COAGULATION TREATMENT OF EFFLUENT FROM MILK-PROCESSING ENTERPRISES WITH WASTE FeSO$_4$

As the world's population grows, the problem of food shortages becomes global, and, for human survival, it is necessary to significantly increase food production, which may increase environmental pollution.

This paper has theoretically and practically substantiated the expediency of coagulation treatment of wastewater from milk-processing enterprises. The coagulant proposed to use is a multi-tonnage waste from industrial enterprises, specifically technical ferrous sulfate.

It is shown that it is advisable to use the dairy effluent imitations based on milk powder for experimental studies.

The potentiometric titration of dairy effluent imitations has established the presence of two points (pH=4.2 and 8.3), which characterize the boundaries of the buffering capacity of solutions. The expediency of carrying out the process of coagulation of dairy effluents in a weakly alkaline environment at pH≥8.3 has been substantiated, and, for the starting effluent to reach such a pH value, a 10-% suspension of Ca(OH)$_2$ should be used. The effectiveness of reagent treatment of dairy effluents has been experimentally confirmed, subject to the alternate introduction of a coagulant (technical FeSO$_4$) and flocculant (polyacrylamide) in the quantities of 120 and 40 mg dm^3, respectively; the degree of clarification of dairy effluents is 90 % while the residual COC value is 76 mg O$_2$/dm^3.

It has been shown that when ultrasound was applied, it was possible to significantly reduce the interaction time and the amount of Ca(OH)$_2$ suspension necessary to achieve pH≥8.3.

Thus, there are grounds to assert the prospects for devising highly effective technology for the coagulation treatment of wastewater from milk-processing enterprises; the results and conclusions reported here about the technological feasibility of using technical FeSO$_4$ as a coagulant could be practically applied for other technologies of coagulation wastewater treatment, provided that its pH value is brought to 8.3

Keywords: dairy enterprises effluents, coagulation treatment, coagulation, flocculation, ultrasonic activation

Oksana Kurylets
Corresponding author
PhD, Associate Professor*
E-mail: oksana.h.kurylets@lpnu.ua

Andriy Helesh
Doctor of Technical Sciences, Associate Professor*

Viktor Vasiichuk
PhD, Associate Professor**

Zenoviy Znak
Doctor of Technical Sciences, Professor,
Head of Department*

Anna Romaniv
PhD, Associate Professor**
*Department of Chemistry and Technology of Inorganic Substances***
Department of Civil Safety*
***Lviv Polytechnic National University
S. Bandery str., 12, Lviv, Ukraine, 79013

1. Introduction

Milk is a valuable food product as it contains almost all the components necessary to ensure normal metabolism. Therefore, the dairy industry is among the leading ones in food production and occupies a prominent place in the consumption of the population; in particular, the share of spending on dairy products is about 15 % of the total food costs [1].

Thus, the dairy industry plays an extremely important role in providing billions of people on Earth with food and has significant economic potential for development, in particular in Ukraine.

One of the main environmental problems in the dairy industry is wastewater. Taking into consideration the results of the studies reported in [2], the most expedient method for cleaning dairy effluent is the biological complex anaerobic-aerobic process. However, there are a significant number of small and medium-sized farms for which it is not economically profitable to install expensive, cumbersome equipment for biological treatment. Usually, this wastewater is discharged into the general sewage system, which

is a gross violation of the norms since its contamination significantly exceeds the norms of discharge of wastewater into the sewer. That is, this issue remains unresolved. To address this problem, it is advisable to use physicochemical treatment methods, in particular with the help of cheap coagulators (coagulants and flocculants). In addition, such physicochemical treatment methods can be used to improve existing or develop new biological treatment methods, in particular at the stage of the so-called chemically enhanced primary treatment (CEPT)). The main task of CEPT is to remove and redirect organic substances and nutrients from wastewater. That makes it possible to significantly reduce the organic load at the stage of biological purification, as well as to obtain concentrated sludge – a valuable energy resource. Depending on the characteristics of wastewater and reagents, it is possible, by using CEPT, to reduce the value of chemical oxygen consumption (COC) by 43.1–95.6 %; suspended substances – by 70.0–99.5 %; and phosphates – by 40.0–99.3 % [3].

Therefore, research aimed at developing new and intensification of existing physicochemical methods for cleaning dairy effluents is extremely relevant.

2. Literature review and problem statement

With the development of "green chemistry", natural coagulants of plant, animal, and microbiological origin (*Moringa oleifera*, guar gum, etc.) are increasingly used [4]. Their main advantage is non-toxicity, the ability to biodegrade, they do not increase the content of chlorides and sulfates in water, which simplifies their application in recycling water use systems. However, it should be noted that "green coagulants" are less effective than synthetic ones, usually have variable composition, require special storage conditions, etc.

Industrial synthetic coagulants are divided into two categories: based on the compounds of aluminum and iron. The high efficiency of these coagulants is due to their ability, as a result of dissolution, to form multi-charge polycore complexes with high sorption properties. Commonly used in the industry are chlorides, aluminum and iron sulfates, as well as aluminum hydroxochloride, sodium aluminate, iron polysilicate, due to their availability and relative cheapness. Highly effective are modern coagulants based on pre-hydrolyzed forms of aluminum and iron: poly aluminum chloride (PAC), ferrous polysulfate (PFS), and iron chloride poly aluminum (PAFC) [5], as well as their combinations with "green coagulants" [6]. Despite the effectiveness of those coagulants, their main drawback is the high price.

Therefore, in work [7], it is proposed to choose the optimal coagulant according to the following criteria: the price of a coagulant, the degree of COC reduction, the volume of the resulting sediment after two hours, the dose of coagulant, the percentage change in the pH of wastewater after the coagulation stage. That is, one of the defining criteria in the choice of a coagulant is its price.

To reduce the cost of coagulation treatment of effluent, it is proposed to regenerate the spent coagulant and reuse it [8]. It is economically feasible to use the waste from other industries as coagulants. In particular, it is proposed to use cement dust as coagulants [9]. All these methods are less effective than those described above and are usually regional in nature. Among the large-tonnage wastes of world industrial production are ferrous salts, which are formed in the production of titanium (IV) oxide (TiO_2). Globally, about 1.3 million tons, or 40 % of the total iron content in titanium ores, is lost [10]. Ukraine's share in the world production of pigment titanium oxide is more than 2 % and, accordingly, a significant amount of waste $FeSO_4$ is formed. Thus, per each ton of product, they receive ~3...5 tons of crystalline $FeSO_4 \cdot 7H_2O$, 5...6 tons of hydrolysis sulfate acid, which contains 5.5...6.5 % by weight of $FeSO_4$ [11].

A powerful factor in the intensification of the wastewater treatment process is acoustic oscillations, in particular the ultrasonic range. Under the influence of ultrasound, complex physical and chemical processes occur in the aquatic environment that contribute to the oxidation of organic substances and reduction of COC, the structuring, compaction, and agglomeration of sediment, etc. Work [12] shows the positive effect of preliminary ultrasonic treatment of $Ca(OH)_2$ suspension on the process of coagulation treatment of wastewater from meat processing enterprises. The efficiency of the COC process, depending on the concentration and dose of acoustically treated $Ca(OH)_2$, increased by 1.3...4.5 times.

Based on a critical review of information sources, it was found that, as a rule, expensive high-purity reagents were used in the above studies. Despite the practical feasibility of introducing the multi-tonnage waste of $FeSO_4$ into the field of water purification, this issue has not been given enough attention; therefore, the issue is relevant and requires additional study. The above necessitates research, which could become a reliable basis for devising highly effective technology for the coagulation treatment of effluents from milk processing enterprises.

3. The aim and objectives of the study

The purpose of this research was to devise the technological foundations of coagulation wastewater treatment with the help of waste $FeSO_4$ and technical $Ca(OH)_2$ to the norms that could make it possible to discharge the above-mentioned effluent into the general sewerage system or environment.

To accomplish the aim, the following tasks have been set:
– to investigate the effect of pH on the process of coagulation of effluents;
– to establish the value of the effective dose of coagulant and flocculant;
– to study the effect of ultrasonic sounding on the effectiveness of the use of the $Ca(OH)_2$ suspension.

4. The study materials and methods

Imitations based on milk powder were used as effluents (DSTU 4273:2003). Milk powder was diluted according to the instructions. Namely, 1 g of milk powder was introduced into a measuring flask with a capacity of 100 ml, hot water was also added (60 °C). The mixture was thoroughly agitated and brought to the label after cooling. Further, an aliquot was taken from the prepared milk, 5 ml, and put in a measuring flask with a capacity of 500 ml. The volume to the label was brought by distilled water. During this dilution, the content of organic compounds of COC≈1,650 mgO_2/dm^3 in the imitation was achieved.

To determine the effect of pH on the coagulation properties of the study system, potentiometric titration with standard 0.1 M solutions NaOH and HCl was used. The values were recorded using the pH-meter of the pH-673M brand and a pair of electrodes, glass ESL-43-07, and chlorine silver EVL-1M. The initial pH value of the examined system was 6.3.

For mixing reagents in the process of coagulation cleaning, a capacitive reactor of 0.5 dm^3 was used, which was equipped with a mechanical agitator with an adjustable number of revolutions. Agitation lasted for 5 minutes. The timing and intensity of the agitation were chosen as a result of previous experimental studies. Initially, with intensive agitation (Re_m=8,000; n=300 rpm), $Ca(OH)_2$ was injected into the imitation and agitated for 2 minutes. Next, we reduced the intensity of agitation to Re_m=4,000 (n=150 rpm) and added the coagulant ($FeSO_4$), which was agitated for 1 minute. At the next stage, the agitation speed was reduced to Re_m=800 (n=30 rpm), after which a flocculant (PAA) was injected into the system and agitated for 2 more minutes. Such a hydrodynamic regime made it possible to achieve sufficient homogenization of the main components of the study system and did not lead to the destruction of the formed coagulation flakes.

The samples settled in measuring cylinders with a volume of 0.25 dm^3. The coagulant and flocculant used were 1-% solutions of technical ferrous sulfate (DSTU 2463-94) and PAA (TU 6-16-2531-81); to stabilize the pH, we used a saturated solution and a 10-% suspension of Ca(OH)$_2$, prepared from slaked lime (DSTU B V.2.7-90:2011).

The concentrations of the coagulant and flocculant solutions were chosen for reasons of convenience of laboratory tests. In addition, at higher concentrations of coagulant solution, the dosage accuracy decreases. For coagulation treatment technology, it is not the initial concentration of coagulant and flocculant that is decisive but their concentration in wastewater. Therefore, when scaling processes to industrial application, it is advisable to adjust the starting concentrations of reagents.

Since pollutants are organic substances different in nature, therefore, the integrated efficiency of purification was estimated on the basis of change in the value of COC. The starting value of COC of the studied system was ~1650 mgO$_2$/dm^3. The value of COC was determined using a standardized procedure (DSTU ISO 6060: 2003), which is based on the oxidation of the organic part of the water phase with a strong oxidizing agent – potassium dichromate in an acidic environment.

The effect of ultrasonic vibrations on the wastewater treatment process was investigated using the US-emitter of magnetostriction type "Ultrasonic Disintegrator" UD-20; radiation frequency – 22 kHz; rated power – 10.2 W.

To characterize the efficiency of wastewater treatment, the following indicators were used: the degree of clarification (the ratio of the height of the clarified part to the total height of wastewater in the cylinder), the degree of purification ((COC$_{initial}$−COC$_{final}$)/COC$_{initial}$·100 %), residual COC.

We analyzed and processed our experimental results using the standard Microsoft Office 2016 software suite. To derive mathematical dependences, the least-square method was applied involving the approximation of values with the corresponding functions. In the cases where the experimentally obtained curves were complex, due to the influence of various, physical, physicochemical, and chemical processes, the results were approximated for the corresponding intervals of input variables. We divided the region of determination into intervals based on general theoretical ideas about the physicochemical essence of the processes studied. The equations and values of the probabilities of approximations (R^2) are given in tables below the corresponding figures.

5. Results of studying the processes of coagulation treatment of wastewater from milk-processing enterprises

5. 1. Investigating the effect of pH on the process of effluent coagulation

The results of studying the effect of pH on the coagulation properties of the studied system are shown in Fig. 1. The differentiation of the curve of acid-base titration ($\Delta pH/\Delta V = f(pH)$ established the presence of two maxima – at pH 4.2 and 8.3. For the mathematical treatment of our experimental results, the region of values was divided into 4 intervals: 1 – pH= 6.3...4.2; 2 – pH=4.2...2.3; 3 – pH=6.3...8.3; 4 – pH=8.3...10.2.
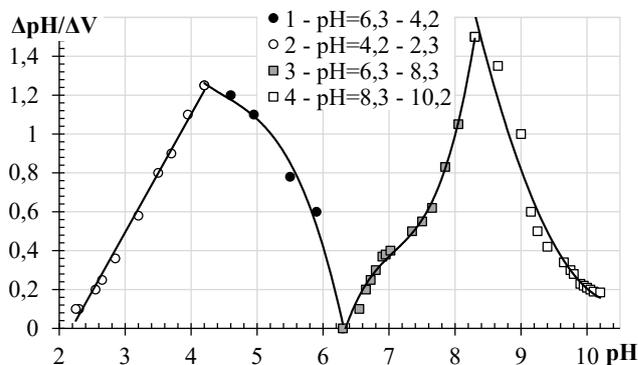
Fig. 1. Results of acid-base titration of dairy effluent imitation

Table 1

Approximation equations of the experimental results from acid-base titration of dairy effluent imitation (Fig. 1)

No. of entry	pH interval	Equations and approximation probabilities values (R^2)
1	6.3 – 4.2	$\Delta pH/\Delta V=-0.1352pH^3+1.8201pH^2-8.3718pH+14.334$; $R^2=0.9898$
2	4.2 – 2.3	$\Delta pH/\Delta V=0.6072pH-1.3275$; $R^2=0.9931$
3	6.3 – 8.3	$\Delta pH/\Delta V=0.3873pH^3-8.2264pH^2+58.565pH-139.34$; $R^2=0.9948$
4	8.3 – 10.2	$\Delta pH/\Delta V=0.3121pH^2-6.5424pH+34.42$; $R^2=0.9611$

At pH=8.3, the wastewater would be low-aggressive, which significantly reduces the requirements for corrosion resistance of the equipment. Accordingly, the cleaning technology is simplified and cheaper. In addition, to bring the wastewater to pH=8.3, one can use a cheap commodity product – construction lime (DSTU B V.2.7-90: 2011). In subsequent studies, the starting effluent was brought to a slightly higher pH value relative to theoretical, which was due to the need to neutralize the residual acidity of the coagulant – technical FeSO$_4$, and sulfate acid, which is formed during its hydrolysis. Therefore, further studies were conducted at pH≥8.3 using a saturated solution (lime water) of 1.5–1.65 g/l and a 10-% suspension (lime milk) of Ca(OH)$_2$. It was expected that in addition to increasing the pH, the use of Ca(OH)$_2$ could contribute to the formation of low-soluble calcium organic and inorganic compounds. The resulting calcium compounds would play the role of coagulation centers while the optimal pH could contribute to the rapid settlement of dispersed particles.

5. 2. Establishing the value of the effective dose of coagulant and flocculant

Our studies have confirmed the assumption that with the use of Ca(OH)$_2$ solution, rapid formation of agglomerates was observed, but their resistance and sedimentation rate were low. Therefore, in order to intensify the process of sedimentation and the formation of stable particles, we investigated the effect of the concentration of the coagulant FeSO$_4$ on the degree of clarification of effluents over time (Fig. 2). The coagulant was introduced in the amount of 1, 3, 5, and 10 cm^3 per 250 cm^3 of wastewater, which was, respectively, 40, 120, 200, 400 mg/dm^3.
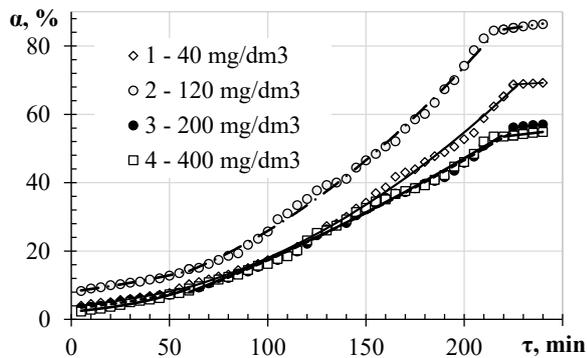
Fig. 2. Time dependence of the effluent clarification degree on the coagulant $FeSO_4$ concentration, mg/dm^3: 1 − 40; 2 − 120; 3 − 200; 4 − 400

tangible effect. Subject to the reverse order of introduction, the process of active particle aggregation was observed in the studied system at the beginning of the experiment. In these search studies, 1, 3, 5, and 10 cm^3 of PAA flocculant for 250 cm^3 of wastewater were introduced into the system. The results of experimental studies are given in Table 4.

Table 4

The effect of PAA concentration on the degree of dairy effluent treatment

PAA amount (1 %)	cm^3/250 cm^3	1	3	5	10
	mg/dm^3	40	120	200	400
Residual COC	mgO$_2$/dm^3	76	140	95	171
Treatment degree	%	95.4	91.5	94.2	89.6

Table 2

Approximation equations of the experimental results from studying the influence of coagulant $FeSO_4$ concentration on the degree of effluent clarification (Fig. 2)

C(FeSO$_4$), mg/dm^3	Stages of the clarification process and their duration		
	Flake formation, 5–60 min	Particle sedimentation, 60–220 min	Sediment compaction, 220–240 min
	Equations and approximation probabilities values (R^2))		
40	$\alpha=3.7564e^{0.0155\,\tau}$; $R^2=0.9753$	$\alpha=0.0011\tau^2+0.0346\tau+3.4095$; $R^2=0.9968$	$\alpha=0.032\tau+61.51$; $R^2=0.9846$
120	$\alpha=8.085e^{0.0094\tau}$; $R^2=0.9854$	$\alpha=0.0014\tau^2+0.0695\tau+5.1097$; $R^2=0.9965$	$\alpha=0.0815\tau+66.927$; $R^2=0.9897$
200	$\alpha=3.1889e^{0.017\tau}$; $R^2=0.9859$	$\alpha=0.0004\tau^2+0.1712\tau-4.0954$; $R^2=0.9944$	$\alpha=0.0692\tau+40.485$; $R^2=0.9723$
400	$\alpha=2.2591e^{0.0231\tau}$; $R^2=0.9812$	$\alpha=0.0005\tau^2+0.1534\tau-3.5951$; $R^2=0.9942$	$\alpha=0.0686\tau+38.392$; $R^2=0.9897$

The technologically expedient concentration of the coagulant, which demonstrated the best clarification indicators, equals 120 mg/dm^3. In the case of an increase or decrease in the concentration of the coagulant, the separation process deteriorated (Fig. 2, curves 1, 3, 4). At a coagulant concentration of 120 mg/dm^3, on minute 230, the degree of clarification (α) was 86.5 %. The resulting clarified effluents were visually transparent without colloidal inclusions.

For these effluents, the value of COC was determined. The average results of the research are given in Table 3.

Table 3

Effect of coagulant concentration on the degree of dairy effluent treatment

FeSO$_4$ coagulant amount (1 %)	cm^3/250 cm^3	1	3	5	10
	mg/dm^3	40	120	200	400
Residual COC of clarified effluent	mgO$_2$/dm^3	1,060	573	968	780
Treatment degree	%	35.7	60.6	41.3	52.6

In order to intensify and deepen the coagulation process, a series of experiments was carried out using a flocculant – a 1-% PAA solution. It has been experimentally established that the alternateness of the addition of reagents (coagulant and flocculant) has a significant impact on the efficiency of the process. Thus, the introduction of first flocculant PAA and then coagulant $FeSO_4$ into the study system did not produce a

Table 4 demonstrates that with an increase in the PAA concentration, the degree of purification in terms of COC decreased. The best result was obtained with a minimum amount of flocculant, which corresponds to the concentration of PAA of 40 mg/dm^3.

To refine the value of the technologically expedient concentration of a flocculant, a study was conducted during which 0.5; 1.0; and 1.5 cm^3 of the PAA flocculant for 250 cm^3 of effluent were injected into the system, which was, respectively, mg/dm^3: 20, 40, 60. Based on the results, we built graphical dependences of the degree of solution clarification over time at the aforementioned concentrations of the flocculant (Fig. 3).
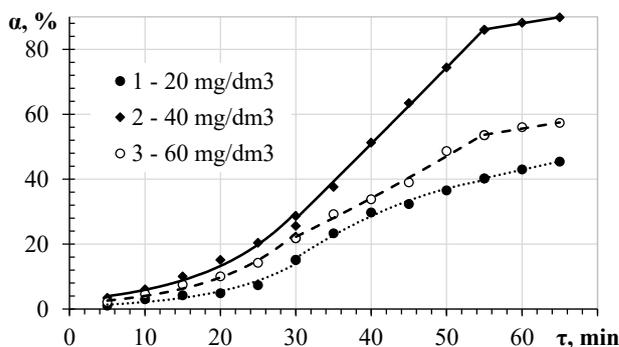
Fig. 3. The dependence of the degree of effluent clarification over time on the concentration of the PAA flocculant, mg/dm^3: 1 − 20; 2 − 40; 3 − 60

Table 5

Approximation equations of the experimental results from studying the influence of the concentration of PAA flocculant on the degree of effluent clarification (Fig. 3)

S(PAA), mg/dm^3	Stages of the clarification process and their duration		
	Flake formation, 5–30 min	Particle sedimentation, 30–55 min	Compaction, 55–65 min
	Equations and approximation probabilities values (R^2)		
20	$\alpha=0.8437e^{0.0936\tau}$; $R^2=0.9575$	$\alpha=-0.0154\tau^2+2.2936\tau-38.94$; $R^2=0.9903$	$\alpha=0.52\tau+11.667$; $R^2=0.998$
40	$\alpha=2.6224e^{0.081\tau}$; $R^2=0.9633$	$\alpha=0.0019\tau^2+2.1827\tau-39.389$; $R^2=0.9982$	$\alpha=0.38\tau+65.2$; $R^2=0.9918$
60	$\alpha=1.6762e^{0.0878\tau}$; $R^2=0.9904$	$\alpha=0.0054\tau^2+0.8126\tau-6.9543$; $R^2=0.9911$	$\alpha=0.38\tau+32.8$; $R^2=0.9678$

At the initial time, for 20–25 minutes, all three samples demonstrated the formation and consolidation of flakes and their slow deposition. Next, after 30 minutes, in all samples there was a rectilinear increase in the degree of clarification, and, after 60 minutes, the degree of clarification changed slightly. As can be seen from the figure, the most intensive deposition process occurred at a PAA concentration of 40 mg/dm^3. On minute 60 of the experiment, curve 2 enters the plateau, the degree of clarification almost reaches 90 %. For other experiments, the degree of clarification does not exceed 45...55 %.

5. 3. The effect of ultrasonic sounding on the efficiency of using the Ca(OH)$_2$ suspension

In the experimental studies, to stabilize the pH, the alkaline reagent used was a saturated solution of Ca(OH)$_2$. Due to the low solubility of Ca(OH)$_2$ (1.65 mg/dm^3), the technological use of such low-concentrated solutions is economically costly. Therefore, in technological processes, Ca(OH)$_2$ is usually used in the form of lime milk – 10 % suspension, the full utilization of which depends on the hydrodynamics of the process and the activity of particles of the solid phase. As noted earlier, an effective way to activate the Ca(OH)$_2$ suspension is the effect of ultrasonic acoustic oscillations on it. Therefore, a study was conducted on the effect of US radiation on the pH value of the reaction medium. The results of the study are shown in Fig. 4.
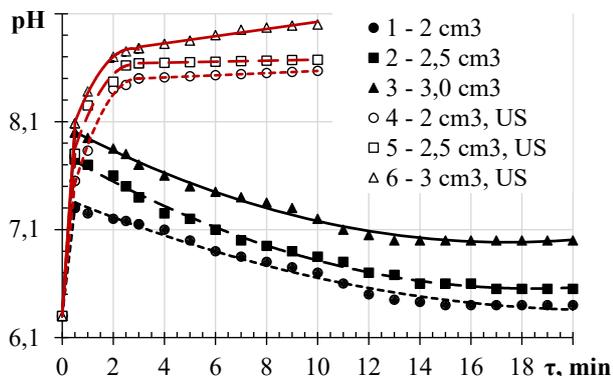
Fig. 4. The dependence of wastewater pH on the amount of a 10-% suspension of Ca(OH)$_2$ and the effect of ultrasound. Ca(OH)$_2$ volume, cm^3: 1, 4 — 2.0; 2, 5 — 2.5; 3, 6 — 3.0. $V_{solution}$=250 cm^3; 1, 2, 3 — mechanical agitation (Re_m=8,000, n=300 rpm); 4, 5, 6 — under the influence of US radiation

In the experiments with mechanical agitation without US sounding during the first 30 s after the introduction of the suspension of Ca(OH)$_2$, we recorded a sharp increase in alkalinity, from pH=6.3 to pH=8, at the volume of the introduced suspension of 3 ml (dependence 3). With a decrease in the volume of the suspension of Ca(OH)$_2$ introduced into the reaction medium, the maximum recorded pH value was naturally reduced (dependences 1, 2). Subsequently, in the process of agitation, the pH value monotonously decreased and stabilized on minutes 13–15 at the level of 6.4–7. In all cases, the required pH≥8.3 could not be reached. Under the action of US radiation, the nature of the change in the pH of the reaction medium over time, regardless of the amount of the Ca(OH)$_2$ suspension introduced, varies significantly (Fig. 4, dependences 4–6). As in the first case, there was a sharp increase in pH at the beginning of the process, but then the nature of the pH change was completely different: the pH of the reaction mixture continued to grow after 2...3 minutes, upon reaching a value of 8.4...8.7, it plateaued. That is, due to the effect of ultrasound, it was possible to significantly reduce the interaction time and the amount necessary to achieve the pH≥8.3 of Ca(OH)$_2$ suspension.

6. Discussion of results of the coagulation treatment of wastewater from milk-processing enterprises

The presence of two peaks on the curves of the acid-base titration of dairy effluent imitation (Fig. 1) can be explained by the buffering properties of milk.

To quantify the buffering property of milk, the concept of "buffering capacity" was introduced. The buffering capacity of fresh milk in terms of acid is 1.7–2.6 cm^3, in terms of alkali – 1.2–1.4 cm^3 [13]. However, the dairy effluent imitations studied were the diluted milk powder solutions; for them, the above indicators were not investigated. It was found that they are also characterized by a "buffering capacity", which, in terms of alkali, is less than that in terms of acid, and reaches its limit at pH=8.3.

In milk, phosphate (pK=7), hydrogen carbonate (pK=6.5), protein (pK=6.0), citrate (pK=5.6 and 4.4), and lactate (pK=3.9) buffers are distinguished. In the process of titration with acid, there is a gradual decrease in pH (curve 1). Accordingly, all the above buffering systems begin to work sequentially. According to the literature [13], in fresh milk, at pH<5.2, the buffering capacity could be exhausted; the pH would decrease sharply. In the studied system (curve 1), this decrease begins at pH=4.2. Such a shift can be explained by the fact that for the preparation of dairy effluent imitation, we used milk powder, which was thermally treated. As it was established in work [14], as a result of heating milk to 100 °C, the buffering capacity shifts from pH=5.1 to pH=4.7. This is explained by changes due to the formation of calcium phosphate, which is chemically different from its native

Table 6

Approximation equations of the experimental results from studying the influence of the amount of Ca(OH)$_2$ and the effect of ultrasound on the pH value of effluent (Fig. 4)

	V(Ca(OH)$_2$), cm^3/250 cm^3	Process stages and their duration		
		stage 1, 0–0.5 min	stage 2, 0.5–20 min	
		Equations and approximation probabilities values (R^2)		
Mechanical agitation	2.0	pH=2τ+6.3; R^2=1	pH=0.0023τ^2−0.0971τ+7.3992; R^2=0.9868	
	2.5	pH=2.9τ+6.3; R^2=1	pH=0.0037τ^2−0.1357τ+7.8025; R^2=0.9951	
	3.0	pH=3.4τ+6.3; R^2=1	pH=0.0036τ^2−0.1244τ+8.0656; R^2=0.9933	
	–	stage 1, 0–0.5 min.	stage 2, 0.5–3 min.	stage 3, 3–10 min.
Mechanical agitation and US	2.0	pH=2.5τ+6.3; R^2=1	pH=−0.1615τ^2+0.9568τ+7.0859; R^2=0.9921	pH=0.01τ+8.47; R^2=1
	2.5	pH=3τ+6.3; R^2=1	pH=−0.1485τ^2+0.8282τ+7.4741; R^2=0.9657	pH=0.0047τ+8.6263; R^2=0.9945
	3.0	pH=3.57τ+6.3; R^2=1	pH=−0.1331τ^2+0.7355τ+7.7607; R^2=0.9977	pH=0.0333τ+8.6908; R^2=0.9652

micellar form. In the process of the further souring of the imitations, a monotonous almost straightforward decrease in the value of $\Delta pH/\Delta V$ occurs, which indicates the absence of a buffering effect (curve 2). When adding alkali to the dairy effluent imitation, we observe a gradual increase in pH (curve 3). The nonlinearity of the resulting dependence can be explained by the presence of protein, hydrogen carbonate, and phosphate buffers. At pH=8.3 (curve 4), there is a sharp rectilinear decrease in the value of $\Delta pH/\Delta V$, which slows down in the interval pH=9.2–10.2, which can be explained by the interaction of milk fatty acids with alkali. The results obtained agree well with the results reported in [15].

In the process of studying the effect of coagulant concentration (FeSO$_4$) on the degree of clarification and process duration, characteristic coagulation dependences were built (Fig. 2). When studying the effect of coagulant concentration (FeSO$_4$) on the degree of clarification and process duration, characteristic coagulation dependences were established (Fig. 2). On all dependences of changing the degree of clarification of the system over time, three characteristic stages of the process can be distinguished. The first stage (from minute 5 to minute 60) is the origin and aggregation of colloidal particles with the formation of flakes.

The second stage is the deposition of the formed flakes (occurs up to minute 220). Subsequently, the resulting precipitate is compacted – this is the final third stage; it is slow. It was found that at a concentration of FeSO$_4$ of 120 mg/dm^3 and the process duration of 230 minutes, the highest degrees of clarification and treatment were achieved – 86.5 and 60.6 % (Table 3), respectively. The residual value of COC in the clarified effluent is 573 mgO$_2$/dm^3. With such indicators, wastewater can be discharged into the general sewerage system for the subsequent biological purification, and the resulting organic-containing sediment (silt) can be recycled (CEPT technology). These dependences agree well with the classic ones for coagulation but we used the exhaust FeSO$_4$ in the process, which is little investigated as a coagulant, and, therefore, we believe that the data obtained are original and necessary for the development of technology.

A significant duration of the coagulation process (230 minutes) necessitates the bulky hardware structure for the process. Therefore, the use of a flocculant (PAA) significantly intensified and deepened the process of coagulation purification (Fig. 3, Table 4). The nature of the clarification curves did not change (Fig. 3) but the duration of the process significantly decreased – 60 minutes. That is, the duration of coagulation treatment of milk effluent has decreased by almost 3 times. In addition, the use of a flocculant significantly improved water purification indicators. Thus, at a concentration of PAA of 40 mg/dm^3, the highest degrees of clarification and purification were achieved – 90.0 and 95.4 % (Fig. 3, Table 4), respectively. That is, a significant role in the cleaning process belongs to the dose of a flocculant. Thus, if there is a shortage of flocculant (C$_{PAA}$=20 mg/dm^3), it cannot bind all coagulation conglomerates, and, therefore, the degree of effluent clarification does not exceed 45 % (Fig. 3). At a technologically expedient concentration of a flocculant (C$_{PAA}$=40 mg/dm^3), separate dense and sufficiently large agglomerates are formed, which are prone to rapid and almost complete sedimentation. In the case of an increased concentration of the flocculant (C$_{PAA}$=60...400 mg/dm^3), the degree of purification is insignificantly, and the degree of clarification significantly, deteriorated. This can be ex-plained by the formation of a three-dimensional spatial grid of PAA molecules, which stabilizes the suspension (Fig. 3, Table 4). The residual value of COC in the clarified effluent is 76 mg O$_2$/dm^3. It should be noted that the residual content of COC in the clarified liquid phase does not exceed the maximum permissible concentrations and such purified effluent can be discharged into the environment without harming it.

In the course of our study, it was found that in the case of using, for coagulation purification, of a 10-% suspension of Ca(OH)$_2$, its significant overconsumption is observed. In particular, in the process of mechanical agitation of dairy effluents and a certain dose of the suspension of Ca(OH)$_2$ (Fig. 4, dependences 1–3), it was not possible to achieve the required pH≥8.3 value. This can be explained by the formation of insoluble interaction products on the surface of the suspended Ca(OH)$_2$ particles, which block the further interaction of the reagent. Instead, under the same conditions, as a result of the acoustic oscillations within a US band, it was possible to significantly reduce the interaction time and reach pH=8.4...8.7. Such a positive effect can be explained by the fact that due to the action of acoustic oscillations in the heterogeneous system, diffusion processes are intensified. In addition, under the effect of US radiation in the aquatic environment, the phenomenon of cavitation is excited, which is accompanied by a number of different effects, in particular, the commutative effect. As a result of the action of cavitation microcurrents, the dispersion of Ca(OH)$_2$ particles and the renewal of their surface as a result of the destruction of low-soluble interaction products occur. All this, in general, leads to an increase in the contact area and an increase in the reactivity of activated particles of Ca(OH)$_2$.

It should be noted that ultrasound exposure studies were conducted for only one frequency and radiation power. This predetermines certain restrictions in the use of our results and can be interpreted as a disadvantage of the current study. At the same time, these restrictions open up new prospects for further research, in particular, it is advisable to investigate the impact of the frequency and power of US radiation on the indicators of the cavitation treatment process.

7. Conclusions

1. It has been established that the process of coagulation treatment of dairy effluents should be carried out in a weakly alkaline environment at a pH of 8.3; the starting effluent was brought to this pH value by using a 10-% suspension of Ca(OH)$_2$.

2. To intensify the process of deposition of the colloid, formed after the alkalization of dairy effluents, it is proposed to alternately introduce a coagulant, technical FeSO$_4$, and a flocculant, PAA, in the following quantities, mg/dm^3: 120 and 40, respectively. Under such conditions, within 1 hour, it was possible to achieve a degree of clarification of 90 % and a residual value of COC in the treated effluent of 76 mgO$_2$/dm^3. These values do not exceed regulatory indicators, and, therefore, such water can be used for household needs, or released into the environment.

3. The use of US sounding for milk effluent at the stage of adjusting the pH to the value of ≥8.3 has made it possible to increase the utilization factor of a 10-% suspension of Ca(OH)$_2$ and significantly reduce the duration of the process.

References

1. Ahmad, T., Aadil, R. M., Ahmed, H., Rahman, U. ur, Soares, B. C. V., Souza, S. L. Q. et. al. (2019). Treatment and utilization of dairy industrial waste: A review. Trends in Food Science & Technology, 88, 361–372. doi: https://doi.org/10.1016/j.tifs.2019.04.003

2. Kumar Awasthi, M., Paul, A., Kumar, V., Sar, T., Kumar, D., Sarsaiya, S. et. al. (2022). Recent trends and developments on integrated biochemical conversion process for valorization of dairy waste to value added bioproducts: A review. Bioresource Technology, 344, 126193. doi: https://doi.org/10.1016/j.biortech.2021.126193

3. Shewa, W. A., Dagnew, M. (2020). Revisiting Chemically Enhanced Primary Treatment of Wastewater: A Review. Sustainability, 12 (15), 5928. doi: https://doi.org/10.3390/su12155928

4. Muniz, G. L., Borges, A. C., Silva, T. C. F. da. (2020). Performance of natural coagulants obtained from agro-industrial wastes in dairy wastewater treatment using dissolved air flotation. Journal of Water Process Engineering, 37, 101453. doi: https://doi.org/10.1016/j.jwpe.2020.101453

5. El Foulani, A.-A., Jamal-eddine, J., Lekhlif, B. (2022). Study of aluminium speciation in the coagulant composite of polyaluminium chloride-chitosan for the optimization of drinking water treatment. Process Safety and Environmental Protection, 158, 400–408. doi: https://doi.org/10.1016/j.psep.2021.12.028

6. Lapointe, M., Papineau, I., Peldszus, S., Peleato, N., Barbeau, B. (2021). Identifying the best coagulant for simultaneous water treatment objectives: Interactions of mononuclear and polynuclear aluminum species with different natural organic matter fractions. Journal of Water Process Engineering, 40, 101829. doi: https://doi.org/10.1016/j.jwpe.2020.101829

7. Qasim, W., Mane, A. V. (2013). Characterization and treatment of selected food industrial effluents by coagulation and adsorption techniques. Water Resources and Industry, 4, 1–12. doi: https://doi.org/10.1016/j.wri.2013.09.005

8. Chakraborty, T., Balusani, D., Smith, S., Santoro, D., Walton, J., Nakhla, G., Ray, M. B. (2020). Reusability of recovered iron coagulant from primary municipal sludge and its impact on chemically enhanced primary treatment. Separation and Purification Technology, 231, 115894. doi: https://doi.org/10.1016/j.seppur.2019.115894

9. Mahmoued, E. K. (2013). Application of cement kiln dust for chemically enhanced primary treatment of municipal wastewater. Desalination and Water Treatment, 52 (25-27), 4698–4704. doi: https://doi.org/10.1080/19443994.2013.810384

10. Sam, J., Kirankumar, P. S., Sanath, K., Prathish, K. P. (2021). Development of saleable chloride free iron oxide from hazardous waste in titanium industries via layered double hydroxide formation. Journal of Environmental Management, 290, 112566. doi: https://doi.org/10.1016/j.jenvman.2021.112566

11. Kalymon, Y., Helesh, A., Yavorskyi, O. (2012). Hydrolytic Sulphate Acid Evaporation by Waste Gases from Burning Furnaces of Meta-Titanic Acid Paste. Chemistry & Chemical Technology, 6 (4), 423–429. doi: https://doi.org/10.23939/chcht06.04.423

12. Savchuk, L., Znak, Z., Kurylets, O., Mnykh, R., Olenych, R. (2017). Research into processes of wastewater treatment at plants of meat processing industry by flotation and coagulation. Eastern-European Journal of Enterprise Technologies, 3 (10 (87)), 4–9. doi: https://doi.org/10.15587/1729-4061.2017.101736

13. Ostroumova, T. A. (2004). Himiya i fizika moloka. Kemerovo, 196.

14. Wang, Q., Ma, Y. (2020). Effect of temperature and pH on salts equilibria and calcium phosphate in bovine milk. International Dairy Journal, 110, 104713. doi: https://doi.org/10.1016/j.idairyj.2020.104713

15. Bai, Y., Zhao, D. (2015). The acid–base buffering properties of Alxa bactrian camel milk. Small Ruminant Research, 123 (2-3), 287–292. doi: https://doi.org/10.1016/j.smallrumres.2014.10.011