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OBSTACLES IN LIME MILK APPLICATION FOR THE TREATMENT OF FOOD INDUSTRY WASTEWATER

ZAKŁÓCENIA PROCESU OCZYSZCZANIA ŚCIEKÓW Z PRZEMYSŁU SPOŻYWCZEGO ZA POMOCĄ MLECZKA WAPIENNEGO

Abstract: It is particularly difficult to treat wastewater from the production of edible oils because of high concentration of phosphates, sulphates as well as organic compounds. What is more, the application of physicochemical methods of purification may be limited due to the varied wastewater character and its chemical properties. Phosphates precipitated by means of calcium hydroxide turn into calcium phosphates, usually in the form of hydroxyapatite (HAP), which together with an excessive amount of calcium hydroxide create well-sedimenting sludge. However, the industrial application of the method for the treatment of the analysed effluent leads to the burdensome floating sludge. The research project was carried out to establish the causes of partial sludge floating. Raw and treated wastewater (after sedimentation process) as well as sludge samples collected in the settling tank were analysed with a view to identify their chemical content. Furthermore, the sludge samples were mixed mechanically and stored in anaerobic conditions and the sedimentation process was studied in laboratory conditions. The research focused on basic physicochemical parameters, including concentration of calcium and fatty substances. It was established that the pretreatment process may be hindered by an excessive amount of fatty substances, which generate lime-fatty complex compounds. Moreover, calcium hydroxide used for phosphates precipitation lead to the release of sulphates into the treated wastewater.

Keywords: food industry wastewater, phosphates removal, coagulation, fatty substances

Food processing companies, including edible fat and oils processing companies, generate wastewater characterized by widely varied chemical composition. The wastewater composition is determined by technology used, the raw materials processed as well as applied reagents.

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The main pollutants produced by edible fat and oils processing companies are fatty substances. Saatci [1] maintains that wastewater generated in the production of sunflower oil is polluted with linolenic acid (52.4 %), oleic acid (29.3 %) as well as arachidic acid, stearic acid and palmitic acid. Apart from fatty substances mentioned above as well as lipids, the wastewater contains total phosphorus in the range of 216–556 mg P/dm^3. The effluent is additionally polluted with substances of CODs – between 5600 and 15300 mg O_2/dm^3. The process of colza oil production also generates effluents polluted with substances of CODs – between 940 and 6364 mg O_2/dm^3; total phosphorus – between 67 and 354 mg P/dm^3, as well as sulphates – between 911 and 4210 mg SO_2/dm^3 [2].

In order to meet quality standards set by municipal sewage treatment plants and avoid high penalties, edible fat and oils companies are forced to pre-treat the wastewater they generate. Fatty substances are generally removed by means of fat traps. Whilst, phosphorus compounds are removed primarily by means of chemical precipitation. It is quite common to remove phosphates in the form of calcium phosphates at increased pH value. Orthophosphates reacting with lime milk precipitate into: amorphous tricalcium phosphatate $Ca_3(PO_4)_2$, or crystalline amorphous $Ca_5(PO_4)_3OH$, or less frequently in the form of tetracalcium phosphatate $Ca_4H(PO_4)_3$. Due to the wide range of precipitated compounds of lime and phosphorous as well as other chemical substances, it is difficult to establish exactly which chemical substances are the product of the precipitation. The types of compounds generated in the process are determined by pH, alkalinity, temperature, initial concentration of Ca/P and other substances, eg carbonates [3–5]. The lime milk added removes also sulphates, however, Ruffer [6] claims that the process of sulphates precipitation is accompanied by the generation of large amount of sludge.

Phosphates precipitated by means of calcium hydroxide in the form of hydroxy-apatite usually create well-sedimenting sludge, but the application of the method for the treatment of the examined wastewater leads to the burdensome floating sludge. Moreover, organic compounds removed become an integral part of the sludge. The main aim of the research project was to established the causes of the partial sludge floating. It was assumed that chemical reactions and biological processes might have changed the chemical composition of the sludge and caused it to float on the surface of the settling tank. In order to verify above assumptions the sedimentation process was studied in laboratory conditions.

The process of wastewater treatment

The technological process of wastewater treatment is divided into three stages: fat removal, phosphorous compounds precipitation as well as dewatering the sludge generated in the preceding stage.

Raw wastewater flows gravitally into a fat trap. The wastewater is pomped out of the last chamber of the fat trap and transferred into a reaction tank. Lime milk and flocculent, which facilitates coagulation, are dosed into that tank. Next, it is transferred into a flocculation tank, where flocs are precipitated. The wastewater leaves the

flocculation tank and is directed into a settling tank. The clarified samples are neutralized to lower pH. The generated sludge is mechanically dewatered by means of a centrifuge and the sludge supernatant is recirculated into the reaction tank (Fig. 1).

Research materials and methods

The research project concerned industrial wastewater (raw and treated) as well as postsedimenting sludge from the pre-treatment plant based on phosphates precipitation by means of lime milk. Raw sewage was collected on a pipe leading to a pretreatment plant while treated sewage – directly from the settling tank. The sludge was collected from the bottom of the settling tank – referred below to as sedimenting sludge as well as from the surface of the settling tank – referred below to as floating sludge. The research materials was gathered irrespective of technological or weather conditions. Chemical analyses were carried out on the day when the samples were collected. The scope of the research project encompassed: oxidic reduction potential (ORP), pH and conductivity measurements; concentration of phosphates and sulphates; COD data; calcium ions concentration as well as fatty substances content [7]. In case of sludge, the concentration of phosphates and sulphates as well as CODs measurement was conducted in the sludge supernatant after it had been centrifuged.

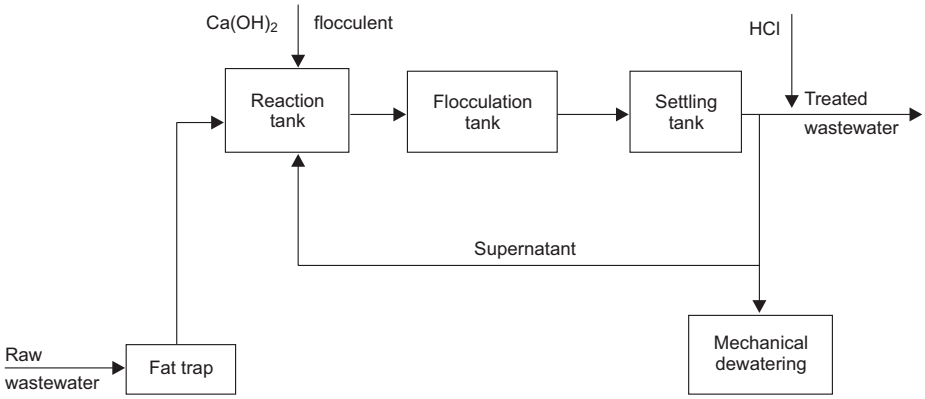

Fig. 1. The process of wastewater treatment

Discussion

The research results show that the applied method quarantees almost complete removal of phosphates – in over 90 % of cases, the average amount of phosphates does not exceed 2 mg PO_4/dm^3 (Table 1). The relatively high sulphates content in the treated wastewater proves that lime treatment is not an effective method of sulphates removal, which confirms Rüffer's explanation, according to which sulphates precipitation by means of lime reduces the content of sulphates to no less than 2000 mg SO_4/dm^3 (Table 1).

Table 1

Results of wastewater analysis

Parameter	Unit of measure	Raw sewage		Treated sewage	
		Range of variation	Average value	Range of variation	Average value
pH	—	5.66–6.05	5.95	8.95–11.05	10.32
ORP	mV	–142– –420	–203	–224– –412	–343
Conductivity	μS/cm	3550–4510	4800	5530–6360	6050
Phosphates	mg PO_4/dm^3	525–1460	1000	0.5–2.96	1.50
Sulphates	mg SO_4/dm^3	1300–3300	1430	500–2100	1890
COD	mg O_2/dm^3	2200–8500	5000	500–3100	1800
Ether extract	g/dm^3	1.20–3.30	2.18	0.04–0.12	0.07

What is more, the lime treatment reduces the amount of CODs by about 60 %. Since fatty substances might have been retained in sludge, the level of fats measured as a ether extract in both raw and treated samples was monitored. It was also confirmed that applied method removes over 95 % of fatty substances (Table 1).

Next, sedimenting and floating sludge were investigated. The sedimenting sludge exhibited ORP at the level of between –210 and –500 mV, while the floating sludge showed ORP at the level of between od –390 do – 450 mV. In case of the floating sludge, a narrow ORP range allows to conclude that the processes involved are exclusively anaerobic in nature. It was also established that there are significant differences between these sludges in terms of conductivity – the supernatant of the floating sludge exhibited conductivity which was higher by about 1000 μS/cm – on average. The difference may be caused by low content of sulphates in the floating sludge.

The average level of sulphates in the floating sludge at 350 mg SO_4/dm^3 was rather unexpected. It cannot be convincingly explained because the raw wastewater, treated wastewater as well as sedimenting sludge contained almost the same amount of sulphates. Taking into account strongly reductive and thus anaerobic conditions, it is assumed that sulphates can be only converted into sulphides and hydrogen sulfide.

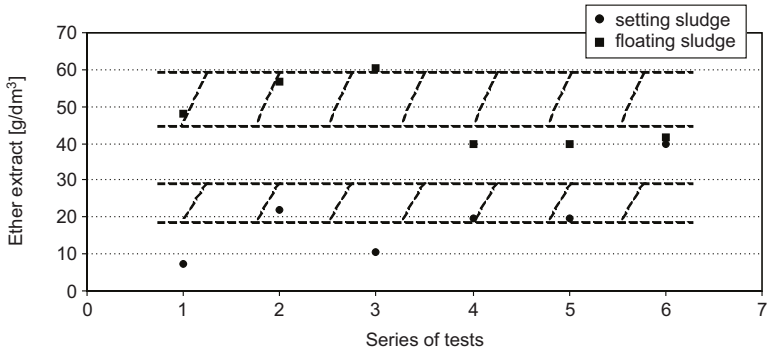

Fig. 2. Fatty substances content – measured as an ether extract

The removal of CODs and fatty substances from the wastewater by means of lime treatment, influences the chemical composition of the sludge. The sedimenting sludge contains between 10 and 20 g/dm^3 of fatty substances, while the floating sludge contains at least three times as much of these compounds– between 40 and 60 g/dm^3 (Fig. 2).

Figure 3 presents the amount of fatty substances in sludge samples – expressed in a different way, ie as a percentage of sludge solids.

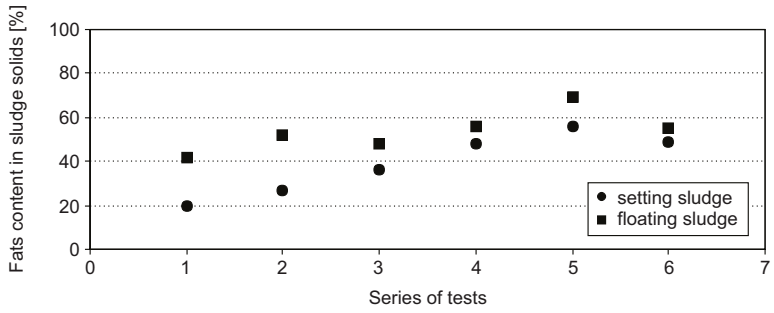

Fig. 3. Percentage of fatty substances in the sludge solids

The amount of calcium ions in the floating sludge fluctuated between 2000 mg Ca^{2+}/dm^3 and 3125 mg Ca^{2+}/dm^3, whereas in the sedimenting sludge – between 937 mg Ca^{2+}/dm^3 and 2681 mg Ca^{2+}/dm^3. The research results presented above allow to conclude that greater amount of calcium ions in sludge is connected with the higher content of fatty substances.

As mentioned above, with a view to investigate the processes in the settling tank, sludge samples were stored in laboratory conditions. It was proved in a series of tests that the pH value decreased slightly and the conductivity value increased. The latter may be associated with an increase in sulphates concentration. Figure 4 presents changes in sulphates concentration in several selected series of tests.

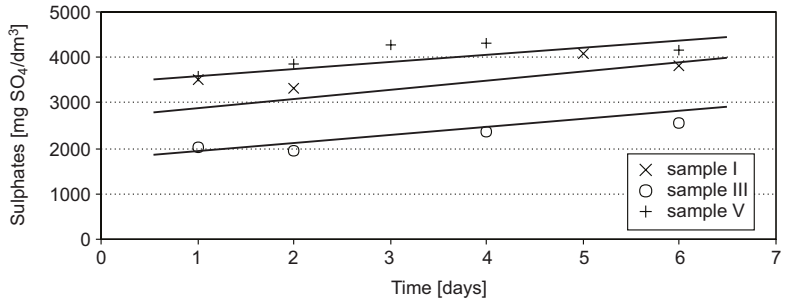

Fig. 4. Changes in sulphates concentration (in selected series of tests)

Moreover, the concentration of CODs increased significantly – Figure 5. It is likely that fatty substances are decomposed in anaerobic conditions into easier oxidating compounds which are also counted as CODs, eg fatty acids.

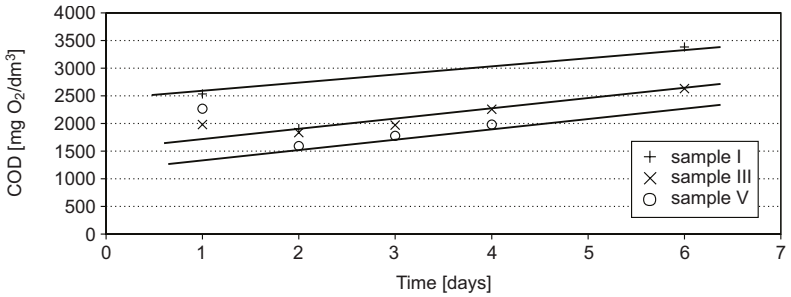

Fig. 5. Changes in CODs concentration (in selected series of tests)

The level of calcium ions recorded throughout the experiment basically does not allow to draw any conclusion as to the character of chemical processes in the sludge. It may only be mentioned that in most cases the level of calcium ions increased in the sludge and decreased in the supernatant phase.

Conclusions

The aim of the research project was to establish the origin of burdensome surface sludge which interferes with the process of chemical pre-treatment. The floating sludge is a side effect of wastewater being treated with lime milk which is used to precipitate phosphates. It is highly probable that flotation may be caused by an increased level of fatty substances in the sludge from the settling tank, which was confirmed by the results of conducted chemical analyses. What is more, greater level of fatty substances in the sludge is connected with higher content of calcium ions. Due to coagulative properties, lime can generate compounds with fatty substances, which may be further modified and deposited on the surface of the sludge.

Moreover, with the view to investigate the technological process, the sludge was stored and mixed mechanically in laboratory conditions. The research results confirmed that the sludge changed its physicochemical properties in the following way: pH value decreased slightly; conductivity value increased; concentration of sulphates increased – it is highly probable that sulphates ions are released from precipitated calcium sulphates. What is more, released sulphates also disrupt the process. It has also been proved that CODs increased throughout the experiment – it may caused by de-composing in anaerobic conditions into easier oxidating compounds which are also measured as CODs. The latter also include fatty substances.

Acknowlegments

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ZAKŁÓCENIA PROCESU OCZYSZCZANIA ŚCIEKÓW Z PRZEMYSŁU SPOŻYWCZEGO ZA POMOCĄ MLECZKA WAPIENNEGO

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Abstrakt: Ścieki pochodzące z produkcji olejów jadalnych są trudne do oczyszczenia ze względu na duże stężenia fosforanów, siarczanów i związków organicznych. Ze względu na zróżnicowany charakter i skład ścieków przemysłowych stosowanie fizykochemicznych metod usuwania zanieczyszczeń może być związane z pewnymi ograniczeniami. Podczas strącania fosforanów za pomocą wapna powstają fosforany wapnia zazwyczaj w postaci hydroksyapatytu (HAP), który wraz z nadmiarem wodorotlenku wapnia tworzy dobrze sedymentujący osad. Zastosowanie tej metody do oczyszczania badanych ścieków w warunkach technicznych powoduje powstawanie uciążliwego osadu flotującego na powierzchni ścieków. Szukając przyczyn wypływania części osadów, wykonano badania obejmujące charakterystykę jakościową ścieków dopływających oraz po procesie sedymentacji, a także osadów zatrzymywanych w osadniku. Zmierzając do lepszego poznania procesów zachodzących w osadniku, badano wpływ mieszania mechanicznego na osady przetrzymywane w warunkach laboratoryjnych. Analizowano podstawowe parametry fizykochemiczne, w tym zawartość wapna oraz substancji tłuszczowej. Stwierdzono, że obecność w ściekach tłuszczy w znacznych stężeniach przyczynia się do powstawania związków wapniowo-tłuszczowych flotujących na powierzchni ścieków, co w rezultacie zakłóca proces podczyszczania ścieków. Ponadto wapno stosowane do strącania fosforanów przyczynia się do uwalniania jonów siarczanowych.

Słowa kluczowe: ścieki przemysłowe, usuwanie związków fosforu, koagulacja, substancje tłuszczowe