

Modern methods of industrial wastewater treatment and softening

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Abstract. The growing demand for clean water has significantly increased the need for coagulants in wastewater treatment, particularly for agricultural production organizations. In response to this pressing issue, the provision of iron-rich raw materials to enterprises producing coagulants has become a critical priority. To address this challenge, the paper focuses on exploring the potential of producing coagulants from local iron ore raw materials available in the Karakalpakstan and Navoi regions. Ongoing scientific research efforts are dedicated to studying the composition of the iron ore resources in these mines and determining their potential applications. By leveraging the local iron ore deposits, this approach aims to develop a sustainable and cost-effective solution for the production of coagulants, ultimately supporting the growing demand for clean water in the agricultural sector.

1 Introduction

In the world, the problem of clean water is growing rapidly as industries, farms, and populations are increasing significantly. Water is one of the main substances in almost all processes of industrial enterprises. Nowadays, it is especially important to clean used wastewater and return it to the process. Discharge of waste water from industrial enterprises into running water is causing not only environmental damage, but also hydrosphere damage. For this reason, world scientists are attaching great importance to wastewater treatment with coagulants, flocculants, float reagents, biological plants and various other methods. At present, great attention is paid to the protection of the environment from anthropogenic influence on a global scale. The rapid development of the industry, including the chemical industry, extensive extraction of raw materials, and the increase in the use of transport cause a lot of waste to be dumped into the environment.

Pollution of the environment (water, air, soil) leads to disruption of the normal functioning of the hydrosphere and biosphere, climate change, extinction of plant and animal species, deterioration of public health. The problem of pollution of the hydrosphere with waste water is becoming urgent in the world, including in Uzbekistan. In order to reduce and prevent environmental pollution, effectively manage and protect water resources, appropriate laws are being developed in our country and in foreign countries, various technological,

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sanitary technical, organizational and other measures are being implemented. Provision of drinking water, drainage and treatment of waste water improves the standard of living of the population and prevents various water-borne diseases. Currently, great importance is attached to the prevention of pollution of water bodies. Wastewater from households and industrial enterprises is treated in facilities and discharged back into water bodies. At the same time, it pollutes water bodies to a certain extent. In recent years, our government has taken a number of practical measures aimed at improving the sanitary conditions of water bodies. In particular, the development of new technologies in the wastewater treatment system, which is considered the most important component of the infrastructure of our country, which forms the necessary conditions for people to live a decent life, and which ensures the comfort and convenience of homes and settlements in all aspects, and the improvement of its activities improvement is one of the important issues [1, 2].

2 Materials and methods

Mechanical, biological and physico-chemical methods are used in the treatment of wastewater, the degree of purification, throughput, sediment treatment methods, composition of wastewater, local conditions and economic indicators are taken into account when choosing treatment methods and facilities. Commonly used wastewater treatment technologies (mechanical and biological) provide for the separation of sizeable impurities, colloidal and dissolved substances. This sequence creates conditions for cleaning. In the world, it is aimed at scientific justification of appropriate solutions for the creation of modern devices for the purification of industrial wastewater from foreign residues, in particular, the identification of raw materials for obtaining coagulant, the determination of the effect of incineration temperature and time on the decomposition of aluminum and other metals, and the improvement of modern technologies of circulating water cooling [3, 4].

Depending on the process of formation and accumulation of water in nature, it is conventionally divided into three types, i.e. underground, atmospheric and surface water. Such waters differ in their physical and chemical properties.

Underground water. These waters are colorless, clear, fresh or salty and contain mainly water-soluble chemicals such as $\text{N}_2\text{S}_2\text{J}_2$ and cations such as Mg^{2+} , Na^+ , K^+ , Ca^{2+} , Fe^{2+} and anions such as Cl , SO_4 , NO_3 , HCO_3 . The chemical composition of such waters depends on the composition of the underground layers, and the more salt content in the soil layers, the more salt content will be in the produced water. The total salt content of underground water is around 50-100 mg per liter, and gases such as O_2 , CO_2 , NO_2 are also partially found in its composition. For use in the field of water engineering, groundwater is brought to the surface through artesian wells. Since the water released in this way is not so much, they will not be enough to supply high-power thermal power plants (TPP) with water. Artesian waters can be used in the energy sector only in low-power TPCs in heat networks that supply steam to production enterprises and heat supply systems.

Atmospheric waters. These waters accumulate on the surface of the earth mainly as a result of precipitation such as rain, snow, etc. Their composition is somewhat cleaner than the composition of underground and surface waters, and the amount of mineral salts in such waters is around 50-60 mg per liter. Atmospheric water is not used in thermal power plants at all due to the fact that atmospheric water in nature is not enough to supply water to thermal power plants.

Surface water. Such waters include streams, rivers, natural lakes, seas and oceans. These waters differ from underground and atmospheric waters by the complexity of their chemical composition and the abundance of various chemical and mechanical substances. Groundwater always contains dissolved organic and inorganic substances, gases, various mechanically mixed small particles. Such waters are formed in nature as a result of the

melting of snow and ice layers accumulated on mountain slopes, and their composition depends on the composition of the surface layers and the extent to which the substances contained in these layers dissolve in water [5-7].

During the accumulation of water flowing down from the mountains, limestone (CaO), marble (CaCO₃), dolomite (CaCO₃, MgCO₃), table salt (NaCl), gypsum (CaSO₄), rock salt (MgSO₄), iron, As a result of contact with sulfur, silicate compounds and other rocks, these compounds enrich natural waters with cations such as Ca²⁺, Mg²⁺, Na⁺, K⁺, Fe²⁺, Fe³⁺ and anions such as Cl⁻. Refined and unrefined salts of aluminum sulfate compounds are used as coagulants in water purification technology. Unrefined aluminum sulfate salt is light gray in color, Gost 5/55-59 compound contains 9.5% Al₂O₃, 2-3% H₂SiO₃ and 23% water insoluble solids. This salt is also called *glycasem* in technology. Its chemical expression is written as follows:



The chemical expression of the purified salt is written as Al₂(SO₄)₃ · 18 H₂O, and according to GOST 1996-75, it contains 16.3% of high grade, 15% of the first grade, and 14% of the second grade of aluminum III oxide.

Iron (II) sulfate salt FeSO₄·7H₂O is a pale bluish substance, GOST 1991-15 contains 47-53% FeSO₄. In water treatment facilities, these salts are stored dry in special reservoirs or in a wet state in special reinforced concrete pools in the amount intended for 2-3 months.

If FeSO₄ salt is used as a coagulant, the dose of alkali added to bring the water pH to an alkaline environment is determined from the following expression:

$$D_i = D_k - I_{um} + I_q, \quad mg - \frac{ekv}{l}. \quad (2)$$

Here: **D_i** - alkali dose, mg-eq/l; **I_{um}** - total alkalinity of water, mg-equiv/l; **I_q** - residual alkalinity, mg-equiv/l.

As a result of coagulation, the amount of residual alkalinity in water is in the range of 0.3-0.5 mg-eq/l.

Table 1 shows how the coagulant dose can be obtained depending on the amount of organic and suspended matter in the water without adding flocculant to the water.

Table 1. Dependence of coagulant dosage on water content.

Permanganate oxidation mg/l, O ₂	Amount of suspended matter, mg/l	Clarity		Anhydrous Al ₂ (SO ₄) ₃ dose
		By "+"	By letter	
5 – 8	Up to 50	45	30	0.3 – 0.5
	30 – 100	30	20	0.4 – 0.6
	100 – 200	20	13	0.6 – 0.8
8 – 12	200 – 400	15	10	0.7 – 1.0
12 – 15	400 – 600	10	7	0.8 – 1.25
15 – 20	600 – 800	8	5	1.0 – 1.0
20 – 25	1000 – 1400	6	4	1.3 – 2.0
When greater than 30	1800 – 2200	3	2	1.4 – 2.2

It can be seen from the table that the higher the amount of organic and suspended matter in the water, the greater the dose of coagulant added to the water.

The amount of liquid coagulant consumed every hour is determined from the following expression:

$$V_K = \frac{QE_K D_K}{100 \cdot C_K \rho_K}, \quad \frac{m^3}{c}. \quad (3)$$

In this case: Q is the amount of purified water, m^3 ; D_K – coagulant dose, $g\text{-eq}/m^3$; E_K – equivalent weight of anhydrous coagulant, $g/g\text{ eq}$; C_K – concentration of coagulant solution, %; ρ_K – density of coagulant solution, mg/m^3 [8-12].

3 Results and discussion

With the increase in the demand for clean water, the need for coagulants in wastewater treatment in agricultural production organizations is significantly increasing. In such situations, providing iron-rich raw materials to enterprises producing coagulants is an urgent issue. In order to find a solution to this problem, first of all, it is considered to be achieved by the production of coagulants from local iron ore raw materials located in Karakalpakstan and Navoi region and currently, scientific research works are being carried out to study the composition of iron ore raw materials available in the mines and to determine the fields of use. The results of a sample taken from a local raw material containing iron ore are shown in Table 2.

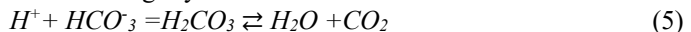
Table 2. Results of a sample taken from a local raw material containing iron ore.

№	1	2	3	4	5	6	7	8	9	10
	Si	Al	Ca	Na	K	Fe	Mg	P	Mn	Ti
mass fraction, %										
1	8.0	0.4	0.06	0.4	0.2	30.0	0.3	0.06	0.1	0.5
2	20.0	1.0	0.06	1.5	0.8	30.0	1.0	0.04	0.08	0.4

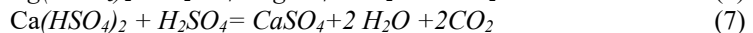
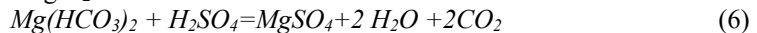
The results obtained from the sample show that the most commonly used substances as coagulants in the water treatment process can be salts such as iron sulfate ($FeSO_4$) and iron chloride ($FeCl_3$). Coagulants obtained by hydrolysis of these salts in water form iron hydroxide ($Fe(OH)_3$).



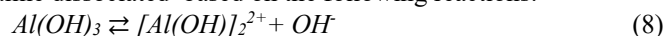
It can be seen from the above reactions that sulfuric acid (H_2SO_4) is formed as a result of hydrolysis of coagulant substances, and hydrochloric acid (HCl) is formed when ferric chloride ($FeCl_3$) is used. These formed acids (if there are no HCO_3 ions in the water) increase the acidity of the water. If there is an HCO_3 ion, then H^+ ions of the acid react with C ions and as a result of mutual neutralization, the bicarbonate alkalinity of water decreases, and the amount of CO_2 in its content increases slightly.



If HCO_3 ions are in the state of $Ca(HCO_3)_2$ or $Mg(HCO_3)_2$ compounds in water, these substances react with acids formed as a result of the hydrolysis of coagulants, resulting in the formation of $CaCl_2$ and $MgCl_2$ salts.



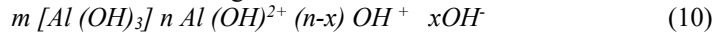
These salts increase the noncarbonate hardness of the water. When adding coagulant to water and settling colloidal particles, the progress of the coagulation process depends on the concentration of H^+ ions in the water, the pH and temperature of the water, the dose of the coagulant, and the amount of turbid substances in the water. Because of $Al(OH)_3$ or $Fe(OH)_3$ formed as a result of hydrolysis of coagulants such as $Al(SO_4)_3$ and $FeCl_3$ during wastewater treatment are ampholyte substances, depending on the pH value of water, these hydroxides are dissociated in two ways. For example, if the pH value of water is less than 7 (acidic environment), $Al(OH)_3$ is alkaline dissociated based on the following reactions:





Since $Al(OH)_3$ is a trivalent compound, its dissociation takes place in three stages. As a result of such dissociation, the process of separation proceeds strongly in the first stage, and in the second and third stages, the process of separation is somewhat less and fewer ions are formed. As a result of the formation of $Al(OH)$, $Al(OH)_3$, Al^{3+} and OH^- ions in water in an acidic environment, the core of the colloidal particle contains the $Al(OH)_3$ molecule and an adsorption layer is formed which consist of $Al(OH)_2$, $Al(OH)_3$, Al^{3+} and partially OH^- ions around this core [7,8].

The diffusion layer of such colloidal particles consists of OH^- ions and if the adsorption layer of the resulting colloidal particle is formed only from $Al(OH)_3$ and OH^- ions, such a colloidal particle can be written in the following form:



On the other hand, if the pH value of water is greater than 7, the alkaline medium $Al(OH)_3$ dissociates acidly based on the following reactions:



In these reactions, as above, in the second and third stages, the separation process is slightly less than in the first stage. As a result of the formation of H^+ and $H_2AlO_3^-$, $HAlO_3^{2-}$, AlO_3^{3-} ions in an alkaline environment, the adsorption layer around the core of the colloidal particle consisting of $Al(OH)_3$ molecules consists of $H_2AlO_3^-$, $HAlO_3^{2-}$, AlO_3^{3-} and partially H^+ ions. The diffusion layer of the colloidal particle consists of H^+ ions.

If the adsorptive layer consists only of $HAlO_3^-$ and partially H^+ ions, the micelle of such a colloidal particle in an alkaline environment can be written as follows:

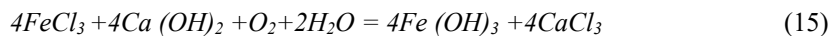


It can be seen from the given reactions that the greater the alkaline or acidic state of water, the greater the degree of dissociation of $Al(OH)_3$, and the more ions are formed. Because of colloidal particles of the aluminum compound formed in the impact of ions have an electric charge even at pH values greater than 7, colloidal particles in water are added to the aluminum micelles, become larger and do not turn into large particles, that is, fragments.

If the pH value of water is in the range of 6-8, that is, a neutral environment, $Al(OH)_3$ formed as a result of hydrolysis of $Al_2(SO_4)_3$ in water is almost not dissociated. Since $Al(OH)_3$ is in an isoelectric state in a neutral environment, its particles do not have a positive or negative charge. Because of $Al(OH)_3$ molecules in the isoelectric state are surface-active substances, as a result of the adhesion of various colloidal substances in the water around them, they become larger, form large fragments in the water, and separate from the water and sink.

When $FeCl_3$ is used as a coagulant to purify water from colloidal particles, the pH value of water should be around 9-10, because the $Fe(OH)_2$ compound formed by the hydrolysis of $FeCl_3$ in a neutral environment is not oxidized to the $Fe(OH)_3$ compound.

Therefore, by adding $FeCl_3$ to the water, $Ca(OH)_2$ and $Mg(OH)_2$ are added to the water to bring the pH to 9-10 as a result of coagulation, and together with the oxidation of $Fe(OH)_2$ to $Fe(OH)_3$ in the water It also reduces the concentration of Ca^{2+} and Mg^{2+} cations and reduces water hardness. Under the influence of $Ca(OH)_2$, the formation of $Fe(OH)_2$ proceeds as follows.



In water treatment, $FeCl_3$ salt is used as a coagulant in cases where it is necessary to simultaneously clean water from colloidal particles and soften it by adding a reagent. The $Fe(OH)_3$ compound formed under such conditions accelerates the coagulation of colloidal particles in water and fully ensures the formation of their large fragments.

The speed of separation of the formed particles from water depends on their size and density. The larger fragments are formed and the greater their density, the faster and more completely such fragments separate from the water and sink to the bottom of the water.

4 Conclusion

If we compare these two $\text{Al}_2(\text{SO}_4)_3$ and FeCl_3 salts as coagulants, the FeCl_3 salt has the following advantages:

1. When FeCl_3 salt is used, the coagulation process can be carried out at the natural temperature of water, that is, heating is not required. When $\text{Al}_2(\text{SO}_4)_3$ salt is used, the water temperature should be 35-40°C, that is, it is required to heat the water. Because the temperature of natural water is not higher than 15-20°C.
2. The sedimentation rate of the $\text{Fe}(\text{OH})_3$ colloidal system is slightly higher than that of the $\text{Al}(\text{OH})_3$ colloidal system, because the density of $\text{Fe}(\text{OH})_3$ is 1.5 times greater than the density of $\text{Al}_2(\text{OH})_3$, that is, colloid particles of $\text{Fe}(\text{OH})_3$ sink 1.5 times faster than those of $\text{Al}(\text{OH})_3$. This feature of $\text{Fe}(\text{OH})_3$ accelerates technological processes in water purification technology and slightly reduces the time of water in the softeners.
3. In the amount of 0.1-0.5 mg.ekv per liter of water, and when using $\text{Al}_2(\text{OH})_3$, the coagulant dose is taken in the range of 0.5-1 mg.ekv, that is, twice as much. The dose of coagulant added to water under operating conditions is determined experimentally in laboratory conditions every day.

In recent times, in addition to the coagulant substances mentioned above, substances such as aluminum oxychloride ($[\text{Al}_2(\text{OH})_3] \text{Cl} \cdot 6\text{H}_2\text{O}$) and aluminum sodium (NaAlO_3) are widely used as coagulants in water treatment technology. It is not required to change the water pH during the coagulation process in the presence of these substances.

References

1. E.N. Kuzin, *The use of a hardened form of aluminum-silicon flocculant coagulant in water treatment processes. Abstracts of the 48th youth scientific and technical conference EPI MAMI. Youth of the 21st century - the future of Russian science. Elektrostal* **5**, 56-57 (2014)
2. T.N. Bokovikova, D.E. Zanin, *Technology. Technologies* **2**, 75-80 (2014)
3. N.E. Kruchinina, E.N. Kuzin, *Bulletin of the Kazan Technical University* **6**, 78-82 (2015)
4. E.N. Kuzin, *Processing of nepheline concentrate to produce a hardened aluminum-silicon flocculant-coagulant. Abstracts of reports of the 49th youth scientific and technical conference EPI MAMI. Youth of the 21st century - the future of Russian science. Elektrostal* **6**, 42-43 (2015)
5. G. Mansourri, M. Madani, *Open Journal of Ecology* **2**, 55-61 (2016)
6. C.G. Lee, M.K. Song, J.C. Ryu, C. Park, J.W. Choi, S.H. Lee, *Chemosphere* **5**, 1-9 (2016)
7. M.A. Elubay, M.A. Suleimenov, A.Zh. Kikueva, D.T. Tolegenov, D. Z. Toleenova, D.E. Nurmakhanbetova, *Science and technology of Kazakhstan* **2**, 114-125 (2019)
8. Z.S. Nazarov, A.B. Jiyanov, L.O. Sharipov, Sh. Sunnatulloev, *E3S Web of Conferences. Geotech* **417**, 01001 (2023)

9. Z.S. Nazarov, A.B. Jiyanov, L.O. Sharipov, A.Z. Nazarov, Science and Education in Karakalpakstan. Karakalpakstan **1/2** (2023)
10. N.M. Akhmedova, I.N. Tursunova, Kh.Sh. Urunova, S.O. Khuzhiev, M.A. Farmanova, Occupational safety in industry **1**, 77-83 (2023). <https://www.doi.org/10.24000/0409-2961-2023-1-77-83>
11. M.A. Askarov, Sh.K. Kurbanov, O.B. Khushvakov, U.Z. Sharafutdinov, N.A. Doniyarov, Gornyi Zhurnal, **2**, 61–62 (2002)
12. K.S. Sanakulov, U.Z. Sharafutdinov, Tsvetnye Metally, **10**, 46–49 (2019)