Matrix-isolated Nanocomposites—Alumina-Silicon and Iron-Silicon Flocculants-Coagulants

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Abstract: This paper presents the research results of cleaning industrial oil-containing wastewater using new nanocomposite flocculants-coagulants ASFC (aluminum-silicon flocculant-coagulant) and ISFC (iron-silicon flocculant-coagulant). The authors made a comparison of new products, with coagulants, widely used for these purposes: aluminum sulfate and iron sulfate. With their help, methods of treating wastewater of industrial enterprises were tested, as well as storm water containing oil products. The concrete examples of the water treatment are the use of new alumina-silicon, and iron-silicon flocculants-coagulants. The authors have developed and patented technology for production of flocculants-coagulants of this type in a solid form. For obtaining such composite materials, authors have used the matrix isolation method of acting active components. This paper assesses the effectiveness of the action flocculants-coagulants ASFC and ISFC on real industrial wastewater. New composite materials are compared with the known analogues.

Key words: Matrix isolation, nanocomposites, flocculants-coagulants, wastewater, water treatment.

1. Introduction

Nowadays oil and oil products are ones of the main types of wastewater pollution. The sources of the wastewater contain oil and products of oil companies processing such as manufacturing, petroleum products delivery, place of their storage and use. Another source of wastewater contains oil products of car washes. Such wastewater is one of the most environmentally hazardous objects because they contain toxic petroleum products. MPC (maximum permissible concentration) petroleum products for discharge into the open water reservoirs is 0.05 mg/L and the biological purification plants on their content varies depending on the load, in the range from 2 to 20 mg/L.

In this regard, for cleaning the wastewater from petroleum products, the technological schemes usually used in coarsely dispersed and fine dispersed states include not only mechanical treatment but also coagulation with application of coagulants.

Coagulants, is used either alone or in conjunction with flocculants. One means of enhancing the efficiency of the coagulation treatment of oil-containing waste water, especially at existing treatment plants, is the use of new more effective reagents and compositions on their basis. Among these reagents there is mix of coagulants ASFC (aluminum-silicon flocculant-coagulant) and ISFC (iron-silicon flocculant-coagulant) that contain silicon compounds and exhibit properties, and as a coagulant and flocculant unlike sulfates, aluminum and iron [1-8].

Therefore, there is practical interest of coagulating properties in comparisons of data mixed coagulants, and individual products when used for cleaning different types of oil-containing waste water. These studies were the aim of the present paper.

First ASFC was formed as a liquid aqueous solution, using a method of the sulfuric acid treatment of nepheline [2]. The disadvantages of this product are its small storage time (within a few days ASFC solution turns into a gel and loses the properties of flocculant-coagulant), the complexity of the manufacturing process and the use of stabilizing

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polymer additives, solid waste generation and significant energy consumption. For this reason and also due to economic inexpediency of transportation solution thereof, using ASFC had to be concentrated only in the places of production. This factor ASFC restrained use in industrial practice of wastewater treatment, so it is topical search of new reagents of this type and conditions for their stabilization.

ASFC is one of the few binary compositions which comprise only inorganic components: a coagulant (aluminum sulfate) and an anionic flocculant (active silicic acid). Actions of ASFC based on the interaction of the primary components ASFC (coagulant and flocculant) thus form the complex compounds, which have a high flocculating ability. They are zeolites-like, nanoscale structured with advanced adsorption surface, which provides water purification mechanism. As a result, there is a synergistic effect associated with an increase in their efficiency, which is due to the integration of individual processes into a unified system.

The authors have developed a method of producing aluminum-silicon flocculant-coagulant as a crystalline product that has higher stability. Shelf life of the developed product is more than 6 months. Furthermore, it is effective and simple to use, easy to manufacture and economical transportation has a higher content of active ingredient: aluminum content, expressed as aluminum oxide: 6.8%-12.7%, the silicon content, expressed as silicon oxide: 10.2%-18.6% [4-7].

Synthesis method laid down the principles underlying the known matrix isolation technique, which was developed at the end of the last century. Implementation of this method is based on the fact that the rate of chemical reactions in the gas and liquid phase by several orders of magnitude is higher than the rate of chemical reactions in the solid phase. Similar processing methods are used to isolate and allow freezing in a matrix of solid phase components coagulant-flocculant—acid salts of aluminum sulfate

and active silicic acid, which is in nanodispersed state with a particle size of 2-10 nm. Quick transfer of active ingredients in solid state can dramatically reduce the rate of diffusion processes and thus preserve the activity of the material.

Among of the known reagents for water treatment there is a separate class of iron coagulants. Among of the iron salts the most common materials are iron sulphate (II) and iron chloride (III). Iron salts have better coagulating properties in the range pH 3.5-6.5 and 8-11. The best discoloration of the water should be carried out at pH 3.5-5.0. Iron salts are preferably used in the purification of hard turbid waters with a high pH, as well as wastewater treatment [1]. They allow eliminating odors and off-flavors due to the presence of hydrogen sulfide to remove the compound of arsenic, manganese, copper, and also promote the oxidation of organic compounds. In comparison with aluminum salts, iron salts may be used in the purification of water with a variety of saline compositions and different pH values, they have a better effect at low temperatures, characterized by high strength and hydrodynamic size of flakes. Application of synthesis methods which are used for producing aluminum-silicon flocculants coagulants with the matrix isolation techniques of active ingredients, has allowed creating similar products, based on iron compounds [7].

2. Methods and Research Facilities

In this paper we used well known standard methods of analysis and studies [1, 9]. Quantitative determination of oil products was carried out by IR spectroscopy, with application of device for determining of oil products, CN-2 model. The method is based on separation from the water emulsified and dissolved oil components, with subsequent extraction with carbon tetrachloride. Oil products are separated from the associated organic compounds of other classes by chromatography on a column filled with alumina. Later we quantitatively determined their

mass concentrations using absorption intensity of C-H bonds in the infrared region of the spectrum on the device CN-2. The range of detectable concentrations of oil products was between 0.02 to 2.00 mg/dm³ [9]. Interfering effect of other substances present in the sample of water is eliminated in the process of sample preparation.

The efficiency of the coagulants was determined by the test of coagulation in a laboratory installing “Drop”, with mechanical stirring under the scheme: mixing, flocculation and sedimentation.

Mixing was carried out for one minute at an average velocity gradient $G = 500 \text{ s}^{-1}$, flocculation during 5 minutes at $G = 50 \text{ s}^{-1}$. Settling was carried out for 5 minutes to extract contaminants having a hydraulic size more than 0.03 mm/s.

Experiments were performed on real wastewater which contained oil products, the characteristics of this water are shown in Table 1.

Wastewater oil refining factory (Yaroslavl, Russia) was a muddy yellowish-greenish liquid with oil products odor. Storm water of oil depot, was a light

gray liquid, and wastewater from carwash had a dark gray color. Both of these wastewater does not become lighten during prolonged storage, and had a strong odor of oil products.

There have been studies of properties of flocculants, coagulants ASFC and ISFC. For comparison, standard products—aluminum sulphate (AS) and iron sulfate (II) (IS, iron vitriol) were taken. Characteristics of studied coagulants are presented in Ref. [8].

3. Effectiveness of Composite Reagents ASFC and ISFC for Cleaning Oil-containing Wastewater

3.1 Comparison of the Ability of Coagulating Reagents in the Purification of Oil Refining Factory Wastewater

Experiment results for determination of the effectiveness of reducing turbidity, color and oil products content in the wastewater, oil refining factory, using coagulants containing aluminum, depending on their doses shown in Fig. 1a. As can be seen from the

Table 1 Characteristics of oil-containing wastewater used as experimental facilities.

Parameter	Total wastewater oil refining factory (NPZ)	Wastewater of carwash	Stormwater of oil depot
pH	7.48	6.92-7.1	7.48-7.6
Oil products	5.5	50.5-139.5	46.7-83.0
Turbidity, mg/L	47	74.8-106.9	84.0-154.0
Chromaticity, degrees*	301	83	47

* Chromaticity is measured in degrees of chromium-cobalt scale.

Fig. 1 The dependence of turbidity (1, 2), the color (3, 4) and the content of oil products (5, 6) in the wastewater, oil refining factory, depending on the dose of reagents: Aluminum sulfate (a) or iron sulfate (II) (b) (1,3,5) and the flocculant-coagulant (2,4,6). a—ASFC; b—ISFC.

Fig. 2 Dependence of turbidity and color of wastewater oil refining factory off pH. ISFC dose was 30 mg/L, the duration sedimentation process was 10 minutes.

data, ASFC and AS have a close coagulating activity and provide an almost equal reduction in turbidity and the content of oil products at independent application, at doses of 10-20 mg/L (based on alumina). However ASFC provides greater reduction in color than the SA in the entire range of reagents tested doses from 5 to 46 mg/L (Fig. 1).

While using the iron coagulants, turbidity and color of wastewater oil refining factory is reduced to the same degree as the flocculant-coagulant ISFC and iron vitriol. The purified water consists of oil products that are much lower in the case of using ISFC than iron vitriol (Fig. 1b). The residual oil content in the purified water is also below during coagulation using ISFC, than by using iron vitriol, at a dose of coagulating agents 5 mg/L. The optimum pH value is in the application of ISFC 8.3-8.7, as is shown in Fig. 2.

Comparison of the coagulating ability has shown that for aluminum and iron-containing coagulating agents, to provide the same effect, purification, waste water, oil refining factory, need 2 times smaller doses of iron coagulating agents (5 mg/L) than the dose of aluminum-coagulating agents (10 mg/L).

3.2 Comparison of the Coagulating Ability of Coagulating Agents in the Purification of Wastewater Car Wash

The experimental results obtained in the evaluation

of the effectiveness of composite flocculants-coagulants ASFC, ISFC and basic coagulants—aluminum and iron (II) sulfates for treatment carwash wastewater are shown in Fig. 3a. As follows from Fig. 3, flocculant-coagulant ASFC in a greater degree reduces turbidity of wastewater than AS, with the same residual oil products content. In this case, coagulant ISFC, in a greater degree reduces the turbidity and oil products content than IS (Fig. 3b).

3.3 Comparison of the Coagulating Ability of Coagulant in the Purification of Oil Depot Storm Wastewater

Experiments of storm wastewater treatment of the oil depot showed high efficiency of flocculants-coagulants, as well as in wastewater treatment of oil refining factory and carwash. Thus it is possible to ensure maximal reduction of oil products content and suspended substances in the coagulant doses of 5-10 mg/L (Fig. 4a). By efficiency, coagulant ASFC operates better than CA (Fig. 4a). However, coagulant-flocculant ISFC provides a significantly lower oil products content in the purified water than IS, while reducing the turbidity of treated water at a dose of only 5 mg/L (Fig. 4b).

Aluminum sulfate (A) or iron sulfate (II) (B) (1, 3) and flocculant-coagulant (2, 4), A—ASFC (at pH 6.4-7.0); B—ISFC (at pH 9.8-10.4).

3.4 The Discussion of the Results

The results shown in Figs. 1-4 are well described by an exponential dependence:

$$P = P_0 - A + A \cdot e^{-\frac{c \cdot \ln 2}{C_{0,5}}}$$

where, P —the measured value of wastewater (turbidity, oil products concentration, color); A —the maximum amount of reduction of the measured parameter under the action of the flocculant-coagulant; c —dose of coagulant-flocculant in wastewater (mg/L); $C_{0,5}$ —dose of flocculant coagulant in the waste water, which achieves a reduction in the magnitude of the measured parameter to 50% of the initial value. From

this we can estimate the parameter A :

$$A = 2 \cdot (P_0 - P(C_{0,5}))$$

where, $P(C_{0,5})$ —the value of the measured parameter at a dose of the flocculant-coagulant in wastewater equal to $C_{0,5}$.

The results of the experimental data using the above equations are presented in Table 2. Based on the data it is possible to make an objective assessment of the impact of each of the reagents used. It is also possible to conclude that the effect of different reagents on various wastewaters is apparent due to differences in the chemical composition of the oil products contaminants present in the different wastewater.

Fig. 3 Dependence of turbidity (1, 2) and oil products content (3, 4) treated of wastewater carwash, depending on the dose of reagents.

Fig. 4 The dependence of the quality of treated water: turbidity (1, 2) and oil products content (3, 4) after the coagulation of wastewater oil depot in a dose dependent coagulants.

Table 2 Parameters that describe the impact on the wastewater of different companies that contain oil products and the resulting for standard coagulants and for developed composite flocculants-coagulants.

	Type of coagulant	Turbidity		Oil Products		Color	
		$C_{0.5}$	$A, \%$	$C_{0.5}$	$A, \%$	$C_{0.5}$	$A, \%$
Wastewater oil refining factory (Yaroslavl)	AS	7.37	37.0	1240	48.6	5.84	24.5
	ASFC	5.22	48.3	8.26	58.3	5.56	37.8
Wastewater carwash	AS	9.76	53.4	2.36	89.9		
	ASFC	9.79	67.5	1.72	98.2		
Wastewater oil depot	AS	2.41	18.2	2.79	26.6		
	ASFC	2.36	30.2	2.38	40.1		
Wastewater oil refining factory (Yaroslavl)	IS	4.29	54.9	2.13	22.1	3.09	29.5
	ISFC	3.32	74.4	1.75	53.4	2.23	28.7
Wastewater carwash	IS	3.17	20.5	0.93	94.3		
	ISFC	4.11	30.0	0.81	96.3		
Wastewater oil depot	IS	1.58	44.8	2.74	16.8		
	ISFC	1.30	63.0	2.68	32.2		

4. Conclusion

It was shown experimentally that the composite flocculants-coagulants ASFC and ISFC are the most effective reagents for the purification of oil-containing wastewater from those reagents which have been tested—AS, IS, ASFC and ISFC. The composite flocculant-coagulant ASFC is more effective for color reduction in wastewater in comparison with ISFC. This is due to lack of coloration of aluminum compounds as compared with iron compounds. The composite flocculant-coagulant ISFC is most effective material to reduce the oil products content in the wastewater.

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