

FEATURES OF WASTEWATER TREATMENT

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Abstract: The authors determined the efficiency of the coagulant-flocculant compositions, which depend on the conditions of reagent introduction, special qualities of wastewater, nature of the coagulant, concentration, molecular weight and charge. The paper explores the issue of optimizing the removal of protein and lipid impurities from wastewater under exposure to the compositions of coagulants and flocculants; in this case anionic acrylamide/sodium acrylate copolymers were analyzed. It has been established that by adding compositions of coagulants with flocculants to wastewater it is possible to significantly reduce the content of protein and lipid impurities.

Keywords: wastewater treatment, coagulants, flocculants

Introduction. In the course of its economic activities, the modern society consumes considerable quantities of water, and as a result, most of it becomes contaminated with various substances. When these substances are released into the environment, they cause an immense harm to it, and, therefore, they must be treated. To ensure this treatment is done as required, it is necessary to use special equipment and technological complexes, which help to meet the established limits for wastewater contamination, as defined by the relevant documents. Over the last years, wastewater-related problems have been getting even more pressing and relevant throughout the world, including the Russian Federation.

Relevance. According to the current legislation, manufacturing enterprises must use waste treatment facilities to correct the adverse effects of wastewater, however, this requirement is not always fully fulfilled. Pollution indexes of discharges coming from industrial facilities are often significantly higher than the established standards. This is caused by the outdated waste treatment facilities, which are subject to reconstruction and reequipment. Manufacturing facilities are the source of many environmental problems associated with wastewater disposal. Production processes of almost all industries involve a generation of effluents contaminated with various substances. Today, industrial pollution of wastewater is one of the paramount threats to the ecological state. The goal of the work is to optimize the removal of protein and lipid impurities contained in wastewater using the compositions of coagulants and flocculants of polyacrylamide nature. As a study subject, the authors examined wastewater of one of the enterprises of Kazan, which is characterized by an over-the-limit content of protein and lipid components. The main characteristics of wastewater

are given in Table 1. As the Table shows, all the core indicators are several times higher than the regulatory criteria.

Table 1 – Main Characteristics of Wastewater

Item	Wastewater I	Wastewater I Regulatory limits *
Lipids, mg/l	750	10
Proteins, mg/l	242	0
COD	1980	265
BOD ₅	1670	177
Suspended substances, mg/l	780	186
pH	6.5-7.0	6.5-8.5

Prevention of the waters contamination, along with protection of surface waters from pollution by wastewater, are the most important tasks for the present-day society. Their efficient and comprehensive solution is only possible with the use of the advanced treatment technologies. The specific aspect of the agricultural industry is that its cattle-breeding and crop-growing sectors produce wastewater, which has a completely different composition of polluting agents: first, organic and biological impurities are predominant and, second, there are pollutants of inorganic origin. Therefore, the approach to their treatment, the used methods and the equipment configuration should be different. The environmental problems of agricultural wastewater are also very grave. Wastewater often discharged into the environment by agro-industrial enterprises has such indicators of the presence of mechanical, chemical and biological impurities, which is many times the maximum permitted concentration. Reducing the concentration of the agricultural runoffs contamination to the required level should be ensured by their thorough treatment using modern equipment. Only this could ensure the quantitative and qualitative pollution indexes of this type of wastewater, which would allow for its discharge without harming the environment.

* Decision of the Executive Committee of the municipal settlement of Kazan No. 2334 dated April 7, 2009, On the Rules for Using the Collecting System of Sewage Waters Discharge and (or) Drainage Water in the City of Kazan (with amendments as of: Oct 14, 2010)

Al₂(SO₄)₃ solution (GOST 12966-85) was chosen as a coagulant (Y), and anionic acrylamide/sodium acrylate copolymers obtained through alkaline hydrolysis of polyacrylamide were examined as flocculants (F). Properties of the flocculants are presented in Table 2.

Table 2 – Properties of flocculants

Grade	CNF	Fr _I	Fr _{II}	Fr _{III}	Fr _{IV}	Fr _V	Fr _{VI}
Amount of ionogenic links, mol %	19.7	28	19	27	27	12	4
Molecular weight M _n *10 ⁻⁶	12.7	4.8	4.4	4.3	4.3	3.8	2.9
Viscosity [η], cm ³ /g	1970	1880	1800	1600	1600	1020	990

The authors used the known methods of physical and chemical analysis (ИТС8 – 2015): primary flocculation, spectrophotometry, sedimentation test, Soxhlet and Kjeldahl methods for determining protein and lipid impurities. Based upon a

comparison of the above methods, the optimal concentrations of flocculants were determined. As a result of a chemical testing on the Soxhlet and Kjeldahl apparatuses, it was revealed that the content of protein and lipid impurities in the wastewater is significantly above the limits (Table 1). The use of flocculants of polyacrylamide nature is one of the most efficient methods of reagent treatment during primary flocculation and sedimentation. From a practical point of view, both flocculants, and coagulant compositions with flocculants are used in optimal ratios for wastewater treatment.

Results. Using the spectrophotometry and sedimentation test methods, the processes of wastewater coagulation and flocculation with various protein and lipid impurities were studied. It has been established that with the introduction of optimal concentrations of coagulant compositions with flocculants, clarification and wastewater purification from impurities is more effective in contrast to using only coagulants. In addition, it was determined that there is a representative decrease in the values of optical density and speed of primary flocculation when the compositions of coagulants with flocculants are introduced. The inflection points on the curves of Figure 1 make it possible to determine the optimal reagent concentration. When a composition of a coagulant with flocculants is added (Fig. 1, curves 2-8) to the systems under consideration, it leads to a noticeable decrease in the values of optical density. Figure 2 shows the kinetic curves of sedimentation test, which indicate an increase in the rate of sedimentation when the optimal reagent concentrations are introduced into the system. The highest sedimentation rate is observed when Y + CNF compositions are introduced into the systems (Fig. 2, curve 2). The obtained result is explained by the high molecular weight of the used polymer additive (CNF) (Table 2).

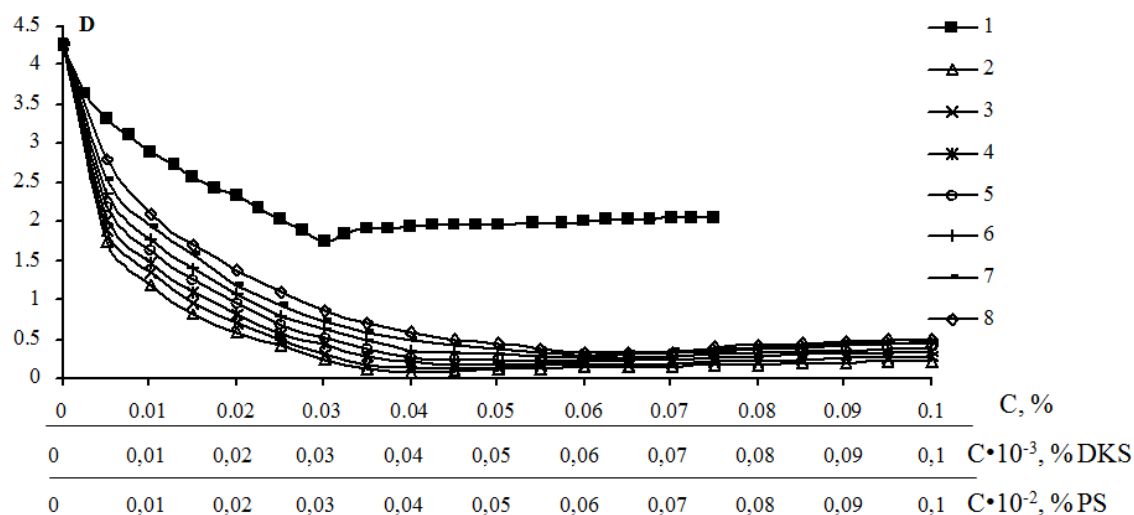


Fig.1. Dependence of Optical Density D on the Optimal Reagent Concentrations
 1- Y – 0.03%; 2- Y +CNF 0.000045%; 3- Y +FR_I 0.0005%;
 4- Y+FR_{II} 0.0005%; 5- Y+FR_{III} 0.0006%; 6- Y+FR_{IV} 0.0006%; 7- Y+FR_V 0.0007%;
 8- Y+FR_{VI} 0.00075%.

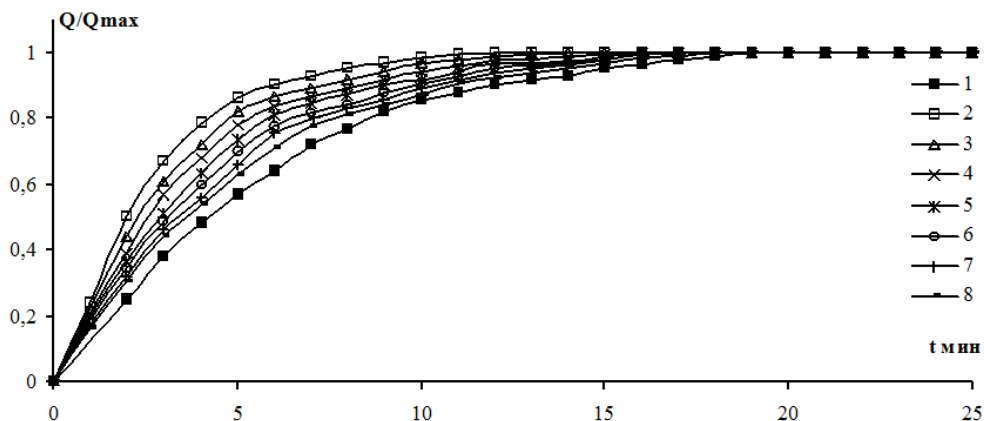


Fig.2. Sedimentation Test Curves in Coordinates Q/Q_{\max} of t (min)

(where Q and Q_{\max} are, respectively, the current and maximum values of the residual matter weight on the torsion-balance pan; t is the exposure time)

- 1- Y - $\text{Al}_2(\text{SO}_4)_3$ 0.03%; 2- Y + CNF 0.000045%; 3- Y + FR_I 0.0005%;
 4- Y + FR_{II} 0.0005%; 5- Y + FR_{III} 0.0006%; 6- Y + FR_{IV} 0.0006%; 7- Y + FR_V 0.0007%;
 8- Y + FR_{VI} 0.00075%.

Using the methods of primary flocculation, clarification, sedimentation and spectrophotometry, the efficiency of the coagulant-flocculant compositions was established: $\text{CNF} > \text{FR}_I > \text{FR}_{II} > \text{FR}_{III} > \text{FR}_{IV} > \text{FR}_V > \text{FR}_{VI}$. Note that a coagulant composition with all the considered polymer reagents is characterized by an effective action in the treatment of the selected wastewater; nevertheless, the best compositions are those of a coagulant with CNF and FR_I flocculants (their molecular weight is, respectively, 12.7 and $4.8 \cdot 10^6$). To verify the choice of optimal concentrations, curves of potentiometric titration of coagulant solutions were obtained in the presence of flocculants of polyacrylamide nature (CNF, FR_I) within the range of $\text{pH } 3 \div 12$. Moreover, the authors created a mathematical model of the main equilibrium processes in the system of Y (III) – $\text{H}_2\text{O} - \text{OH}$ – flocculant, which made it possible to estimate the values of the equilibrium constants, as well as to take into account the presence of polynuclear entities and heteroligand compounds in the system. By combining the experimental and theoretical titration curves, the existence domains of the compounds were established depending on the solution pH , and the initial coagulant and flocculant (F) concentrations. The values of equilibrium constants were evaluated; the importance of taking into account polynuclear entities and heteroligand compounds in the system simulation is shown.

It was determined that when the molarity of a flocculant is less than the optimal concentration, being within the range of $\text{pH } = 2.7 - 4.8$, the destruction of polynuclear coagulant entities is observed, manifesting in the transformed potentiometric titration curves (PTC) through a shift into the alkaline region. With an increase in the flocculant concentration, the PTCs shift into the acidic region due to the formation of new polynuclear entities with the flocculant. If flocculants (CNF, FR_I) are added within the $\text{pH } = 4.5 - 12$ range, it leads to sedimentation of the constant composition. Processing of potentiometric titration curves using the method of mathematical modeling allows for a determination of the type, number and nature of distribution of the resulting complexes. Mathematical modeling demonstrated that in the acidic region of $\text{pH } = 2.7 -$

4.8, the flocculant forms the compounds $Y_{12}(\text{OH})_{24}\text{F}_{12}$ and $Y_{32}(\text{OH})_{64}\text{F}_{32}$. This composition was determined by the shape of the curves within the range of $\text{pH} = 2.7\text{--}4.8$.

Conclusion. In the course of this work it was revealed that when the flocculant concentration is less than optimal, a shift of PTC to the alkaline region is observed. When the flocculant concentration is optimal, the PTCs shift to the acidic region, and when the flocculant concentration is higher than the optimal by more than 2 times, no shift of the curves is observed. Apparently, this is due to the formation of heteroligand compounds of the coagulant with all the flocculant compounds. The influence of the compositions of coagulants with flocculants on the behavior of wastewater containing protein and lipid impurities was studied. The efficacy of the compositions of coagulants with flocculants was established. Using the method of sedimentation test and spectroscopy, the optimal concentrations of the compositions of coagulants with flocculants were determined. Using the method of mathematical modeling, the structure of the compounds formed in the considered pH range was determined.

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