid mono/dimer. This, in turn, leads to an increase in the size of the flakes during the hydrolysis of the coagulant in water, their larger hydraulic coarseness and, accordingly, faster and more complete sedimentation, Fig. 2–10. The presence of an anionic group of orthosilicic acid in aluminum hydroxide flakes during hydrolysis in water serves as an additional flocculating factor during coagulation. This fact is confirmed by significantly lower concentrations of residual aluminum than when using unmodified aluminum hydroxychlorides, Fig. 6–10, which demonstrates the effect of orthosilicic acid as an inorganic flocculant, which is especially characteristic of coagulation at a temperature of 2 °C, while at the time of coagulation at a temperature of 20 °C and above, the influence of the content of orthosilicic acid on the concentration of residual aluminum is insignificant compared to initial coagulants. This is explained by the fact that in warm water the hydrolysis of aluminum hydroxychloride occurs more completely and the effect of the composite coagulant is comparatively less noticeable.

The composite coagulant was also shown to be effective in removing turbidity and dissolved organic and inorganic substances. This effective effect is confirmed by the reduction of the Al/Si ratio in the sediment after coagulation compared to the composite coagulant used in the laboratory test, Table 2.

The obtained results of coagulation efficiency allow for the development of technological conditions for the industrial production of alumino-silicon composite coagulants with a shelf life similar to or longer than that of conventional aluminum hydroxychlorides. In addition, the obtained results make it possible to develop coagulants with higher efficiency in removing insoluble and soluble impurities in the process of drinking water preparation. This is explained by the interaction of aluminum hydroxychloride and orthosilicic acid monomer/dimer with the formation of a stable adduct that is not prone to polymerization or destruction when stored under normal conditions.

This study was carried out using aluminum hydroxychlorides of the Alumofloc brand, which were obtained by dissolving aluminum in a hydrogen chloride solution. Accordingly, when creating composite coagulants with orthosilicic acid monomer and aluminum hydroxychlorides obtained by other technologies, the stability and efficiency results may deviate from those given in our work.

Coagulation efficiency was also determined on water from a surface source with high turbidity, coloration, and low hardness. When conducting similar tests on water from underground sources, process or waste water, the results may differ from those obtained in our research.

The drawback of the study is that the structure and form of the adduct of aluminum hydroxychloride and orthosilicic acid in the coagulant solution was not experimentally confirmed. Further research is planned to focus on the establishment and instrumental confirmation of the existence of the adduct in the solution. This can be complicated by the fact that the adduct can exist in the form of ionic associates that are not determined by IR or NMR spectra.

7. Conclusions

1. The stability of the obtained samples was studied, and it was shown that orthosilicic acid with a high monomer content (above 50 %) obtained precisely with the use of methanesulfonic acid has the best effect on the stability of the composite coagulant. It was established that the technologically appropriate ratio of Al/Si in the composite coagulant is from 100 to 20. Above this ratio, the efficiency of the coagulant increases slightly, and below it negatively affects the stability of the coagulant in commercial form.

2. It is shown that composite alumino-silicon coagulants modified with orthosilicic acid with a high monomer content (above 50 %), obtained using methanesulfonic acid, have a better efficiency in coagulation purification of water from turbidity and in the content of residual aluminum compared to the original aluminum polyhydroxychlorides. It is shown that the greatest efficiency is achieved by coagulation in cold water (2 °C) with high turbidity.

3. It has been proven that orthosilicic acid monomer forms an adduct with aluminum hydroxychloride in an aqueous solution, and they also co-precipitate during coagulation. This allows us to consider orthosilicic acid monomer as an effective modifier of aluminum hydroxychlorides and an inorganic flocculant.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

Funding

The study was conducted without financial support.

Data availability

All data are available in the main text of the manuscript.

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