Cleaning of natural and sewage water using new composite flocculants-coagulants

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Abstract: The present work relates to the topic of green chemistry and technology of inorganic substances. In particular, it is devoted to the development of new materials for the reagent treatment of natural and waste water. The authors developed a technology for manufacturing composite materials - flocculants-coagulants on aluminum-silicon and iron-silicon base. Based on these reagents, methods were proposed for purifying natural waters, industrial wastewater and storm sewage. The authors have developed and patented a technology for producing flocculants-coagulants of this type in solid form. When creating these composites, matrix isolation methods of existing active components were used. The experimental evaluation of the effectiveness of the developed flocculants-coagulants ASFC and IFSC on real natural water and industrial wastewater is carried out. Their comparison with known analogs produced by industry is made.
Key words: composite flocculants-coagulants; water treatment agents; aluminum-silicon and flocculants-coagulants; iron-silicon flocculants-coagulants; matrix isolation.

INTRODUCTION

In the modern world environmental problems get a global scale. The actual problems of modernity are a qualitative and quantitative depletion of water resources on Earth. Domestic or industrial wastewater, which are discharged into rivers and ponds, greatly degrade the quality of water from surface sources. In this regard, the priority is the development and widespread using of closed water cycles in industry and also desalination and complex treatment of natural and waste waters. As a result of increasing demands to reduce emissions of modern industrial enterprises, and also other objects involved in the problem of wastewater, it is required to make new, more effective and cheaper reagents allowing solving the assigned tasks.

In various industrial processes require the separation of the liquid and solid phases (thickening, filtration, centrifugation, flotation, etc.). As in the case of water purification from suspended solids, and the concentration and phase separation in suspensions great difficulties arise due to the small particle size and high aggregative and sedimentation stability of the resulting dispersed systems. The intensification of these processes can be achieved by consolidation of the particles in the aggregates under the action of special chemical reagents, coagulants and flocculants and their mixtures. The prospect of increasing consumption of these reagents will be preserved for the future thanks to the simplicity, versatility and reliability of this method.

Low-molecular inorganic or organic electrolytes, leading to aggregation of the particles, referred to as coalesces. A particular case of coalesces are coagulants — hydrolyzed salts, such as sulfates and halides of multivalent cations (aluminum, iron, titanium and others). The flocculants are inorganic or organic high molecular weight compounds contributing to the formation of aggregates by combining multiple particles through macromolecules adsorbed or chemically bound polymer [1-3].

Development and application of new more coagulants that are effective and flocculants in order to accelerate phase separation of dispersed systems with minimum consumption and cost of reagents is an actual problem.

Use of flocculant-coagulant for the treatment of industrial and storm drains on the basis of natural mineral nepheline is known since the 1960s At the moment there is increased interest in the flocculant-coagulant (only since 2000 has about 10 patents on the application of flocculant-coagulant on the basis of nepheline).

N.E. Kruchinina and V. Kim and co-authors developed a method of processing nepheline with sulfuric acid [4], resulting in a liquid aluminum-silicon flocculant-coagulant (ASFC). This method of obtaining aluminum-silicon coagulant, in which the aluminum-silicon raw material is treated with 6 ? 14 % sulfuric acid and the resultant solution was added a stabilizing additive in an amount of 0.05 ? 1.0 *g/l*, which take water-soluble surfactant, polyphosphate, sodium, or urea. The authors recommend to take sulfuric acid with the addition of hydrochloric acid at a weight ratio of (80:20) ? (99:1) accordingly, when the total concentration of 6?14 wt. %. The disadvantages of this method are the insufficient shelf life of the finished product, the complexity of the process, the use of a stabilizing polymer additives and considerable energy.

1. Matrix-Isolated Flocculants-Coagulants

Aluminum-silicon flocculant-coagulant ASFC is one of the few binary compositions comprising only inorganic components: coagulant – aluminum sulfate and flocculant anionic – active silicic acid. The action of the ASFC based on the fact that as a result of interaction of primary components ASFC – coagulant compounds of aluminum and flocculant active silicic acids form complex compounds with a higher flocculation ability of nanosized zeolite like structure with well-developed sorption surface. There is a synergistic effect - increasing the efficiency of the impact resulting from integration of individual processes into a single system. The mechanism of water treatment is realized by volumetric adsorption of pollutants on self-organizing of aluminosilicate complexes.

Sulfuric acid solution ASFC was described as a reagent for the purification of water [5]. The significant disadvantages of the aqueous solutions of ASFC are certain difficulties arising from the carriage, and the limited duration of its use (within a few days the ASFC solution turns into a gel and loses the properties of flocculant-coagulant). For this reason and because of economic inexpediency of transportation solution application aluminum-silicon flocculant-coagulant is concentrated at the sites of production. This factor hindered the practical use of the ASFC practice in industrial wastewater treatment. So important is the search for new reagents of this type and conditions for their stabilization. For comparative characteristics, we obtained the liquid aluminum-silicon flocculant-coagulant from nepheline concentrate by decomposition of sulfuric acid [4, hereinafter referred to as ASFC-1, and a new aluminum-silicon flocculant-coagulant ASFC-2 - white substance in pellets allocated in certain technological conditions of the sulfuric acid solution of flocculant-coagulant ASFC-1.

Our task was to develop a method of obtaining aluminum-silicon flocculant-coagulant is in the form of a crystalline product, which has a higher stability, so the shelf life of the product should be not less than 6 months It needs to be easy to manufacture and cost-effective transport and to have a higher content of active component. So the content of aluminum, calculated as aluminum oxide — 6.8?7.9 % of silicon, calculated as silicon oxide — 10.2?12.0%. Must be efficient and simple in use for wastewater treatment

The task was solved by using in the processing of aluminum (nepheline) of the raw material with sulfuric acid, separation of the liquid phase from the solid and liquid phase dehydration [6]. The processing carried out with concentrated sulfuric acid under conditions allowing obtaining concentrated 20?30%, aqueous solution of flocculant-coagulant. Dehydration of resulting solution carried out at a temperature below the boiling point of water, the method of evaporation under vacuum or high velocity dispersion in high-temperature gas stream of the coolant. The product was dried and separated from the coolant temperature lower than the boiling point of water.

The basis of this method of synthesis, which based on the principles underlying the known method of matrix isolation was developed at the end of the last century. Matrix isolation method allows you to freeze and study of reactive particles with a short lifetime in an inert solid matrix. As is known, the intermolecular interaction is most pronounced in the case of chemically reactive species such as most atoms, free radicals and molecules that are Monomeric only at high temperatures can be investigated in the gas phase only at low concentrations. However, even in such extreme conditions, some particles are so reactive that exist for a very short time after formation; therefore the study of their molecular properties is very difficult.

Matrix isolation method has arisen as attempt to overcome the above difficulties in the study of reactive molecules. It consists of freezing of the studied molecules in a rigid environment (the matrix) at low temperatures. The rigidity of the matrix prevents diffusion of active molecules, i.e., hampers their interaction with other similar particles. In turn, the inertia matrix substances are necessary to prevent the interaction of active particles with the matrix [7]. This situation can be seen when you receive aluminum-silicon flocculant-coagulant.

The use of such technological methods allowed «freezing» and isolating in the matrix of the solid phase components of the flocculant-coagulant. In this method acidic salt of aluminum sulfate and active silicic acid are in nanosized state. Quick active components in the solid state can dramatically reduce the rate of diffusion processes and thus to maintain the activity of the material.

The resulting material was named ASFC-2. It contains: aluminum (in terms aluminum oxide) is not less than 11.1?12.7 wt. %; silicon (in terms of silicon oxide) is not less than 16.3?18.6 wt. %. When dissolved in water to form a 1% solution, its pH was 3.5.

ASFC-1 and ASFC-2 have been testing for water purification on model samples and on samples of waste waters of oil refineries. For this purpose the water samples were added different concentrations of ASFC and samples were bubbled for a certain period of time and monitored the quality indicators by standard methods.

Tests were carried out with the addition of ASFC-1 in the form of a solution and ASFC-2 in the form of a solution or in a powdery state thereby enabling its benefits.

To compare the effectiveness ASFC-1 and ASFC-2 were tested the effect of flocculants-coagulants in the following indicators: turbidity, chromaticity, mass concentration of iron (III), chromium (III) phosphate ions and the concentration of oil in water. The definition of the indicator of turbidity was carried out photometrically by comparing samples of the investigated water with standard suspensions of kaolin. The results of the measurements are presented in figure 1 and table 1.

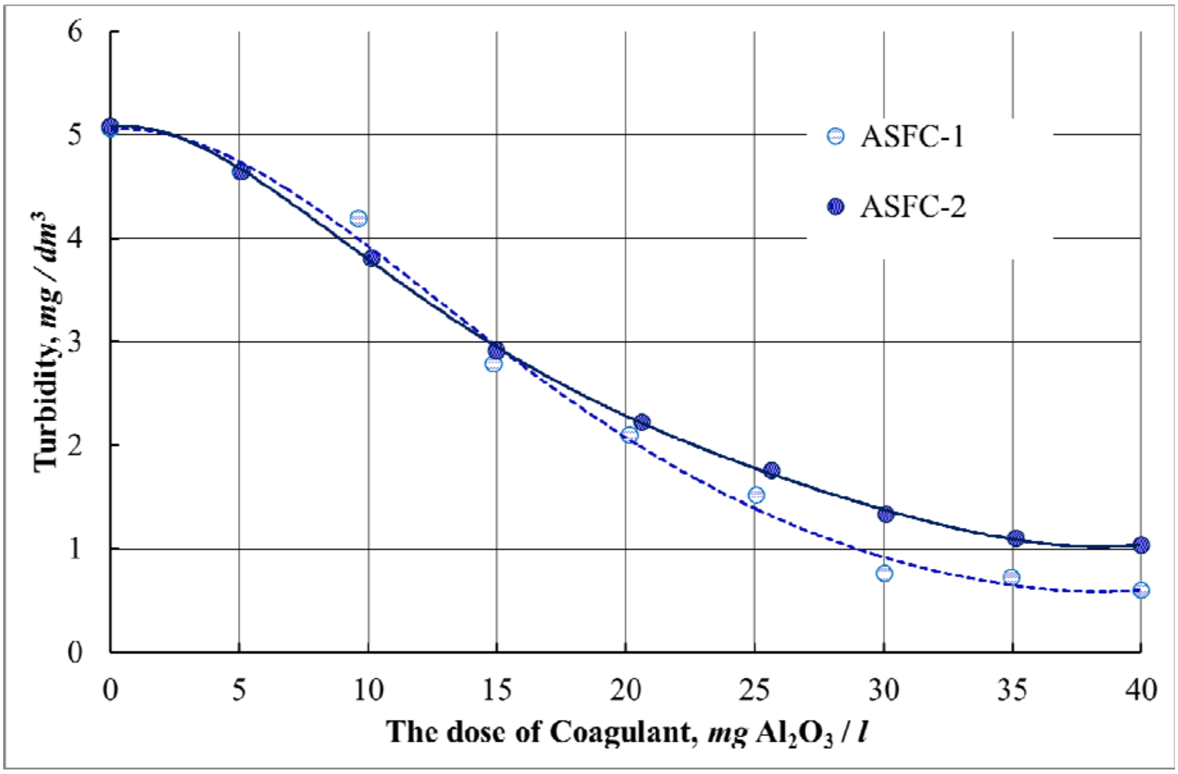

Figure 1. The dependence of turbidity of treated water and the coagulant dosage

The figure shows that the optimum dose of ASFC-1 to achieve turbidity equal to 1.5 *mg/dm*^{3} lies in the range of 23?30 *mg* Al_2O_3/*l*, and for ASFC-2 - 25?35 *mg* Al_2O_3/*l*. These data show that the use of ASFC-2 allows achieving the same purity as when using ASFC-1. From the experimental data on the efficiency of water discoloration determined that when the concentration of the ASFC-1 and ASFC-2, equal to 30?40 *mg* Al_2O_3/*l*, chromaticity of water reaches the maximum permissible concentration.

Comparison of the effectiveness ASFC-1 and ASFC-2 for removing iron from water is presented in table (initial concentration of iron (III) was 5.1 *mg/l*). From the tabular data shows that the degree of purification by 70-80% required a lower dose of ASFC-2 than ASFC-1. This confirms the more efficient use of ASFC-2 compared to ASFC-1. Positive dynamics in the advantages of ASFC-2 is observed in wastewater treatment from pollution by oil products, while ASFC-2 can be used as a pre-dissolved and in powdery state. Thus resulting in new technology in the form of powder ASFC-2 is superior on a number of parameters before a liquid sulfuric acid ASFC-1. In addition, storage and transportation of ASFC-2 is easier and economically more profitable. This implies that the use of its in water treatment is preferable.

Table 1.

The degree of extraction of iron (E, %) depending on the coagulant dosage and settling time

ASFC	Concentration, %	The dose of the coagulant in terms of Al_2O_3, *mg/l*	The time of sedimentation, *min*				
			10	20	30	40	50
ASFC-1	2	12.85	15.70	25.23	35.49	36.23	36.23
		25.28	18.64	27.43	39.16	39.16	41.36
		34.20	23.77	38.42	52.35	54.55	56.02
		42.80	55.14	63.36	67.10	70.09	72.34
		64.30	70.09	75.32	78.32	81.31	81.31
ASFC-2	2	5.80	34.17	42.29	44.73	49.61	51.24
		13.92	42.30	45.55	56.92	65.05	68.30
		23.20	58.55	70.74	78.87	84.55	86.99
		46.40	82.12	90.89	91.87	91.06	91.87
		69.60	83.74	91.87	93.49	93.49	92.68

As shown by experiments the resulting material can be stored for a long period of time. During the time warranty period of storage 0.5 years we did not observe significant changes in the properties of the material. For individual samples was observed saving up to 90% activity for more than 2 years. The aqueous solution ASFC in a concentration of 0.1 to 2.0% is stable for a relatively long time. For effective cleaning of reagent water are required in much smaller quantities. An important feature is the possibility of using powdered ASFC in water purification from oil products and heavy metal compounds.

2. Development of Technology for Matrix-Isolated Flocculants-Coagulants

Further development work on the improvement of industrial production technology ASFC has identified a number of significant disadvantages of this method. These disadvantages are the complexity of the process of obtaining aluminum-silicon flocculant-coagulant, multistage, considerable costs of the energy and necessity to use expensive equipment for quick drying of the solutions. In this regard, the task of further development was to create a simple and fast method of obtaining aluminum-silicon flocculant-coagulant with a pre-defined ratio of the active component in terms of aluminum oxide and silicon oxide; to use it in a crystalline powder form; to have constant composition; to be highly stable; to be easy use for water treatment.

The task of receiving the flocculant-coagulant as a compositional reagent was solved by solid-phase mixing of the initial components [8]. As initial components used aluminum sulfate, sodium sulfate (anhydrous) and the sodium hydrogen sulfate or aluminum sulfate and sodium hydrogen sulfate or aluminum sulfate, sodium sulfate (anhydrous) and concentrated sulfuric acid (96%). Then on the 2nd stage was to the obtained dry mixture by adding fine ground solid sodium silicate ("Monasil" is a liquid glass in the dry state) with module 1.5?3.0 while stirring. Obtained mixture had the following ratio of components respectively for the first option parts by weight: 3.4:2.1:1.4:1, or for the latter parts by weight: 3.4:1.4:1 or to a third embodiment parts by weight: 3.4:2.9:0.6:1. This produces a dry powder flocculant-coagulant with the concentration of the active components 57?75%.

The technical result from the above combination of features is achieved by using the ASFC components in different ratios is a product with pre-set parameters of the content of active components in terms of oxide of aluminum and oxide of silicon that allows you to receive the flocculant-coagulant with the most effective composition for water purification with different types of contaminants.

The positive effect is achieved by the fact that the final product is a crystalline substance characterized by high stability (shelf life at least 12 months), ease of obtaining and economical transportation. In addition when natural products were obtained from nepheline raw materials and from sufficiently large amount of solid waste constitute the insoluble portion of nepheline concentrate. In this regard the technology of processing nepheline raw materials has problem of washing the resulting solid phase from technological solutions and to its subsequent disposal. Obtained by the proposed method the product has a name ASFC-3. The effectiveness of the ASFC-3 was tested on such factors as the color of water, the content of phosphate ions, the content of Cu (II), etc.

Comparison of the effectiveness of flocculants-coagulants ASFC-2 and ASFC-3 at the waste water treatment facilities of Perm (Russia) on the parameter “color” is presented in figure 2. Presented data shows that aluminum-silicon flocculant-coagulant ASFC-3 was obtained by the new method. The effectiveness of the product is not inferior to the ASFC-2 derived from nepheline raw materials.

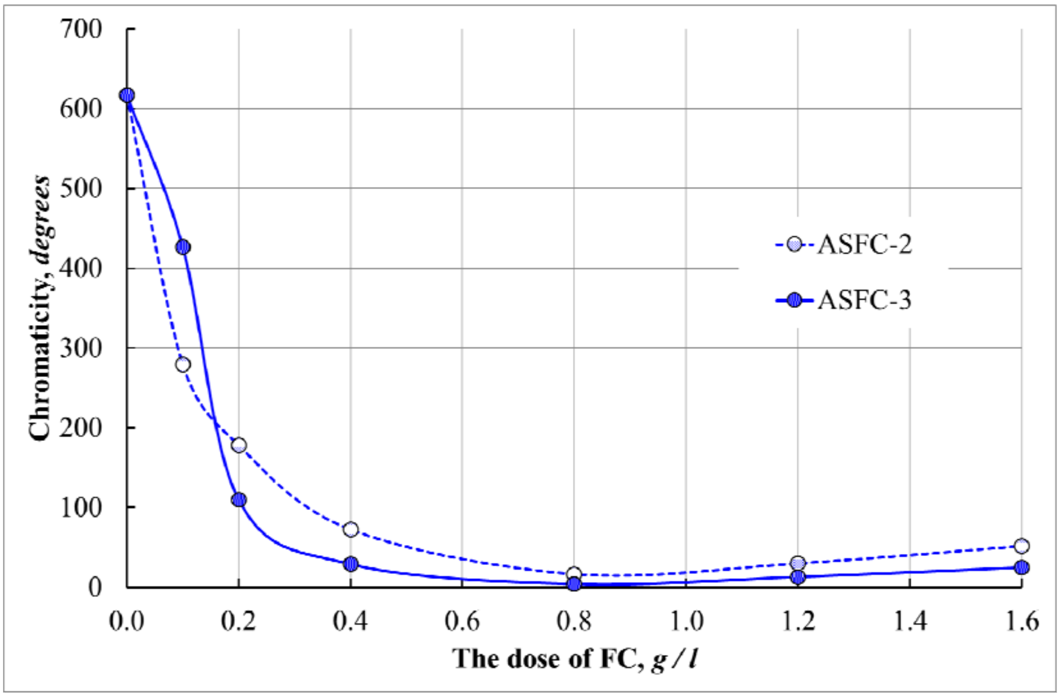

Figure 2. Presents the dependence of the chromaticity of the treated water on the dose of flocculant-coagulant

We compared the effectiveness of coagulants ASFC-2 and ASFC-3 at the waste water treatment facilities of phosphate ions in Perm (Russia). The data obtained are presented in figure 3. Comparison of the efficiency of coagulants

ASFC-2 and ASFC-3 at in purification from ions of copper (II) of the waste water treatment facilities of Perm (Russia). The data obtained are presented in figure 4.

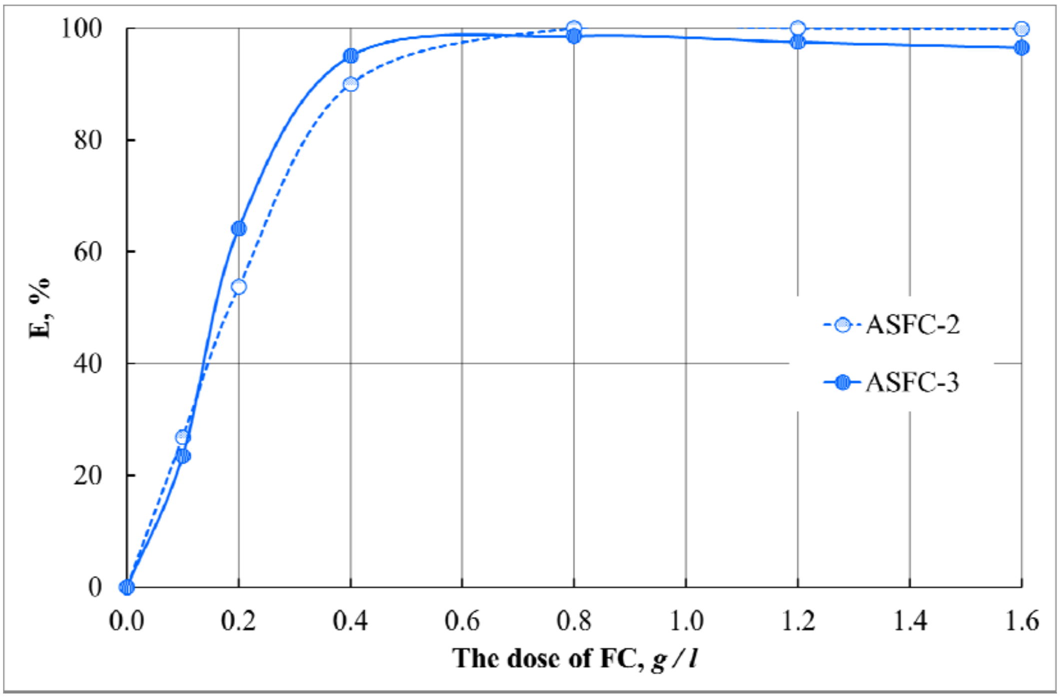

Figure 3. The dependence of the degree of extraction phosphate-ions on the dose of flocculant-coagulant

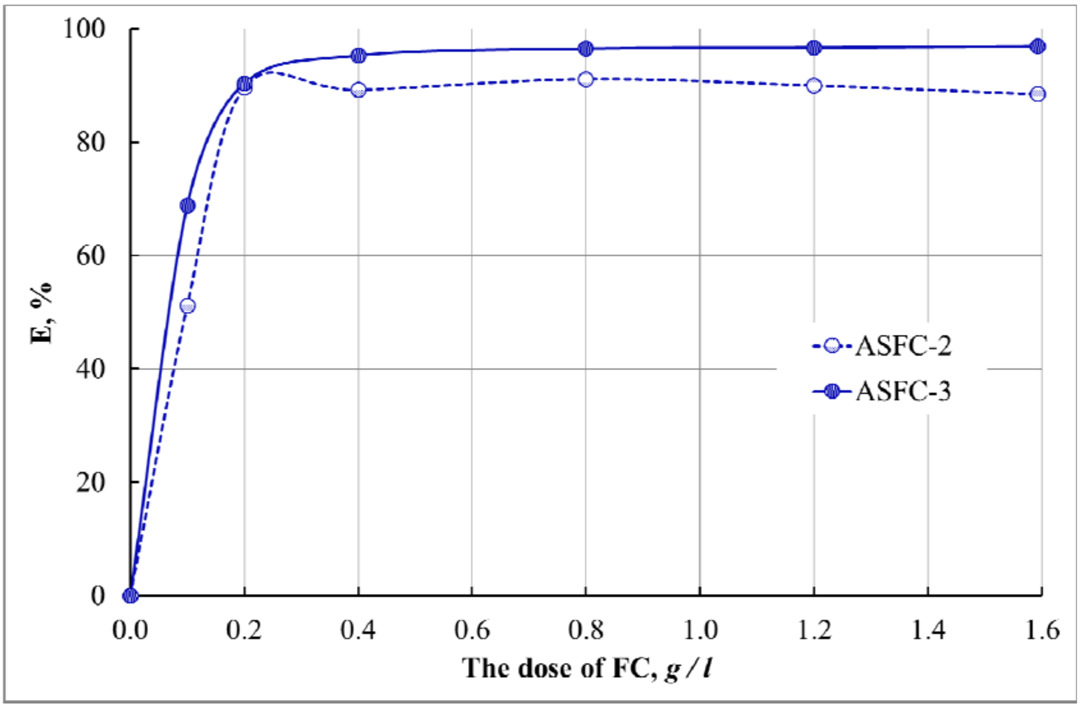

Figure 4. The dependence of the degree of extraction of copper (II) on the dose of flocculant-coagulant

From all data presented above shows that ASFC-3 is not inferior by the effectiveness of action to the product obtained from natural nepheline raw materials.

3. Comparison of the Properties Developed Flocculants-Coagulants with Existing Analogues

The objects of the research were the following manufactured industrial products:

ASFC – aluminum-silicon flocculant-coagulant, produced in accordance with the technical documentation developed by the authors.

AHC – the aluminum hydroxochloride ($Al(OH)_{(3-m)}Cl_m$, m≈0.8, the content of the basic substance – 95%);

AS – aluminum sulphate $Al_2(SO_4)_3 \cdot 18H_2O$, content of the basic substance – 96%.

For example, during the spring floods period the water of the city and Gaiva-river (Perm region, Russia), were compared of the effectiveness of flocculants-coagulants. In Figures 5 and 6 are shown properties of water after chemical treatment. Recalculation of doses of coagulants on the amount of active oxides in the calculation of commodity products was carried out as follows: The required dose of the flocculant-coagulant needed for effective purification of the water was 15 *mg* $(Al_2O_3+SiO_2)/l$ of purifying water. The appropriate doses compared flocculants-coagulants were: ASFC - 130 $g/м^3$ of water; AHC - 32 $g/м^3$ of water; AS - 100 $g/м^3$ of water.

It is seen that the ASFC is more effective than an aluminum sulfate and aluminum hydroxochloride.

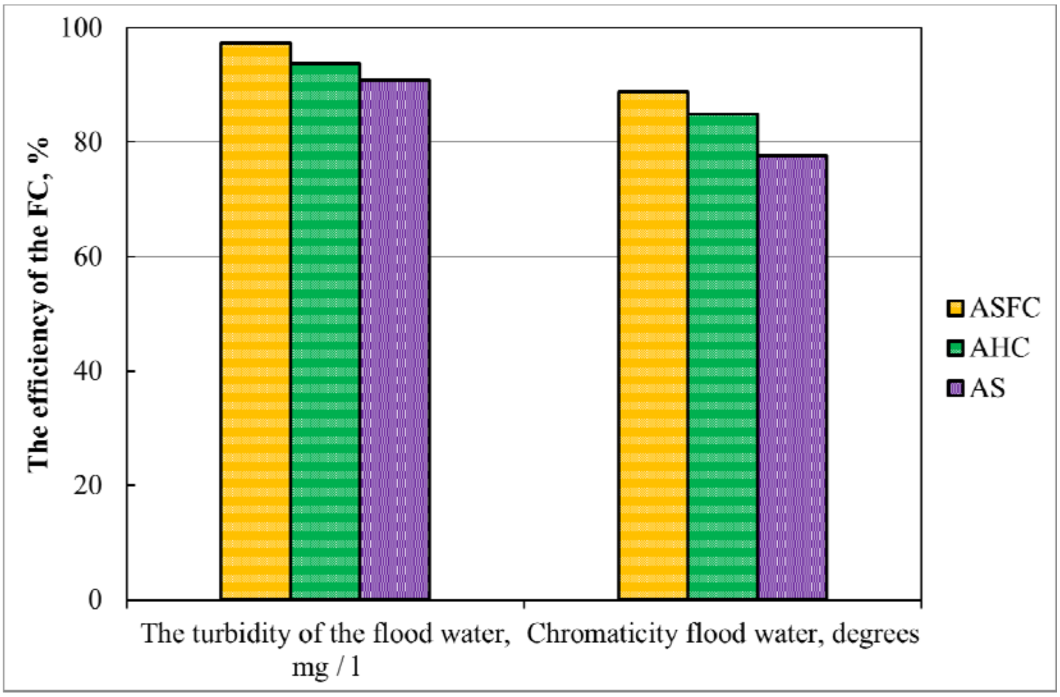

Figure 5. Comparison of the flocculants-coagulants efficiency for flood water.

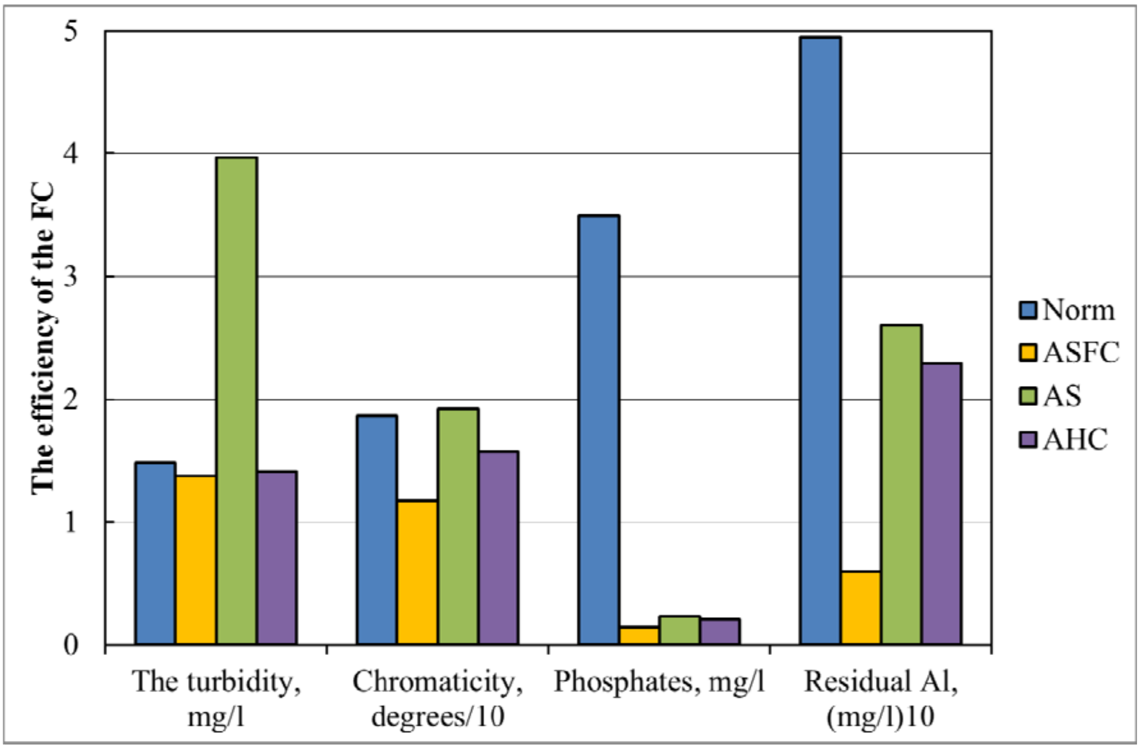

Figure 6. Comparison of the coagulating action effectiveness of ASFC, aluminum sulfate (AS) and aluminum hydroxochloride (AHC). The tests were conducted on the waste water taken at water treatment. The results are given for the content of the coagulant at doses of 15 *mg* Al_2O_3/*l* of water.

A particular challenge is the treatment of drinking water intakes and water treatment plants. In this regard the tests were conducted using the flocculant-coagulant ASFC, in the purification of river water entering from the water intake station. The results of these tests are presented in table 2.

Table 2.

The test results of flocculant-coagulant ASFC in comparison with existing in the Russian Federation sanitary rules and regulations

Index	Standard	Influence of ASFC
Parameters for which the experimental data		
Hydrogen ion exponent, pH	6?9	Remains within the normative values
Aluminum, *mg/l*	0,5	Remains within the normative values
Iron, *mg/l*	0.3	Falls below the standard values Soluble compounds are formed from the components of the flocculant-coagulant (FC)
Chemical oxygen demand (COD), *mg* O_2/*l*	15	Falls below the standard values
Chrome, *mg/l*	0.1	Cr(III) - Falls below the standard values Cr(VI) - Falls below the standard values
Copper, *mg/l*	1.0	Falls below the standard values Soluble compounds are formed from the components of FC
Petroleum products, *mg/l*	0.3	Falls below the standard values
Indicators for which further has an effect of ASFC		
Total hardness, *mEq/l*	7	Falls below the standard values Soluble compounds are formed from the components of FC
Strontium, *mg/l*	7	Falls below the standard values Soluble compounds are formed from the components of FC
Barium, *mg/l*	0.7	Falls below the standard values Soluble compounds are formed from the components of FC
Sodium, *mg/l*	200	Are introduced together with FC
Fluorides, *mg/l*	1.5	Falls below the standard values Soluble compounds are formed from the components of FC
Sulfates, *mg/l*	500	Are introduced together with FC

The data represent averaged values obtained for the concentration range ASFC per 10?40 *mg* Al_2O_3/*l* of treated water. As regulatory parameters presents the data existing in the Russian Federation sanitary rules and norms. The obtained results indicate the possibility of using the flocculant-coagulant ASFC, including diversion of water for purification in the preparation of drinking water

4. Synthesis and Properties of Iron-Containing Flocculants-Coagulants

Among known agents for water treatment there is a specific class of iron-containing coagulants. From iron salts is the most common iron (III) sulphate and iron (III) chloride. Iron salts have better coagulating properties in the pH range 3.5?6.5 and 8?11. Discoloration of water is better occurs at pH 3.5?5.0. Iron salts preferably should be used in the purification of turbid hard water with high pH value, as well as in wastewater treatment [3]. They eliminate the smells and odors due to hydrogen sulfide to remove arsenic compounds, manganese, and copper, also they promote the oxidation of organic compounds. In comparison with aluminum compounds, iron compounds can be used in the purification of water with salt composition and different pH values, can have a better effect at low temperatures, can characterized by high strength and hydraulic dimensions of a cereal.

It should be noted the increased corrosive effect on process equipment as disadvantages of iron (III) compounds as coagulant. Has been formed soluble complexes with strong color in the interaction of iron ions with some organic compounds are. It is necessary to apply lime and chlorine to oxidize iron into the trivalent state when individual iron (II) salts uses as a coagulant. Otherwise we are observing a strong slowdown in the flocculation. However a synergistic effect can be appeared if you combine the coagulating action of salts of iron with the flocculation action of the silica by an analogy with composite flocculants-coagulants such as ASFC. Thus it is possible to enhance the dignity of coagulants based on iron salts and to reduce their disadvantages.

The purpose of this study was to develop of method of obtaining iron-siliceous flocculant-coagulant (hereafter ISFC) with a predetermined ratio of the content of active components in terms of oxide of iron (II) and silicon dioxide. The product must be in the form of crystalline powder, must have a constant composition and high stability. The storage period should be not less than one year. The resulting product should be cost-effective transport and application for simpler and more efficient purification of water from pollution. The task was solved using the methods described in section 2, in particular using approaches matrix isolation of active components. Synthesis of iron-silicon flocculants-coagulants was carried out by mixing the starting components. On the 1st stage as initial components used ferrous sulfate (II) ($FeSO_4 \cdot 4H_2O$), sodium sulfate anhydrous (Na_2SO_4) and concentrated sulfuric acid (96%), or ferrous sulfate (II) and sodium hydrosulfate ($NaHSO_4 \cdot H_2O$). Then on the 2nd stage anhydrous sodium silicate ("Monasil") with module 1.5?3.0 was added to the resulting dry mix under continuous stirring. The ratio of the components is maintained at: 1.5:2.1:0.6:1 (mass parts), either: 1.5:1.4:1 (mass parts) respectively. The result is a dry powder flocculant-coagulant with the concentration of the active components of 45?48% [9]. Depending on the anticipated applications the obtaining of Iron-silicon flocculant-coagulant lead by the mixing of the source components in the form of dry powders to produce different ratios of the active components.

The obtained flocculant coagulant ISFC includes the sparging or mechanical stirring of the flocculant-coagulant and separation of the resulting precipitate. The achievable positive effect is that the resulting product is a crystalline substance having high stability (shelf life at least 12 months), ease and economy of transportation. The introduction of the product in the purified water is provided in the form of powder or 0.1?1.0% aqueous solution to create a concentration of 0.09?0.8 *grams* of the flocculant-coagulant to 1 *liter* of treated water.

The technical result from the above combination of features is achieved by the use of components of ISFC in various proportions. The result is a product with a predefined content of iron (II) oxide and silicon oxide. This allows obtaining a composite flocculant-coagulant with the most effective composition intended for water purification with different types of contaminants.

The results obtained is illustrated by examples of tests on model and real contaminated waters, which are presented in table 3

Table 3.

The test results flocculant-coagulant ISFC on model and on real contaminated waters.

Remove the impurity	Impurity concentration	Content of ISFC		Bubbling time by air	Time of sedimentation	Water purification degree, %	Type of the investigated water body
	mg/l	*g/l*	*mg* FeO*/l*	*minute*	*minute*		
Cu^{2+}	5.0	0.1?0.2	6.3?12.5	15	20-30	88?98	Artificial sample
Cu^{2+}	1.43	0.2?0.4		15	30	84?88	Waste water of industrial enterprises
V (V)	1.93	0.1?0.2	6.3?12.5	15		80?90	Waste water treatment plants
Cr^{3+}	1.2		4.4?5.5	15	40	95?99	Artificial sample
Cr (VI)	0.4		0.07?0.09	15	30	90?99	Waste water treatment plants
Turbidity	14.3	10	20	15	30	90	Waste water treatment plants
Petroleum content	50.5	1		5	5	90?98	Storm runoff tank farm

CONCLUSION

As a result of the conducted researches the following facts. The flocculant-coagulant ASFC and ISFC are a composite of powdered reagents are white or gray in color, soluble in water, stable during storage 0.1?5% aqueous solutions with an acid reaction medium.

ASFC compared with aluminum sulfate has the following advantages:

- during the purification of natural waters is increased, the content of residual aluminum in purified water is decreased, the removal efficiency of turbidity, chromaticity and permanganate oxidizability at low temperatures reduced the dose ASFC comparable with aluminum sulfate at 20?25%;

- the dose of ASFC by 25?30% reduced in wastewater treatment, the efficiency of purification from oil products, dissolved organic substances (COD), ions of heavy metals is increased.

ASFC is recommended to be used instead of aluminum sulfate on existing and newly designed treatment facilities.

ASFC without making additional flocculants can be used in common with separation of the products of coagulation of contaminants in natural and waste waters by filtration and pressure flotation.

ISFC compared with the iron compounds has the following advantages:

ISFC provides getting iron-silicon flocculant-coagulant with a predetermined ratio of the content of iron oxide (II) and silicon oxide in the form of a crystalline powder, possessing a constant composition and high stability (at least one year), fuel efficiency in transportation and efficiency in the application of effective water purification from contamination

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