

Для локальної очистки стічних вод підприємств харчової промисловості широко застосовуються фізико-хімічні методи очистки, які при правильно підібраних реагентах та їх дозах дозволяють досягти високої ефективності очистки. При цьому дози реагентів та умови їх застосування можуть різко відрізнятися між підприємствами, тому закономірності перебігу очистки повинні бути вивчені на конкретному стоці.

У даній роботі розглянуті закономірності перебігу процесу коагуляції стічних вод коагулянтами і флокулянтами різного хімічного складу на прикладі стічних вод підприємства по переробці м'яса індички. Досліджено закономірності перебігу процесу коагуляції стічних вод в широкому діапазоні значень рН середовища. Експериментально визначено, що найбільш сприятливий рН середовища для застосування поліоксихлориду алюмінію знаходиться в діапазоні 5,9÷6,4, хлориду заліза 6,2÷6,7, сульфату заліза 5,1÷5,7. Встановлено закономірності впливу дози коагулянту на ефективність очищення стічних вод від зважених речовин і кольоровості. На підставі отриманих даних визначені раціональні дози коагулянтів. Так для поліоксихлориду алюмінію це 140 мг/л, сульфату заліза – 110 мг/л і хлориду заліза – 80 мг/л. Досліджено закономірності перебігу процесу флокуляції стічних вод із застосуванням флокулянтів різних зарядів і молекулярних мас. Визначено найбільш ефективні типи флокулянтів, встановлені раціональні дози реагенту. Визначено найліпші умови проведення фізико-хімічної очистки стічних вод із застосуванням коагулянтів і флокулянтів. Отримані дані дозволяють оптимізувати роботу локальних очисних споруд підприємства по переробці м'яса птиці: підвищити ефективність їх роботи, а так само зменшити експлуатаційні витрати. Підібрані бінарні комбінації реагентів дозволяють досягти ефективності очищення за зваженими речовинами 99,4 % і 82,4 % по кольоровості

Ключові слова: стічні води, коагулянт, флокулянт, доза реагента, фізико-хімічна очистка, зважені речовини

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A STUDY OF WASTEWATER TREATMENT CONDITIONS FOR THE POULTRY MEAT PROCESSING ENTERPRISE

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1. Introduction

The food industry is one of the most developed and largest sectors of the national economy of Ukraine, which not only provides the domestic market, but is also a major exporter of products. One of its largest branches is processing of meat products, where poultry meat production prevails, about 49 %, which is more than 700 thousand tons of finished products per year [1]. In the production of meat products, from 6 to 30 m³ of pure water per ton of finished products is used [2]. At the current production level, it is more than 2 million m³ of wastewater a year.

At the same time, most enterprises have low-efficiency treatment facilities or do not have them at all. This situation leads to the fact that untreated or poorly treated wastewater is discharged into a municipal sewage system or a nearby water body, thus worsening the ecological condition of water basins [3].

A total of 92 % of fresh water used by mankind, in one way or another, accounts for the food industry, more than a third of which is spent for production of meat products [4, 5].

2. Literature review and problem statement

Wastewater from the enterprises for the production of meat products represents complex high-concentrated systems [6, 7]. The main types of pollutants are blood, wool, mineral inclusions, paunch manure, skin, feather [8, 9].

For the local treatment of wastewater of food industry enterprises, pressure flotation units with preliminary physicochemical processing are the most widely used [10]. As reagents, coagulants based on aluminum and iron salts are most often applied [11], which, when properly dosed, give a high treatment efficiency [12]. At the same time, the review of recent studies shows that it is very difficult to determine the doses based on the available results due to a considerable variation of the data obtained. So, in [13], using iron chloride for removal of dyes from wastewater, it has been found that the optimum pH range of the medium is 3÷4 and the coagulant dose is 40 mg/l.

When using the same coagulant for dairy's wastewater, it turned out that at almost the same pH value, namely 4.5, the coagulant dose of 200 mg/l was required [10]. That is

5 times more. For slaughterhouse wastewater, according to [14], the working range of pH was within 5.83–6.28 (significantly higher than in [13]), and the coagulant dose reached 600 mg/l.

A similar variation of results occurs in studies on the use of iron sulfate as a coagulant for the dairy's wastewater treatment. Thus, in [10], it has been found that the optimum pH is 7.6, and the coagulant dose is 200 mg/l. Other studies have found that pH=5 is optimum for the treatment of the same wastewater, and the coagulant dose reaches 1,000 mg/l [15]. As for wastewater of the pig meat processing plant, as found in [16], the coagulation workflow proceeds most intensively at pH=10 and the coagulant dose of 350 mg/l.

This variation of data is associated with many factors, beginning with the reagents and production standards used, ending with the quality of tap water at the enterprise [17, 18].

From the above, it becomes obvious that the optimum conditions for the application of coagulants for each particular enterprise are highly individual and are subject to study and testing at a particular drain.

3. The aim and objectives of the study

The aim of the study was to increase the efficiency of local sewage treatment facilities by rationalizing the operating conditions of physicochemical wastewater treatment facilities. In particular, by experimental substantiation of rational doses of reagents and conditions of their application.

To achieve the aim of the study, the working ranges of pH of the medium for each of the studied types of coagulants were determined first, coagulation thresholds were identified, and rational doses of reagents were established. At the second stage of the study, the regularities of the action of flocculants with different charge and molecular weight were studied and the most preferable combinations thereof were determined.

4. Materials and methods of the study of chemical wastewater treatment efficiency when using coagulants and flocculants

The subject of the study was wastewater of the slaughterhouse of the turkey meat processing enterprise. The major amount of wastewater of the enterprise results from slaughter and evisceration of poultry, preparation of natural chopped semi-finished products, washing and disinfection of equipment and premises.

Industrial wastewater contains fats, proteins, organic particles, as well as mechanical impurities and sand. To ensure trouble-free operation of the general sewage system at the slaughterhouse outlet, before wastewater discharge into the general sewage system, local treatment facilities – grease trap and sand trap are installed.

The characteristics of the wastewater subject to treatment are given in Table 1.

The following reagents were used in the study:

1. Coagulants: AQUA-AURAT-18 polyaluminum chloride TU 2163-069-00205067-2007; ($\text{Al}_2\text{O}_3=17\pm 0.5\%$) FER-AQUA-17 ($\text{Fe}_2(\text{SO}_4)_3$ iron-containing coagulant TU U 20.1-03327724-006: 2013, the mass fraction of Fe^{3+} not less than 13.7 %; FeCl_3 iron chloride coagulant TU 2152-081-56856807-08, the mass fraction of iron chloride not less than 40 %.

2. Flocculants: Flopam AN 934 SH polyacrylamide anionic flocculant with an average charge density, very high molecular weight, Flopam AN 926 SH polyacrylamide anionic flocculant with an average charge density, very high molecular weight; Flopam FO 4490 SH and Flopam FO 4440 SH polyacrylamide cationic flocculants with an average charge density and high molecular weight.

3. Reagents for pH adjustment: sodium hydroxide NaOH by GOST R 55064-2012; hydrochloric acid (HCl 35–38 %) by GOST 3118-77.

Table 1

Composition of industrial wastewater subject to treatment

Parameter	Unit of measure	Value
Suspended solids	mg/l	2,200±4,000
COD	mgO ₂ /l	6,000
BOD ₅	mgO ₂ /l	2,500
Fats	mg/l	950
Ammonium nitrogen (NH ₄ -N)	mg/l	40
Phosphates	mg/l	70
pH	–	6.5±8.5
Maximum water temperature	°C	35
Minimum water temperature	°C	24

To determine the pH, the wastewater collected from a neutralizer was poured into 0.5-liter beakers. Then, a coagulant, a pH adjuster (acid or alkali) were added, and two-step mixing was performed: first fast and then slow. The resulting suspension was settled for 30 minutes, followed by sampling the treated water and measuring its quality.

Similarly, the coagulant dose was selected. In experiments on the selection of a rational dose in the binary coagulant – flocculant system, the coagulant dose found above was first added, the results of suspended solids removal and color reduction were estimated, then a flocculant was added and the result was estimated by the same wastewater treatment quality parameters.

The measurements were carried out using standard measuring instruments: portable waterproof pH Meter Hanna HI 9124 and HACH DR/890 colorimeter. Total suspended solids were measured in milligrams per liter and the color of the studied samples was determined in color degrees according to the Pt-Co scale by the photometric method.

The removal efficiency of suspended solids in percent was determined as the ratio of total suspended solids in the treated sample to those in the initial wastewater. The efficiency of color reduction in percent was determined as the ratio of the optical density of the treated sample to that of the initial wastewater.

The obtained experimental data were processed by means of spreadsheets on the MS Office Excel software.

5. Results of studies of the regularities of the course of chemical wastewater treatment depending on the pH of the medium and reagent dose

The results of determining the effective pH range for wastewater treatment using coagulants: polyaluminum chloride, iron sulfate and chloride are shown in Fig. 1, 2. The

curves shown in the graphs below are not considered as an approximation of the experimental data and are given only to illustrate the possible nature of dependencies.

From the graph in Fig. 1, it can be seen that for all the coagulants studied, there is almost the same regularity in the effect of pH on the removal efficiency of suspended solids. At low pH values of 2÷4, low treatment efficiency is observed, while with an increase in pH to 5.5÷6.5, the suspended solids removal efficiency grows. The subsequent alkalization leads to a decrease in treatment efficiency. Similar regularities are also observed for the color reduction efficiency, as shown in Fig. 2.

The most acceptable pH range for the coagulation process when using the polyaluminum chloride coagulant is the range of values of pH – 5.9÷6.4; iron sulfate – 5.1÷5.6; iron chloride – 6.2÷6.7. Deviation from these ranges, both to lower and higher values, leads to a deterioration in treatment efficiency.

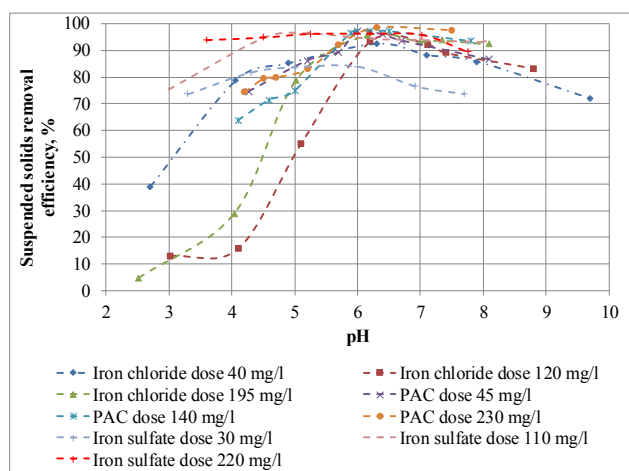


Fig. 1. Suspended solids removal efficiency when using polyaluminum chloride, iron sulfate and chloride coagulants with different doses and pH

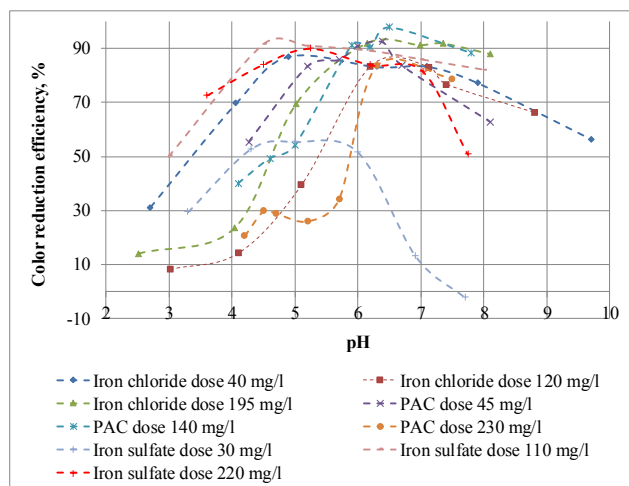


Fig. 2. Color reduction efficiency when using polyaluminum chloride, iron sulfate and chloride coagulants in the pH range of 2.5÷9.5

The results of determining the rational coagulant dose are shown in Fig. 3. Polyaluminum chloride at a dose of 45 mg/l provides the suspended solids removal efficiency of 56.5%. With the subsequent increase in the amount of reagent,

the quality of treatment is improved, reaching the value of 91.8% at a dose of 185 mg/l. The subsequent increase in the coagulant dose, up to 230 mg/l, does not significantly improve the quality of treatment.

The dependence of wastewater treatment efficiency on the coagulant dose when using iron chloride is qualitatively similar. However, at a dose of 40 mg/l, the suspended solids removal efficiency is much lower – 24.4%. With the subsequent increase in the reagent dose, the quality of treatment is improved and reaches 72.9% at a dose of 80 mg/l, but still remains lower than when using polyaluminum chloride. The subsequent increase in the coagulant dose to 195 mg/l does not significantly improve the quality of treatment.

Iron sulfate at a dose of 30 mg/l provides a 40.6% suspended solids removal efficiency. With the subsequent increase in the reagent dose to 110 mg/l, treatment rate is increased to 73.7%. Treatment efficiency is better than with the use of iron chloride, but worse than with polyaluminum chloride. The subsequent increase in the coagulant dose to 220 mg/l, as with the use of other coagulants, leads only to minor improvements in the quality of treatment.

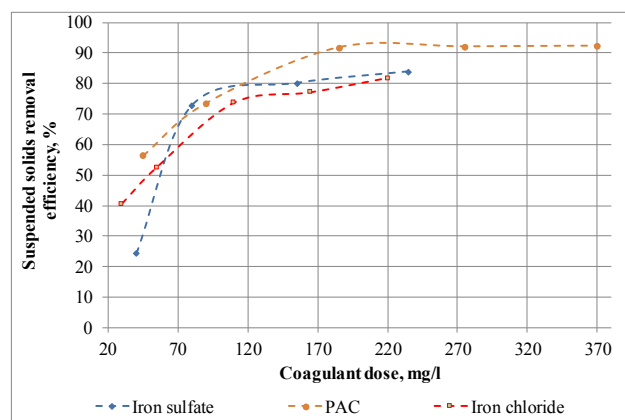


Fig. 3. Suspended solids removal efficiency when using polyaluminum chloride, iron sulfate and chloride coagulants with different doses at the optimum pH

When using the binary coagulant – cathode flocculant system, an increase in the suspended solids removal efficiency for all types of flocculants and coagulants used is observed (Fig. 4).

The efficiency of combined use of polyaluminum chloride (a dose of 140 mg/l, pH=5.9÷6.4) and cationic flocculants (FO 4440 and FO 4490) is shown in Fig. 4. When adding the flocculant at a dose of 1.5 mg/l, an increase in the suspended solids removal efficiency to 97.0 and 94.4%, respectively, is observed. The subsequent increase in the flocculant dose to 3; 4.5; 6 mg/l does not significantly increase the efficiency.

The efficiency of combined use of iron sulfate (a dose of 110 mg/l, pH=5.1÷5.7) and cationic flocculants with different charge densities (FO 4440 and FO 4490) is similar (Fig. 4). At the flocculant dose of 1.5 mg/l, the suspended solids removal efficiency is increased to 98.5% and 91.9%, respectively. The subsequent increase in the flocculant dose to 6 mg/l does not significantly increase the removal efficiency of suspended solids.

The combined use of iron chloride (a dose of 80 mg/l, pH=6.2÷6.7) and cationic flocculants (FO 4440 and FO 4490) at a dose of 1.5 mg/l increases the suspended solids removal efficiency to 98.7 and 93.9%, respectively. The subsequent

increase in the flocculant dose to 6 mg/l does not improve the efficiency (Fig. 4).

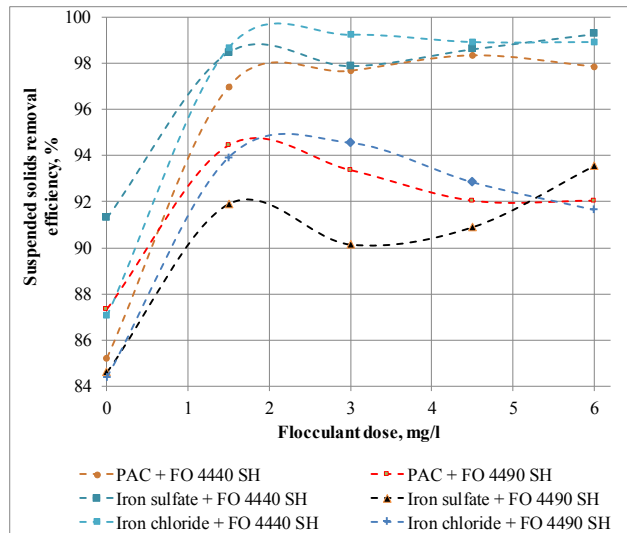


Fig. 4. Efficiency of suspended solids removal from wastewater when using the binary coagulant – cationic flocculant system

The results of color reduction when using the binary coagulant – cationic flocculant system are shown in Fig. 5.

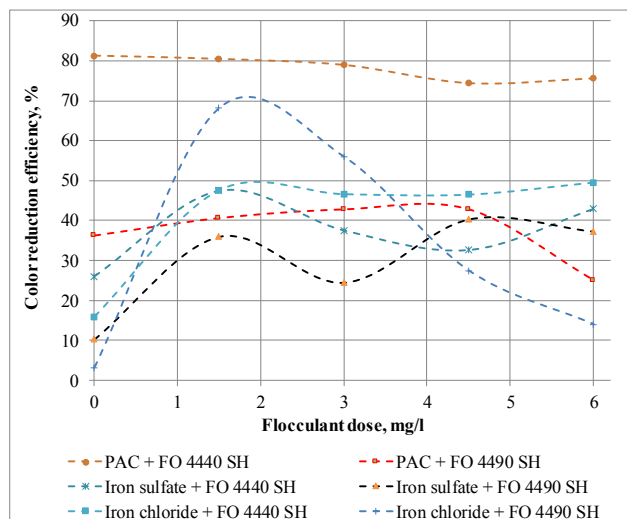


Fig. 5. Color reduction efficiency when using the binary coagulant – cationic flocculant system

For the iron sulfate coagulant, the color reduction efficiency when adding FO 4440 and FO 4490 cationic flocculants at a dose of 1.5 mg/l is increased to 47.5 % and 39.5 %, respectively. The subsequent increase in the flocculant dose to 3 mg/l somewhat reduces efficiency to 37.5 % and 24.5 %. With an increase in the flocculant dose to 4.5 mg/l, the efficiency is increased again and accounts for 42.9 % and 37.2 %, respectively.

For the binary system of iron chloride and FO 4440 cationic flocculant at a dose of 1.5 mg/l, the efficiency is increased to 47.6 % and with the subsequent increase in the dose to 4.5 mg/l remains practically unchanged. When using FO 4490 flocculant at a dose of 1.5 mg/l, the dramatic increase in the color reduction efficiency to 68.1 % occurs, the subsequent increase in the flocculant dose gradually

reduces the effect and at a dose of 4.5 mg/l the efficiency is already 14 %.

For the polyaluminum chloride coagulant, the introduction of FO 4440 and FO 4490 cationic flocculants has little effect on the color reduction efficiency.

When using the binary coagulant – anionic flocculant system, an increase in the suspended solids removal efficiency for all types of flocculants and coagulants used is observed (Fig. 6).

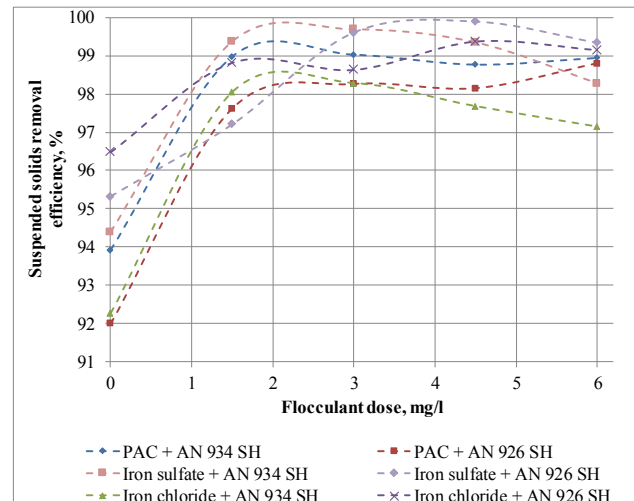


Fig. 6. Efficiency of suspended solids removal from wastewater when using the binary coagulant – anionic flocculant system

The efficiency of combined use of polyaluminum chloride (a dose of 140 mg/l, pH=5.9÷6.4) and anionic flocculants (AN 934 SH and AN 926 SH) is shown in Fig. 6. When adding the flocculant at a dose of 1.5 mg/l, the suspended solids removal efficiency is increased to 99.0 and 97.6 %, respectively. The subsequent increase in the flocculant dose up to 6 mg/l does not increase the efficiency, but also no significant changes in efficiency occur.

When using the binary system of iron sulfate (dose – 110 mg/l, pH=5.1÷5.7) and anionic flocculant (AN 934 SH and AN 926 SH) at a dose of 1.5 mg/l, the suspended solids removal efficiency is increased to 99.4 % and 97.2 % respectively. The subsequent increase in the flocculant dose up to 6 mg/l does not affect the efficiency.

The combined use of iron chloride (a dose of 80 mg/l, pH=6.2÷6.7) and anionic flocculants (AN 934 SH and AN 926 SH) at a dose of 1.5 mg/l improves the suspended solids removal efficiency to 98.0 and 98.8 % respectively. The subsequent increase in the flocculant dose does not significantly increase the efficiency.

When using the binary coagulant– anionic system, the results shown in Fig. 7 were obtained.

For the iron sulfate coagulant, the color reduction efficiency, when adding AN 926 SH anionic flocculant at a dose of 1.5 mg/l, is reduced to 43.8 %. The subsequent increase in the dose to 3 mg/l increases the efficiency to 83.8 %, and this efficiency remains with the subsequent dose increase up to 6 mg/l. With the addition of AN 934 anionic flocculant at a dose of 1.5 mg/l, the color reduction efficiency is increased to 82.5 % and remains up to a dose of 4.5 mg/l. With the subsequent increase in the flocculant dose to 6 mg/l, the efficiency is reduced to 61.1 % (Fig. 7).

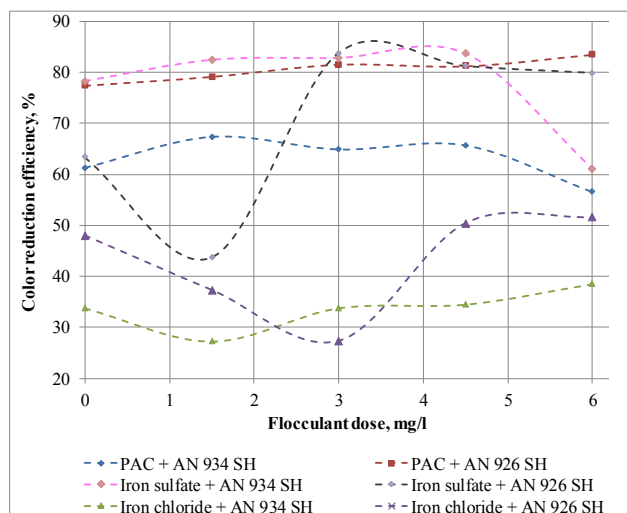


Fig. 7. Color reduction efficiency when using the binary coagulant – anionic flocculant system

For the binary system of iron chloride and AN 934 flocculant, in the range of flocculant doses from 0 to 6 mg/l, the color reduction efficiency was 30.0÷38.5%. When adding AN 926 flocculant with a lower charge density at low doses (1.5÷3 mg/l), a decrease in the color reduction efficiency to 37.3% and 27.3%, respectively, is observed. The subsequent increase in the flocculant dose to 4.5 mg/l increases the efficiency to 50.4%. The subsequent increase in the flocculant dose does not significantly increase the treatment efficiency (Fig. 6).

For the polyaluminum chloride coagulant, the introduction of AN 926 SH and AN 934 SH anionic flocculants hardly affects the color reduction efficiency.

6. Discussion of the results of the study of the effect of pH of the medium and reagent dose on the process of wastewater coagulation

The results of studies on the determination of rational doses of coagulants and pH of wastewater are given in Table 2.

Table 2

Optimum pH values of wastewater and coagulant doses

Coagulant	Optimum pH	Coagulant dose mg/l
Iron sulfate	5.1÷5.7	110
Iron chloride	6.2÷6.7	80
Polyaluminum chloride	5.9÷6.4	140

As can be seen from this table, the maximum values of treatment rate for all investigated coagulants are achieved in weakly acid solutions with pH in the range of 5.1÷6.7. The lowest pH is characteristic of sulfate, and the highest – iron chloride. At the specified pH values, along with the formation of the hydroxide of the corresponding metals, hydrocomplexes with a high degree of polymerization and polycations, which are capable of being adsorbed on the surface of negatively charged colloids can be formed [16]. This fact allows achieving a high removal efficiency of suspended solids.

The coagulation threshold for the studied coagulants is the dose in the range from 80 to 140 mg/l. When the coagulant dose is reduced, the efficiency of treatment decreases and its increase does not lead to a noticeable improvement in the treatment quality, while the consumption of reagents increases.

An interesting fact is the presence of a correlation between the rational pH and the coagulant dose. So, if the application of iron chloride, as already noted, requires a higher pH than for other coagulants, then the rational dose of this substance is the smallest. At the same time, the minimum pH characteristic of iron sulfate is combined with its maximum dose.

On the basis of the data obtained, it can be said that the use of iron-containing coagulants is more effective for treatment of wastewater of turkey meat processing enterprises. The removal efficiency of suspended solids, both with the use of aluminum-containing and iron-containing coagulants, is comparable. However, when using polyaluminum chloride, the color of the treated sample remains from pale pink to burgundy, which indicates an insufficient depth of the coagulation process.

Among iron-containing coagulants, iron sulfate is more effective because it has a high efficiency of suspended solids removal and color reduction. Its considerable advantage, in comparison with iron chloride, is that it remains highly efficient in a wider range of pH values of the medium. This is a significant advantage in the conditions of industrial wastewater, the composition of which can change drastically.

The quality of treatment when using cationic and anionic flocculants is almost the same, however, a rational dose of the cationic flocculant is somewhat lower. The suspended solids removal efficiency when adding the flocculant after wastewater coagulation is increased, on average, by 5÷7%. There is also a significant increase in the size of flakes, which leads to a faster settling of the coagulated agglomerates, decrease in the volume of sediment and reduction in its moisture content. The rational dose of the cationic flocculant is 1.5 mg/l.

The results of the study can be used in the design of local treatment facilities of food industry enterprises, where the composition of wastewater is close to that studied in this work. An important area of further research is the identification of the factors that significantly affect the process conditions of physicochemical treatment of waste liquids and quantitative assessment of this effect.

7. Conclusions

1. Rational pH ranges of the medium for coagulation are: 5.1÷5.7 for iron sulfate; 6.2÷6.7 – for iron chloride; 5.9÷6.4 – polyaluminum chloride.

2. The coagulation threshold is the coagulant dose: 110 mg/l for iron sulfate; 80 mg/l – for iron chloride; 140 mg/l – polyaluminum chloride.

3. Cationic flocculants, the application of which increases the efficiency of suspended solids removal by 5÷7% and color reduction by 10÷13% are the most preferable.

4. The best result of wastewater treatment was achieved when using the binary system of coagulant – iron sulfate at a dose of 110 mg/l, pH of the medium of 5.1÷5.6 and anionic flocculant at a dose of 1.5 mg/l. The efficiency of suspended solids removal achieved in the laboratory was 99.4% and color reduction – 84.2%.

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