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Colloid-Chemical Regularities of Reagent Wastewater Treatment of Dairies

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Abstract. A comparative characterization of chemical reagents $Al_2(SO_4)_3$, $FeSO_4$ and $FeCl_3$ in the process of wastewater treatment of dairies. The colloid-chemical regularities of the course of hydrolysis of chemical reagents depending on the nature, concentration and acidity of wastewater are established. It was found that the greatest degree of purification from ether-soluble substances 87-88% is provided by the addition of $FeCl_3$ at a concentration of 150-200 mg / l at a pH of 9.5-10.

Introduction

One of the first places in terms of volume and concentration of wastewater pollution is occupied by the dairy industry, which consists of different types of enterprises: milk collection points, separators, municipal dairies, cheese and butter factories [1-3]. In the dairy industry, wastewater accounts for about 90% of the pure water used by enterprises. With an average specific water consumption of 5 m^3 per ton of milk, depending on the capacity of the enterprise, about 500 m^3 of wastewater is generated per day.

Wastewater from milk processing enterprises belongs to the category of highly concentrated water with unstable composition. The main normative indicators that characterize the danger of wastewater are chemical oxygen demand (COD) (1000–5000 mg O_2 / l), biochemical oxygen demand (BOD) (700–3700 mg O_2 / l), total content of ether-soluble substances (200–400 g / l), total nitrogen content (20–170 mg / l), pH acidity index (3.6–10.4), transparency (0.8–2.0 cm). In addition to the mentioned indicators, wastewater from milk processing technologies is characterized by an increased content of suspended solids (1200–2900 mg / l), sulfate ions SO_4^{2-} (140–160 mg / l), chloride ions Cl^- (168–400 mg / l), ammonium ions NH^{4+} (6–12 mg / l), phosphate ions PO_4^{3-} (100–145 mg / l), calcium ions Ca^{2+} (150–200 mg / l), as well as dry (2500–8000 mg / l) and calcined (500–1500 mg / l) residues. The dispersed phase of wastewater is represented by water-insoluble fats and particles of coagulated protein [4, 5]. For primary wastewater treatment of dairies, the most common are methods of treatment with chemical reagents – sulfates, chlorides and oxochlorides of aluminum or iron, calcium chloride and more. The addition of chemical reagents provides not only the removal of ether-soluble substances, but also compounds of nitrogen and phosphorus, which is of great importance for further biological purification [6-8].

Literature Review

Primary reagent treatment methods are not effective enough and require dehydration of a large volume of sludge (sludge), which is formed during further settling. Therefore, to achieve the maximum effect of wastewater treatment in dairies, reagent treatment is often combined with subsequent, for example, pressure flotation [9, 10], electrocoagulation [11-15] or other physicochemical methods. In some works, after reagent treatment for the removal of organic contaminants it is recommended to use sorbents based on mineral materials - bentonites, kaolinites, zeolites, etc. [16-19] or filters and membranes made of synthetic polymeric materials. The main disadvantages that complicate the use of reagent and reagent-sorption methods are cumbersome reagent tanks and the formation of large amounts of sediment, which require further processing [12, 14]. In addition, when using sorbents, filters or membranes, there is a need for regeneration or, if it is impossible to restore efficiency, disposal of used materials. It should also be noted that due to stricter requirements for the quality of treated water, a limiting factor in the use of reagent treatment methods is the limitation of chloride and sulfate ions, which are usually introduced when adding common chemical reagents [12, 17, 18].

The combination of reagent and physicochemical treatment methods requires a detailed study of the processes occurring in wastewater at each stage. An idea of the colloid-chemical regularities and mechanisms of these processes will help to most effectively form a set of technological techniques and equipment for the most effective treatment of dairy wastewater. From the analysis of literature sources, it follows that the technological and economic efficiency of wastewater treatment of dairies largely depends on the stage of primary reagent treatment. The efficiency of this stage is determined by the following factors: the acidity of the environment, the nature and concentration of chemical reagents, the technology and sequence of addition of reagents, and so on. Therefore, the detection of colloid-chemical regularities of primary wastewater treatment with chemical reagents is an important scientific and practical task.

Materials and Methods of Research

The wastewater of the milk processing enterprise of Sumy region (Ukraine) was selected for the study.

The most common chemical reagents were selected for reagent treatment: aluminum sulfate $Al_2(SO_4)_3$, iron sulfate $FeSO_4$, iron chloride $FeCl_3$ in the form of 5% aqueous solutions. Sodium NaOH hydroxide in the form of a 5% aqueous solution was used as an alkaline additive. To accelerate the formation of sediment (sludge) used flocculant nonionic polyacrylamide (PAA) in the form of 0.05% aqueous solution.

The efficiency of treatment was studied by the following indicators of wastewater: hydrogen index pH, transparency and amount of ether-soluble substances. The pH was determined at room temperature (18–20^{0}C) using a portable pH meter brand SX 711 (China) with a measurement accuracy of ± 0.01pH. The transparency of the water was determined using a Snellen instrument, which is a glass cylinder with a flat bottom [20]. Determination of the amount of soluble substances (fats and mineral oils) was carried out by the method of multiple extraction with petroleum ether as an extractant [20].

Discussion of the Research Results

Wastewater after addition of reagents (metal salts and alkaline additives) was stirred for 5–10 minutes, then added flocculant PAA in an amount of 5 mg / l. After stirring, the wastewater was defended for 1 hour. The deposition rate and the volume of sediment formed were recorded. The filtrate was determined by the transparency and amount of ether-soluble substances.

After the addition of metal salts of aluminum sulfate $Al_2(SO_4)_3$, iron sulfate $FeSO_4$ and iron chloride $FeCl_3$ in wastewater, the process of hydrolysis of metal cations with the formation of insoluble hydroxides and the release of protons:

$$Fe^{2+} + 2H_3O^+ \leftrightarrow Fe(OH)_2 \downarrow + 4H^+ ; \quad (1)$$

$$Fe^{3+} + 3H_3O^+ \leftrightarrow Fe(OH)_3 \downarrow + 6H^+ ; \quad (2)$$

$$Al^{3+} + 3H_3O^+ \leftrightarrow Al(OH)_3 \downarrow + 6H^+ . \quad (3)$$

As a result of hydrolysis, sparingly soluble metal hydroxides are formed, which are able to adsorb various contaminants on the surface. Particles of hydroxides with adsorbed contaminants over time become larger and precipitate as a precipitate (sludge). The hydrogen index pH of wastewater is reduced.

In Fig. 1 shows the change in pH of wastewater after the addition of metal salts (reagents).

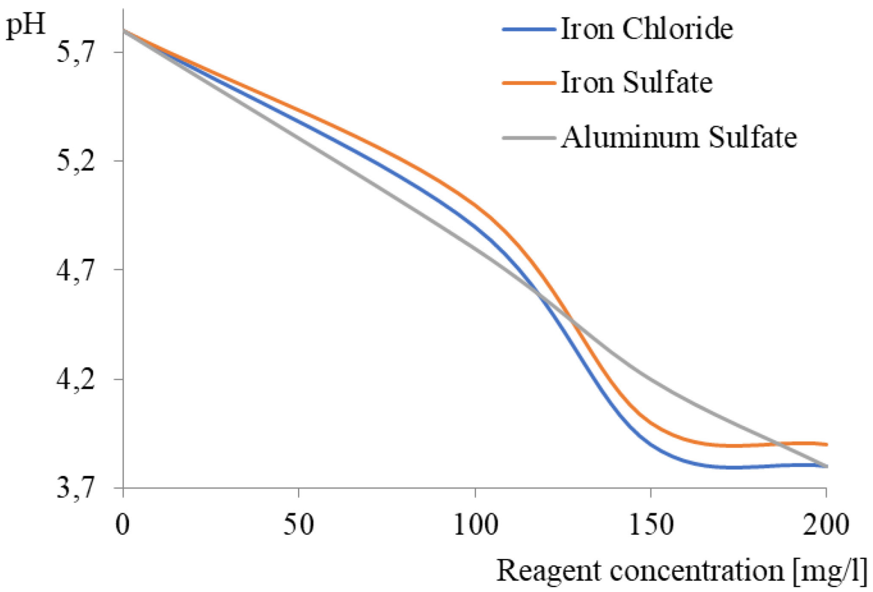
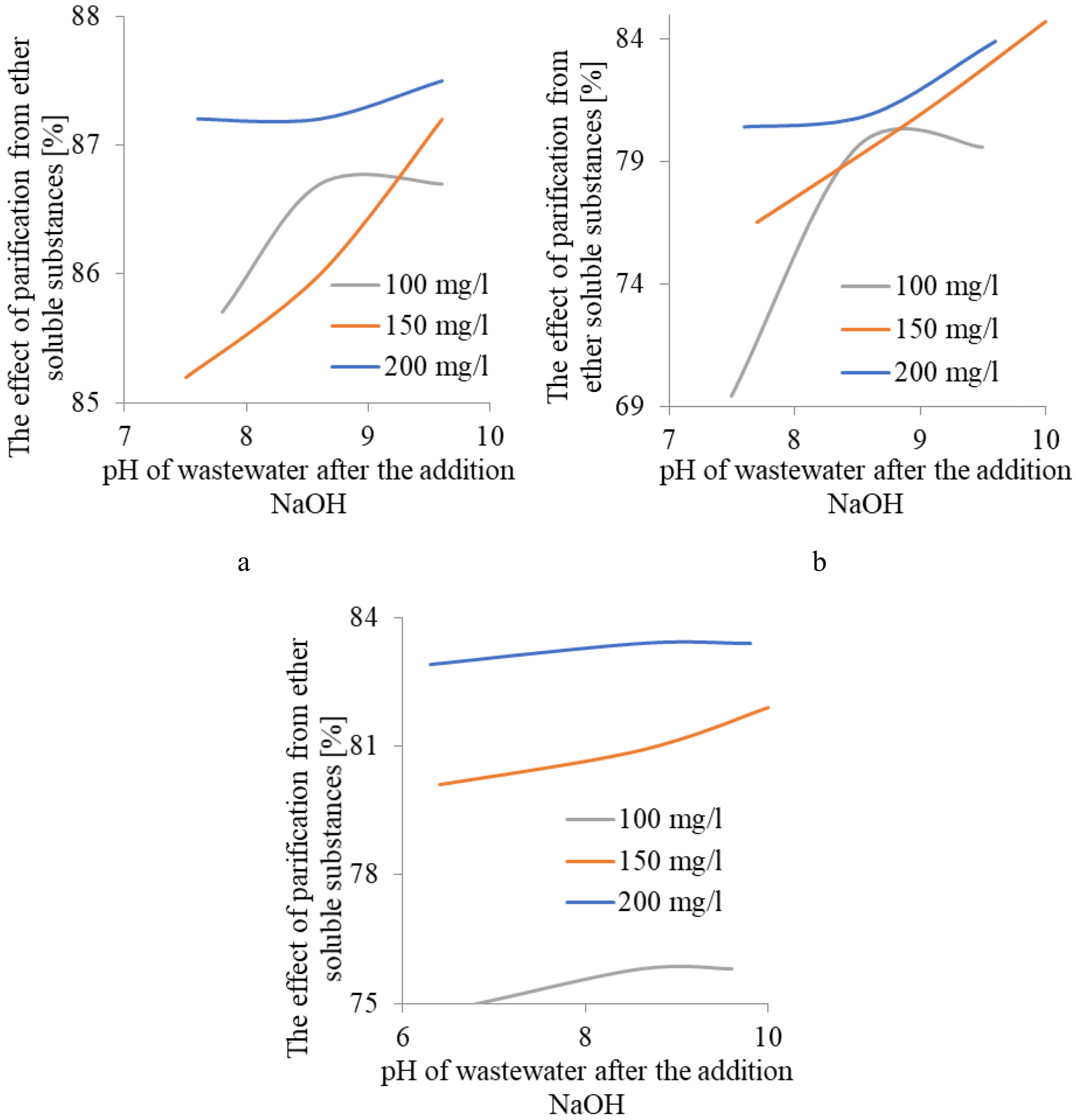


Fig. 1 Change in the hydrogen index pH of wastewater after the addition of metal salts

As can be seen from the results presented in the graph, with increasing concentration, the hydrolysis of iron salts occurs by a different mechanism than the hydrolysis of aluminum salts. The process of hydrolysis of iron salts proceeds unevenly and its nature does not depend on the cation charge. With increasing concentration of iron salt in the range up to 100 mg / l hydrolysis is slow, in the range of 100–150 mg / l there is a jump in pH, and in the range of concentrations greater than 150 mg / l - the acidity of the medium does not depend on salt concentration, ie hydrolysis does not happen. Hydrolysis of aluminum sulfate throughout the concentration range occurs uniformly and the pH of the medium decreases almost directly proportionally with increasing salt concentration.

Analyzing the schemes of hydrolysis equations (1-3), it can be argued that the greatest reduction in the pH of wastewater should provide the addition of aluminum sulfate and iron chloride. But the results presented in Fig. 1, indicate the following: the greatest increase in the acidity of the medium is provided by the addition of salts of iron, namely, iron chloride. The minimum pH value = 3.8 is achieved at a salt concentration of more than 150 mg / l. The same pH value when adding aluminum salt is achieved only when the salt concentration is more than 200 mg / l. Therefore, the highest degree of hydrolysis is characterized by iron chloride, the addition of which to wastewater, obviously, should provide the highest degree of purification. To increase the pH of wastewater after the addition of chemical reagents, a solution of sodium hydroxide was used. In fig. 2 shows graphs of the dependence of the purification effect (on the content of ether-soluble substances) on the nature and concentration of the added metal salt and the pH of the medium after the addition of sodium hydroxide.



c

Fig. 2 Dependences of the purification effect on the pH of the medium, the concentration and nature of the salt: a – $FeCl_3$; b – $FeSO_4$; c – $Al_2(SO_4)_3$.

As can be seen from the presented dependences, the mechanism of adsorption of ether-soluble substances on the surface of iron hydroxides differs from the mechanism of adsorption on the surface of aluminum hydroxide. In the case of iron hydroxides, the process of extraction of ether-soluble substances largely depends on the pH of the medium and increases with increasing alkalinity of wastewater (Fig. 2a, 2b). The cleaning effect increases by 2–10%. The process of adsorption of ether-soluble substances on the surface of aluminum hydroxide is practically unaffected or insignificantly affected by the pH of the medium (Fig. 2c). The cleaning effect increases by 0.5–2%. The greatest influence of pH of the environment is observed at concentration of reagents of 100–150 mg / l. When adding reagents with a concentration of 200 mg / l, the cleaning effect does not depend on the pH of the medium. But this concentration provides the maximum cleaning effect in all cases. The greatest degree of purification from ether-soluble substances 87-88% is provided by addition of iron chloride in concentration of 150-200 mg / l at pH of 9,5–10.

Table 2 shows the results of the influence of nature and the concentration of the chemical reagent on the transparency of wastewater and the volume of sediment (sludge) formed after settling.

Table 2 The effect of nature and concentration of the chemical reagent on the transparency of wastewater and the volume of sediment (sludge) after settling

Reagent concentration [mg / l]	pH of wastewater	Transparency, cm	Sediment volume (sludge) [%]
Wastewater without reagents	5.8	1.6	-
$FeCl_3$			
100	9.6	8.3	14
150	9.6	11.0	17
200	9.6	14.0	18
$FeSO_4$			
100	9.5	6.0	18
150	10.0	9.0	25
200	9.6	11.0	30
$Al_2(SO_4)_3$			
100	9.6	7.3	18
150	10.0	8.5	22
200	9.8	8.0	24

As can be seen from the presented results, the addition of iron chloride provides the formation of the smallest amount of sediment (sludge) of about 18%, as well as the greatest transparency of treated wastewater. The greater effect of purification with the addition of iron chloride can be explained by the following reasons. Obviously, in contrast to $FeSO_4$ and $Al_2(SO_4)_3$, the hydrolysis of $FeCl_3$ produces a colloidal dispersed system with dispersed phase particles with a large specific surface area. This provides their greatest adsorption capacity and, accordingly, the highest degree of wastewater treatment.

Conclusions

Colloid-chemical regularities and conditions of hydrolysis of chemical reagents $FeSO_4$, $Al_2(SO_4)_3$ and $FeCl_3$ in dairy wastewater have been studied. Differences in the processes occurring in wastewater during treatment have been established. The relationship between the degree of purification, the pH of the medium, the mechanism of hydrolysis and the concentration of various chemical reagents is shown. As a result of the conducted researches it is established that at sewage treatment of dairies from ether-soluble substances the addition of $FeCl_3$ in concentration of 150–200 mg / l at pH of 9,5–10 is the most effective. However, it should be noted that the addition of chemical reagents has negative aspects. When metal chlorides or sulfates are added, a large amount of chloride or sulfate ions, respectively, enters the wastewater. Due to the fact that dairy wastewater usually contains 170-400 mg / l of chloride ions and 150-160 mg / l of sulfate ions [3], the use of metal salts is not always justified. In this case, it is necessary to search for and use reagent-free physic-chemical cleaning methods.

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