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Method of Water Purification Using Sulfate-Chloride Aluminum-Iron Coagulant from Substandard Bauxite

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One of the main methods of natural water and wastewater treatment is coagulation. Water purification from suspended solids is very difficult due to their small particle size and flocculation stability. In many cases, enhancement of these processes can be achieved by enlargement of the particles in flocculence under the action of flocculants, especially mixtures (mixing) of them. Both pure chemical salts and mineral raw materials are used as initial raw materials for flocculants. The technique of obtaining coagulant from mineral raw materials (alunite, nepheline, slag, ash and clay, bauxite) and unconditioned natural ores that are considered technical waste is much cheaper than obtaining reagents from pure chemical salts. A technology is presented that simultaneously solves the problem of obtaining low-cost, cost-effective alumina iron coagulant and reducing bauxite mining waste. This information is confirmed by the study of the physicochemical and thermodynamic conditions of the process, the validation of mathematical models, and estimated data on the efficiency of industrial wastewater treatment when a given coagulant is applied. This scientific paper presents original research on the development of coagulants-flocculants based on sulfate-chloride alumina coagulants and substandard bauxite. The novelty of the work lies in the selection of substandard materials for the extraction of effective coagulant products.

Keywords: water treatment, recoagulant, flocculant-coagulant, mixed flocculant, sulfate-aluminum chloride flocculant, off-specification bauxite, natural flocculant.

Introduction

Due to the constantly increasing volumes of various industrial wastewater (Bijekar et al., 2022, Koul et al., 2022), there is a continuous emphasis on the development of flocculating reagents for its treatment, both from natural flocculants, which are raw materials of natural origin, and from chemical inorganic flocculants, which are components of mineral raw materials (Zouboulis and Avranas, 2000).

Natural flocculants are desirable in terms of their low environmental impact and low cost, but they are not profitable for treating large volumes of industrial wastewater. For this reason, the most effective is the use of chemical flocculants (Scholz, 2016), the most important selection criteria being low cost and reduced impact on environmental components.

This paper presents research data on the development and creation of low-cost technology for producing chemical flocculants from substandard bauxite.

The purpose of the scientific research is to prove the possibility of using substandard bauxites as raw materials for producing a coagulant, as well as to determine the technical parameters of the coagulant production process and to investigate the possibility of using a mixed sulfate-alumina-chloride-ferric coagulant for wastewater treatment.

The difference of this research from already known ones is in obtaining the development and creation of a technology for low-cost production of chemical coagulant from substandard bauxite due to low economic costs for the technology of its production, profit from the use of waste and reduction of costs for the maintenance of landfills for these wastes. Also in this scientific research, optimal conditions for obtaining coagulant from natural bauxites "Krasnooktyabrskoe deposit", (Kazakhstan) are developed.

Analysis of literature data and problem statement

Efficient treatment of industrial wastewater and implementation of water-saving technologies (recycled water supply) are fundamental requirements for environmental users. The use of coagulants in industrial wastewater treatment is an essential step in wastewater treatment systems (Wei et al., 2018). The coagulation process itself is used to remove suspended particulates along with other contaminants, and the advantages of this method are simplicity, high efficiency, and low energy consumption.

Industrial wastewater contains many impurities, and both dissolved and insoluble forms may be present in the water. The insoluble portion can be divided into colloids and suspended solids. The suspended matter can be removed by filtration or sedimentation processes, but removal of the colloidal portion requires the use of flocculants.

In the past two decades, natural flocculants (eggshells, rice starch, chitosan, and banana peels) have become widespread worldwide, with attributes such as biodegradability, environmental friendliness, low cost, and ease of availability.

However, natural flocculants, although economical and environmentally friendly, are less preferred than inorganic flocculants, especially for treating large volumes of wastewater in the mining and processing industries (Gautam and Saini, 2020).

Pure chemical salts containing aluminum (Colvin and White, 1991) or iron can be used as raw materials for inorganic flocculants, and bauxite, nepheline sienite, clay, kaolin, alumina-containing materials-TPP ash and residual claystone can be used as inexpensive raw materials. The activity of these flocculants is evaluated by the content of water-soluble oxides (Al_2O_3 and Fe_2O_3) (Panhwar et al., 2021).

Inorganic chemical flocculants can be divided into simple flocculants, which contain either aluminum or iron salts as active ingredients, and mixtures of these salts (Yang et al., 2016).

The raw materials used to obtain simple coagulants are, for example, aluminum sulfate, which is obtained mainly from expensive aluminum hydroxide, or natural raw materials such as alunite ore, kaolin, nepheline, and other aluminosilicates, which are decomposed with sulfuric acid. Aluminum hydroxochloride is obtained by dissolving aluminum oxide or aluminum hydroxide in a stoichiometrically insufficient amount of hydrochloric acid or aluminum chloride (aluminum-containing coagulant). Anhydrous chlorite iron is obtained by chlorinating steel scrap at 700°C, and also as a byproduct of the production of metal chlorides by high-temperature chlorination of ores. Iron sulfate is obtained by dissolving iron oxide in sulfuric acid (iron-containing coagulant).

An analysis of the obtaining and application of simple coagulants shows that the technological process of obtaining them is multi-step and characterized by high material costs. Wastewater treatment by application of simple coagulants does not always meet the specified requirements (Yang et al., 2016).

Research on the production of mixed flocculants has become widespread only relatively recently. For many years, mixed flocculants have been referred to as mixtures of pure salts of aluminum and iron, representing alum-iron, an aluminum salt without iron, and iron-aluminum flocculants (sulfate and chloride), an iron salt without aluminum (Tahraoui et al., 2023, Kadooka et al., 2016, Sheffe, 1958).

Water treated with mixed flocculants usually does not produce precipitates, even at low temperatures. This is because flake formation and precipitation are almost complete before filtering.

Mixed flocculants are prepared in advance or by dosing their solutions simultaneously or sequentially into the treated water itself. Mixed aluminum-iron flocculant is prepared from a solution of aluminum sulfate and ferric chloride at a ratio of 1:1 (by weight). The recommended ratio may vary depending on the specific conditions of the treatment plant. The maximum ratio of $FeCl_3$ to $Al_2(SO_4)_3$ when using mixed flocculants is 2:1 by mass.

The use of mixed flocculants can significantly reduce reagent consumption. The components can be introduced separately or pre-mixed mixed coagulant solutions. The first method is more flexible in transitioning from one optimal ratio of reagent to another, while the second method is easier to achieve dosing.

However, it is preferable to use the same salts of aluminum and iron, but in a form where the iron and aluminum are not separated from each other in solution, the typical raw material for this process is bauxite.

These coagulants can be obtained by acid decomposition of bauxite containing water-soluble aluminum and iron compounds: for this purpose, the ore is treated with 60% sulfuric acid in 90% of its stoichiometric volume at 100 to 150°C for 1 to 2 hours. The resulting melt is granulated and dried at 1500–2000°C. The extraction rate of Al_2O_3 and Fe_2O_3 as sulfate in solution was 90%. The obtained coagulant was characterized by the following composition: the application of this technique simplifies the bauxite treatment process, since the operations of precipitation, evaporation, and renormalization of the sulfuric acid solution are eliminated. It was formed by treating montmorillonite clay with mineral acid and contained about 16 g/L Al^{3+} and an acidic solution containing about 6 g/L of divalent and trivalent Fe is described.

Scientific research by scientists who also synthesized coagulants-flocculants based on the use of bauxite was analyzed. In the work (Yang et al., 2016), the prepared PAFC based on bauxite residue demonstrated optimal performance in terms of color and chemical oxygen demand (COD) removal rate. In addition, the combination of bauxite residue-based PAFC and PFC for synergistic coagulation (Gao et al., 2022) of such wastewater demonstrated obvious positive effects. The results of the study (Cheng et al., 2022) confirmed that PAFC obtained at a polymerization pH of 2.5, an Al/Fe molar ratio of 8, and a polymerization temperature of 70°C had the optimal coagulation effect (Krishnan et al., 2018). The grafting effects of PAFC and commercial polyaluminum iron chloride (CPAFC) under different coagulation conditions were compared and it was found that PAFC has excellent coagulation performance and can be used as a simple, potentially low-cost agent for wastewater treatment for industrial purposes.

RNA coagulant (solution of nepheline coagulant), obtained from nepheline and mineral acids (hydrochloric or sulfuric acid), has been certified and patented as a reagent for industrial wastewater. In these studies, it was confirmed that it is the silicic acid present in dissolved form that gives nepheline its special properties, but the use of silicic acid requires more care in the implementation of this technique. The characteristics of nepheline flocculants combine the properties of aluminum sulfide flocculants with those of silicic acid flocculants, greatly increasing the range of action of aluminum sulfide in terms of both temperature and pH. There are methods to produce mixed flocculants by acid treatment of slag, ash, and clay with reduced iron and aluminum content. These methods are reflected in many studies. Methods for obtaining iron-aluminum flocculants from ash and clay from thermal power plants involve leaching of the metal oxides with solutions of sulfuric acid and chloride-containing components, precipitation or filtration of the reaction mass, and heating of the reaction mass by DC or AC with carbonaceous iron alloy electrodes. This technique is also characterized by high material and time costs.

Current analysis of the use of aluminum-containing raw materials indicates that there are a number of sulfuric acid and hydrochloric acid decomposition methods to obtain alumina, but they have not been implemented industrially due to the multistage process, large material flow, and high cost of alumina. In this case, the problems of using off-specification raw materials and storage of aluminum production waste are solved. The preferred raw material in this process is a small amount of off-specification bauxite (a rock composed mainly of aluminum and iron hydroxides, mixed with aluminosilicates, titanium, calcium minerals, and other impurities), from which mixed flocculants can be obtained by decomposition with mineral acids.

This paper presents the results of the development of a technology for the production of mixed sulfate-aluminum chloride-iron coagulant (MSCAIC) obtained from substandard bauxite formed during the mining of aluminum ores.

Materials and methods

Physicochemical study to obtain sulfate-aluminum chloride-iron coagulant from substandard bauxite

In the study, bauxite from the Krasnooktyabrskoe deposit in RK was chosen as a typical substandard bauxite, which includes gibbsite $Al(OH)_3$, hematite α-Fe_2O_3, siderite $FeCO_3$, anatase TiO_2, kaolinite $Al_2Si_2O_5(OH)_4$ goethite FeOOH, and quartz α-SiO_2. Chemical composition, %: $A1_2O_3$ – 41.0; Fe_2O_3 – 25.0; SiO_2– 20.0; CaO – 3.9; MgO – 0.2; TiO_2 – 2.4; Na_2O + K_2O – 0.5.

The completeness of the mineral-acid interaction of red October bauxite and the composition of the final product can be determined by the possibility of chemical conversion processes (by changes in Gibbs free energy values).

Thermodynamic analysis of the interaction reactions between bauxite minerals and hydrochloric and sulfuric acids in the temperature range of 298–473 K confirms that the Gibbs energy does not change much as the temperature increases above 100°C. It is reasonable to assume that the decomposition of the main bauxite minerals occurs at temperatures up to 100°C.

For the mathematical description and analysis of these processes, a mathematical design of experiments based on a five-step four-factor matrix was used.

Study of physicochemical properties of sulfate-alumina chloride-iron flocculants

The study of the physicochemical properties of flocculants was carried out using samples of model solutions of industrial (Mao et al., 2020) wastewater (*Table 1*). The selection of the required amount of flocculant and its correction were made according to the results of the trial tests.

Table 1. *Characteristics of model solutions of industrial wastewater*

Sample number	pH	Content, mg/L		
		Weighed substances	Petroleum products	Chemical oxidation of acid
1	8.2	2824	120	974
2	7.9	2667	160	870
3	9.4	6207	83	1873
4	8.8	4831	46	1402
5	9.1	4040	28	1796
6	8.7	3020	78	1516

Results and Discussion

Physicochemical process for obtaining sulfate-alumina chloride-iron coagulant from substandard bauxite

The main parameter for obtaining the reagent MSCAIC (mixed sulfate-chloride aluminum-iron coagulant) is the value of aluminum and iron extractability in salt and sulfate decomposition in solution, which is explained by the fact that the activity of the coagulant is due to the presence of Al_2O_3 and Fe_2O_3 in it. Therefore, the value of metal extractability is the main output parameter of the four-factor matrix of the plan, and the following factors (*Table 2*) influence the degree of bauxite degradation:

- Leaching temperature, 0°C;
- Treatment time, minutes;
- Acid concentration, %;
- Mass ratio, solution: solid phase.

Private functions describing the influence of the different study factors on the degree of aluminum and iron extraction were obtained. Based on the private level, a generalized function describing the influence of all factors on the degree of Al_2O_3 and Fe_2O_3 extraction was obtained.

The private dependence of the degree of Al_2O_3 and Fe_2O_3 extraction on the individual factors in hydrochloric acid decomposition is described by the equation:

By degree of extraction Al_2O_3

$Y_1 = -55.25 + 1.3X_1$	(1)
$Y_2 = 84 - 0.07(X_2 - 40)^2$	(2)
$Y_3 = 64.7 + 3.4X_3$	(3)
$Y_4 = 72.4 + 0.77X_4$	(4)

By degree of extraction Fe_2O_3

$Y_1 = 40 + 0.3X_1$	(5)
$Y_2 = 60.2 + 0.26X_2$	(6)
$Y_3 = 63.62 + 1.75X_3$	(7)
$Y_4 = 68.0 + 1.8(X_4 - 1.5)$	(8)

Table 2. *Factor space area*

Factor	Level				
	1	2	3	4	5
Hydrochloric acid decomposition					
Temperature, °C (X_1)	85	90	95	100	105
Duration, min (X_2)	5	30	40	50	60
ConcentrationHCl, % (X_3)	2	3	4	5	6
Solution: solid phase (X_4)	1	2	3	3.5	4
Sulfuric acid decomposition					
Temperature, °C (X_1)	85	90	95	100	105
Duration, min (X_2)	5	30	40	50	60
Concentration HCl, % (X_3)	45	50	55	60	65
Solution: solid phase (X_4)	0.5	1	1.5	2	2.5

Based on particular dependencies, generalized equations were obtained:

$$Ygen(Al_2O_3)_{HCl} = (1/76.12) * (-55.25 + 1.3X_1) * [84 - 0.07 * (X_2 - 40)^2]*(64.7 + 3.4X_3) * (72.4 + 0.77X_4), \quad (9)$$

$$Ygen(Fe_2O_3)_{HCl} = (1/71.44^2) * [(40 + 0.3X_1)* (60.2 + 0.26X_2)*(63.62 + 1.75X_3) * (65.3 + 1.8X_4)], \quad (10)$$

During sulfuric acid decomposition, the partial dependencies on the degree of extraction of aluminum and iron are described by the equations:

By degree of extraction Al_2O_3

$Y_1 = 55 - 0.06(X - 97)^2$	(11)
$Y_2 = 51.5 - 0.1X_2$	(12)
$Y_3 = 46 + 0.005(X_3 - 45)^2$	(13)
$Y_4 = 48.5 - 0.25(X_4 - 1)^2$	(14)

By degree of extraction Fe_2O_3

$Y_1 = 96 - 0.5X_1$	(15)
$Y_2 = 58.5 - 0.3X_2$	(16)
$Y_3 = 53.98 - 0.11X_3$	(17)
$Y_4 = 50.49 - 1.7X_4$	(18)

Generalized equation:

$$Ygen(Al_2O_3)_{H2SO4} = (1/47.5^3)* (55.25 - 0.06* (X_1 - 97)^2*[50 - 0.004 * (X_2 - 20)^2] * (46 + 0.005(X_3 - 45)^2 (48.5 - 0.25(X_4 - 1)^2, \quad (19)$$

$$Ygen(Fe_2O_3)_{H2SO4} = (1/47.93^3)* [(96 - 0.5X_1)* [58.5 - 0.3X_2] * (53.98 - 0.11X_3)* (50.49 - 1.7X_4)], \quad (20)$$

According to the analysis of generalized equations, the optimal conditions for bauxite decomposition by hydrochloric acid are as follows:

- Temperature: 90 to 100°C;
- Hydrochloric acid concentration: 5–6%;
- Treatment time 30–60 min;
- solution(liquid): solid phase = 2:1 ratio.

Bauxite decomposition by sulfuric acid:

- Temperature: 85–100°C;
- Hydrochloric acid concentration 50–60%;
- Treatment time 30–40 min;
- Solution(liquid): solid phase = 1.5:1.

The process of interaction of Krasnooktyabrskoe bauxite with hydrochloric acid and then sulfuric acid was studied and validated by simple lattice programming according to Scheffe. The validity of the obtained model was evaluated by additional control points.

The effect of the mixed composition of HCl and sulfuric acid on the extractability of aluminum and iron in the system Al_2O_3-Fe_2O_3-(HCl)H_2SO_4 is described by the fourth order equation:

$$Y = \beta_1 \times X_1 + \beta_2 \times X_2 + \beta_3 \times X_3 + \beta_{12} \times X_1 \times X_2 + \beta_{13} \times X_1 \times X_3 + \beta_{23} \times X_2 \times X_3 + \gamma_{12} \times X_1 \times X_2 \times (X_1 - X_2) + \gamma_{13} \times X_1 \times X_3 \times (X_1 - X_3) + \gamma_{23} \times X_2 \times X_3 \times (X_2 - X_3) + \delta_{12} \times X_1 \times X_2 \times (X - X_2)^2 + \delta_{13} \times X_1 \times X_3 \times (X_1 - X_3)^2 + \delta_{23} \times X_2 \times X_3 \times (X_2 - X_3) + \beta_{1123} \times X_1^2 \times X_2 \times X_3 + \beta_{1223} \times X_1 \times X_2^2 \times X_3 + \beta_{1233} \times X_1 \times X_2 \times X_3^2 \quad (21)$$

The experiment was conducted according to a design matrix with the components of the system as independent variables X1, X2,... Xp were conducted according to a planned matrix with the independent variables X1, X2.

As a result of the experiments, process data on the extraction of aluminum and iron were obtained and a composition-property diagram of the system Al_2O_3-Fe_2O_3-(HCl)H_2SO_4 at 950°C was constructed according to the composition of the mixture (*Fig 1* and *2*).

The interaction in the Al_2O_3-Fe_2O_3-(HCl)H_2SO_4 system involves the formation of a modified sulfate-aluminum chloride-iron flocculant in solid fusion, whose crystal chemical formula can be expressed as [Al, Fe] [SO_4-2,Cl_2-1,$(OH)_2$-1] The composition of MSCAIC The triangulation diagram can be used to determine schematically the metal extraction in the MSCAIC compositions.

Analysis of the composition-property diagram of the Al_2O_3-Fe_2O_3-(HCl)H_2SO_4 system at 950°C shows that complete extraction of aluminum and iron is achieved at the optimal ratio of Al_2O_3:Fe_2O_3:(HCl)H_2SO_4=(40:20:40) Al=(30:30:40)Fe.

The kinetic analysis of the decomposition process of bauxite by mineral acids (HCl and H_2SO_4) was performed to determine the chemical interactions. The results show that in the decomposition of aluminum and iron-based minerals by hydrochloric acid, the process proceeds in the diffusion zone (E=55.7 kJ/mol(Al_2O_3) and E=28.4 kJ/mol(Fe_2O_3)). In the decomposition of ferrous minerals by sulfuric acid, the process proceeds in the chemical kinetics regime of Fe_2O_3 (E=389.3 kJ/mol), while in the decomposition of aluminum-containing components of the raw material, the process proceeds in the diffusion regime (E=21.8 kJ/mol). The measurement of the activation energy (E) gives information on the minimum energy of the process that must be brought to the system in order to move to the decomposition process and helps to determine the correct choice of technological mode.

Fig. 1. *Isothermal section 95°C of the Al_2O_3-Fe_2O_3-(HCl)H_2SO_4 system along the isolines of the degree of Al_2O_3 extraction*

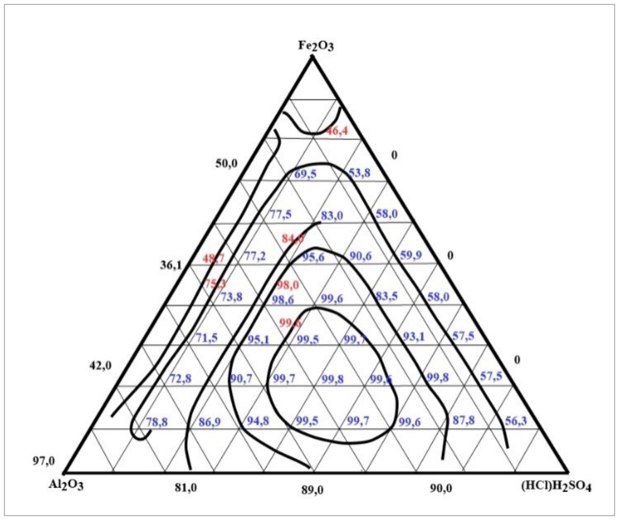
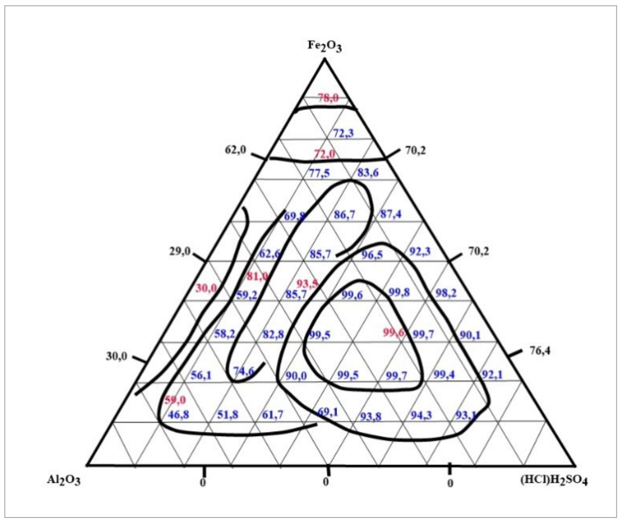


Fig. 2. *Isothermal section 95°C of the Al_2O_3-Fe_2O_3-(HCl)H_2SO_4 system along the isolines of the degree of Fe_2O_3 extraction*



Based on the results of the study of the physicochemical process of obtaining sulfate-chloride mixed alumina-iron coagulant from substandard bauxite, the following conclusions were formulated:

1 Thermodynamic analysis of the reaction equation for the decomposition of bauxite with hydrochloric acid at 298–473 K indicates that virtually all reactions are thermodynamically probable and form aluminum and iron chloride in the products of the interaction, with the exception of kaolinite. Thermodynamic analysis of the

reaction equation with sulfuric acid showed that the reaction is thermodynamically favorable for 7 of the 10 major minerals, and that increasing the temperature above 100°C is of little significance because ΔCfº(T) changes little.

2 Based on the generalized equations describing the influence of the studied factors on the degree of aluminum and iron extraction in the final product, the optimal conditions for HCl interaction were determined: temperature 90–100°C, process time 30–60 min, HCl concentration: 5.6 %, L:S = 2:1; for sulfuric acid degradation: temperature 85–100°C, process time 30–40 min, H2SO4 concentration 50–60%, L:S = 1.5:1.

3 Simple lattice planning method confirmed that the most complete decomposition of the initial off-specification material with formation of MSCAIC in the solid phase occurs under the conditions of Al2O3:Fe2O3:(HCl)H2SO4 = (40:20:40)Al = (30:40:30)Fe.

4 Kinetic analysis allowed us to select a technical regime for the preparation of MSCAIC.

Technical scheme for obtaining sulfate-aluminum chloride-iron coagulant from substandard bauxite

Based on the analysis of theoretical and experimental studies of physicochemical and technological properties of Krasnooctyabrsk bauxite, optimal conditions for obtaining mixed sulfate-aluminum chloride-iron coagulant from low-quality bauxite were established.

The following conditions were found to be optimal: Stage I – hydrochloric acid decomposition (HCl concentration: 5.6 %; temperature 95–100°C; decomposition time 30 min; ratio Liquid(L) : Solid(S) = 2:1; extraction of Al_2O_3– 94 %; Fe_2O_3– 65 %; Stage II – sulfuric acid decomposition of the insoluble residue (H_2SO_4 50–60 % concentration; temperature – 100°C; treatment time – 40 min; ratio L:S = 1.5:1; extraction of Al_2O_3 – 97 %; Fe_2O_3 – 87 %).

Chemical composition of MSCAIC, %: Al_2O_3 – 11.18; Fe_2O_3 – 6.66; sulfuric acid – 6.8; HCl-insoluble residue – 6.5.

The main technical operations required for the production of sulfuric acid-alumina chloride-iron mixed coagulant (*Fig. 3*): preparation of raw materials, hydrochloric acid decomposition, sulfuric acid decomposition, crystallization.

1 Raw material preparation. Bauxite after crushing in jaw crusher and grinding in ball mill is fed to the pulp collector. The resulting pulp is fed into an acid-resistant lined steel reactor.

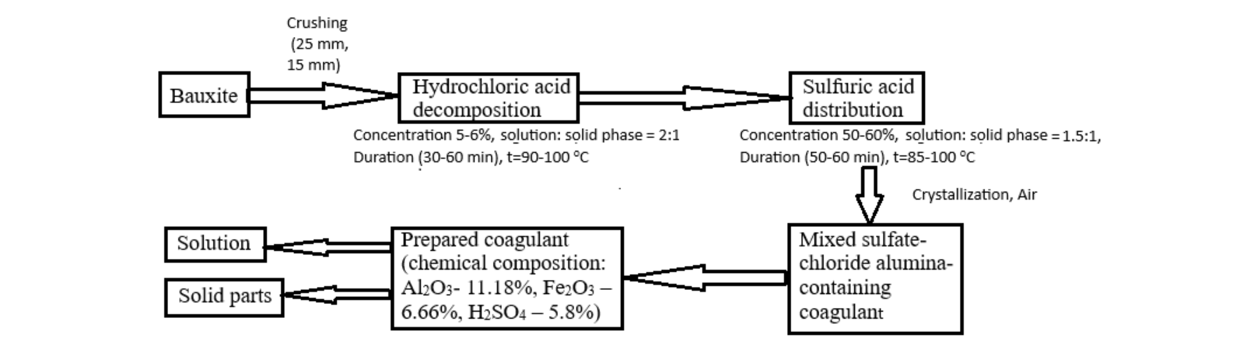
2 Hydrochloric acid decomposition. In an acid reactor equipped with a flame stirrer, 5–6% hydrochloric acid is added from a tank collector to the crushed bauxite, the temperature of which is maintained between 90 and 1000°C by external air effects and partial heating with acute steam. The drain pipe of the stirred reactor is heated by high temperature steam. The stirring speed is no more than 50–70 rpm. The resulting suspension is filtered through a drum vacuum filter and diatomaceous earth is used as filter media. It should be noted that the resulting filtrate is a mixed aluminum and iron chloride flocculant and can be used as an independent inorganic flocculant for wastewater treatment.

3 Sulfuric acid decomposition. The resulting insoluble residue (after sulfuric acid decomposition) is fed in small portions to the next sulfuric acid reactor equipped with a similar stirrer to avoid foaming. It should be noted, however, that 93% H_2SO_4 is first fed into the reactor, diluted with wash water to a concentration of 50–60%, and heated to boiling (steam heating is also used). The stirring speed of the flame stirrer is 60–80 rpm. The sulfate-chloride suspension as the finished product of the sulfate-chloride mixed alumina-iron coagulant is fed for crystallization.

4 Crystallization. The finished product – mixed sulfate-chloride alumina-iron coagulant received from the reactor through the tank-collector is gravity fed to the conveyor-crystallizer at a float thickness of 15–29 mm on the belt of the crystallizer and its surface is cooled by blast air at a rate of 800–1200 m^3 per ton of finished product The crystallizer belt is covered with a cover. The crystallizer belt is covered. To improve melt removal, the belt is pre-wetted with water.

Thus, in contrast to the effect on the root system, the sensitization of plants by hyperthermic factor on the 5^{th} and 7^{th} day of observation increases the negative impact of the contaminant on the growth activity of the stem part. This fact means that in the case of observation of the growth activity of the stem part of the test plants, it is necessary to take into account the possible influence of sensitizing factors. In other words, in the practice of the normalization of acceptable levels of load, it is necessary to use sensitized test organisms that would simulate real stressful conditions.

Fig. 3. *Technological scheme for obtaining MSCAIC*



In further studies of the impact of petroleum products on the environment using the biotesting method, it is advisable to use multispectral and hyperspectral studies. In particular, under the influence of oil pollution of water bodies, the pigment characteristics of plants used as test objects change, namely, the ratio between chlorophyll a and total chlorophyll, as well as between carotenoids and total chlorophyll. The use of the ratio between pigments as a test parameter will make it possible to assess the complex effect of petroleum products on model ecosystems. When assessing damage to the leaf cover of plants, methods of fuzzy logic and neural networks can also be used.

Physicochemical analysis of sulfate-alumina chloride-iron flocculant application

Experiments to measure the effectiveness of water treatment were performed on model solutions (*Table 3*) and industrial wastewater (IW) containing petroleum products, suspended solids, and organic impurities (*Table 4*).

As can be seen from *Table 3*, the flocculation properties of MSCAIC at low temperatures (110°C) by several indicators (color, turbidity) are superior to some conventional flocculants, i.e., MSCAIC reagents can be used at 110°C.

Table 3. *Comparison of flocculation properties between MSCAIC and conventional flocculants in model solutions*

Coagulant	coagulant dose, mg/L	flocculation			Color,°	Turbidity, mg/L	pH
		15 min	30 min	1 hour			
Model solution: turbidity 14 mg/L, color 120, pH 7.8, t 11°C							
$Al_2(SO_4)_3$	200	large flakes, lightening begins		means lightening	30	0.6	5.2
$FeSO_4$	200	small flakes	lightening begins	slight lightening	35	1.1	3.5
MSCAIC	200	large flakes, lightening begins		significant lightening	23	0.7	5.0
$NaAlO_2$	300	small flakes		slight lightening	37	1.8	6.5
$FeCl_3$	200	small flakes		slight lightening	27	2.5	3.8

Impurities in bauxite, such as clay minerals and organic matter, can significantly affect the chemical coagulation reactions during water treatment or bauxite processing. Clay minerals (kaolinite, $Al_2Si_2O_5(OH)_4$) increase turbidity and can adsorb the coagulant, reducing its effectiveness. It also contributes to the formation of small flakes that do not settle well. Organic matter – humic and fulvic acids, contained in bauxite, form complexes with coagulants, reducing their activity. They also increase the turbidity and color of the water. These problems are solved by more precise adjustment of the coagulant dosage and careful pH control.

Several batches of flocculants were tested in sewage (SW), a multi-component solution containing up to 80% of fine dispersed impurities with high flocculation stability due to its composition; contaminants in SW were suspended solids, soluble organic impurities and petroleum products (*Table 4*).

Table 4. *Results of wastewater treatment with different flocculants*

Coagulant	Optimal dose of coagulant (ODC), mg/L	Snellen transparency, cm	Degree of purification, %			Sediment volume, %	pH
			Suspended substances	Oil products	chemical oxygen consumption		
$Al_2(SO4)_3$	600.0	12.0	90	98.2	85	16.5	5.0
MSCAIC	800.0	10.0	94	98.0	82	16.0	5.5
$FeCl_3$	850.0	5.0	79	97.0	58	15.5	3.5
$NaAlO_2$	900.0	3.5	51	67.0	46	14.5	6.5
$Fe_2(SO_4)_3$	1000.0	11.0	90	93.0	80	17.0	3.2

The results of the experiments conducted on wastewater by the most typical pollution levels (*Table 4*) show that the maximum depth of CB treatment by suspended particles, organic matter (COD) and petroleum products is achieved when the flocculant dosage is 600 mg/L aluminum sulfate, 850 mg/L and 1000 mg/L iron sulfate and chloride respectively, MSCAIC – 800 mg/L were found to be achieved.

Purified water is characterized by variations in pH values. For example, the pH of water purified with ferric chloride is 3.5, that of water purified with aluminum sulfate is 5.0, that of water purified with ferrous sulfate is 3.2, and that of water purified with MSCAIC is 5.5. To maintain the pH at a given level (5.5 to 7.5), coagulant dosages should be carefully selected. The pH value of the coagulant should be carefully selected. Higher values, for example, of ferrous sulfate, which undergoes hydrolysis in the first stage, give large concentrations of hydrogen ions. As a result, the pH shifts to the acidic side above 5.5 and soluble iron complexes are formed instead of the required iron hydroxide, which increases the residual iron content in the water, simultaneously reducing flocculation efficiency, increasing residual color, and becoming more corrosive.

According to the physicochemical analysis data of the improved flocculant MSCAIC, has flocculation ability, works for clarification of wastewater, significantly accelerates the clarification process, and is not inferior to the quality of purification commodity flocculants (aluminum sulfate, ferric chloride, ferrous sulfate, etc.). The range of optimum pH values is due to the diversity of hydrolysis products and the physicochemical properties of the flocculant. Another advantage is the fact that low temperature treatment of MSCAIC does not cause "hardening" (precipitation of iron oxides) and the flakes formed precipitate more uniformly than with the application of conventional flocculants.

It is important to know the effect of DC on the pH of the treated water in order to select a reasonable dosage of flocculant and to compare and evaluate its effectiveness.

It has been observed that with increasing DC, the pH of the treated water decreases significantly, and the characteristics of the changes in the curve of the studied salts are different and depend on the nature of the flocculant.

Comparing bauxites (*Table 5)* with commercial coagulants (such as aluminum sulfate, ferric chloride, polyaluminum chloride) in the context of their use for coagulation, for example in water treatment, allows us to assess their efficiency, cost-effectiveness and practicality. Bauxites containing aluminum hydroxides (gibbsite, boehmite) can be a source of coagulant after processing, but are not a finished product, unlike commercial coagulants.

Therefore, bauxites are economically viable in regions with accessible deposits, but require pre-treatment (acid dissolution, thermal activation), which reduces their practicality. Impurities make coagulation control difficult, making them less versatile. However, they are well suited for industrial applications or as a raw material for the production of coagulants, and, under certain conditions, as their replacement.

It is also worth considering the environmental and economic aspects of using bauxite (processed as a coagulant source), aluminum sulfate ($Al_2(SO_4)_3$), ferric chloride ($FeCl_3$), and polyaluminum chloride (PAC) as coagulants for water treatment (*Table 6*).

Table 5. *Comparative table of advantages and disadvantages of bauxite compared to commercial coagulants*

Characteristic	Bauxite	Aluminum sulfate	Ferric chloride	Polyaluminum chloride
Main component	Al_2O_3, Fe_2O_3, SiO_2	$Al_2(SO_4)_3$	$FeCl_3$	$[Al_2(OH)_nCl_{6n}]_m$
Efficiency	Average (after processing)	High	High	Very high
pH range	Depends on processing (≈5.5–7.5)	5.5–7.5	4.0–8.0	5.0–9.0
Cost	Low (raw material), high (processing)	Medium	Medium/high	High
Amount of sediment	High (due to impurities)	High	Medium	Low
Ease of use	Complex (requires processing)	Simple	Simple	Simple
Environmental friendliness	Potentially high (waste recycling)	Medium	Medium	Medium
Versatility	Low (depends on impurities)	High	High	Very High

Table 6. *Environmental and economic comparison of bauxite with common coagulants*

Aspect	Bauxite	Aluminum sulfate	Ferric chloride	Polyaluminum chloride
Resource extraction	High impact (mining, red mud)	High (bauxite mining)	Moderate (iron mining)	High (bauxite mining)
Production emissions	High (acid/thermal processing)	Moderate (SO_2, CO_2)	Moderate (Cl_2, CO_2)	Moderate (HCl, CO_2)
Sludge volume	High (impurity-driven)	High	Moderate	Low
Sludge reuse potential	Low (contaminated)	Low	Moderate	High
Residual impact	Moderate (impurities)	Moderate (aluminum)	Moderate (iron)	Low (minimal aluminum)
Raw material cost	Low	Moderate	Moderate/High	High
Production cost	High (processing)	Low	Moderate	High
Operational cost	High (variable dosing)	Low	Moderate	Low (efficient dosing)
Market availability	Limited (needs processing)	High	Moderate	Moderate

In terms of environmental priority, PAC is preferred for minimal sludge and residues, followed by ferric chloride for dense sludge. Bauxite and aluminum sulfate are less favorable due to large waste.

In terms of economic priority, aluminum sulfate is the most cost-effective for general use, followed by ferric chloride. Bauxite requires investment in processing, while PAC is justified only for premium applications.

Summary of the eco-economic value of bauxite: in regions rich in bauxite, processed bauxite can supplement aluminum sulfate production to reduce costs, but the environmental impacts need to be carefully managed.

Bauxite containing aluminum hydroxides and impurities can be an alternative to commercial coagulants, but their use has both positive and significant limitations. In particular:

1 Environmental consequences. The use of low-grade bauxite, unsuitable for alumina production, reduces the accumulation of mining waste, such as red mud. This contributes to the rational use of resources. In regions with bauxite deposits (e.g. Ukraine, Guinea, Brazil), the method can reduce dependence on imports of commercial coagulants, reducing transport emissions of CO_2. Bauxite mining leads to soil degradation, deforestation, disruption of ecosystems and pollution of water bodies. The red mud remaining after processing is toxic and difficult to dispose of. Bauxite processing requires significant energy, which contributes to emissions of CO_2, SO_2 and other greenhouse gases. Due to the high content of impurities (silica, iron), bauxites generate large amounts of sludge, which is often contaminated and difficult to dispose of. This can lead to the accumulation of waste in landfills. Improper treatment or excess impurities can lead to residual contaminants in water, which reduces its quality.

2 Economic implications. Bauxites are cheaper than synthetic coagulants, especially in regions with a de-

veloped mining infrastructure. The use of local bauxites can stimulate the economy of the region, creating jobs and reducing import costs. Activation processes require capital investments in equipment, energy and reagents, which can exceed the savings from the raw material. The unstable composition of bauxites requires regular laboratory tests to determine the dosage, which increases operating costs. Bauxites are not a standardized product for coagulation, which makes it difficult to compete with commercial coagulants.

3 Technical implications. The presence of aluminum and iron allows bauxite to act as a complex coagulant, which can be useful for waters with various contaminants. After optimizing the process, bauxite can be effective in industrial water treatment systems. Impurities (silica, titanium minerals) make it difficult to form strong flakes, which worsens precipitation compared to pure coagulants. Iron can cause discoloration of the water, and silicagel-like precipitates, which reduces the quality of the purified water. Aluminum in bauxite is less reactive than in synthetic coagulants, which prolongs the coagulation and flocculation time.

There are also limitations to the coagulation method using bauxite, including the need for pre-treatment, unstable composition, certain problems with the presence of impurities, and high sediment. There are also regulatory barriers to the use of bauxite, since it contains an unstable composition, there is a difficulty in developing regulations and standards for its use.

Conclusions

When MSCAIC was used, the optimal dose of coagulant was 800 mg/L, with 94% cleanliness of suspended solids, 82% for COD, and 98% for oil products. The application of MSCAIC expanded the range of optimal pH values in wastewater treatment. In several indicators (color, turbidity, pH), MSCAIC outperforms conventional flocculants, and another important advantage is the fact that the reagent can be used at low temperatures.

The following conditions are optimal values: Stage I – hydrochloric acid decomposition (hydrochloric acid concentration: 5.6 %; temperature 95–100°C; decomposition time30 min; ratio L:S = 2:1), extraction of Al_2O_3 – 94 %; Fe_2O_3 – 65 %; Stage II – sulfuric acid decomposition of insoluble residue (H_2SO_4 – 50–60 % concentration, temperature 100°C, treatment time – 40 min, ratio L:S = 1.5:1), extraction of Al_2O_3 – 97 %; Fe_2O_3 – 87 %.

Chemical composition of MSCAIC, %: Al_2O_3 – 11.18; Fe_2O_3 – 6.66; sulfuric acid – 6.8; HCl-insoluble residue – 6.5. Appearance: isometric solid fragments, dark brown, matte color.

The possibility of using substandard bauxite as raw material for obtaining mixed sulfuric acid-alumina chloride-iron coagulant was proved.

Technical parameters of the mixed sulfate-alumina chloride-iron coagulant production process based on physicochemical studies were determined.

The application of mixed sulfate-alumina chloride-iron coagulant was confirmed on the basis of physicochemical analysis of wastewater treatment processes.

The use of bauxite for coagulation has potential in terms of resource savings and local application, but its consequences and limitations are significant. Environmental risks (mining, sediment, emissions), technical complexity (processing, impurities) and economic barriers (activation costs) make the method less competitive compared to commercial coagulants such as polyaluminium chloride or aluminium sulphate.

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