Abstract. The pretreatment of the wastewater from the edible production based on calcium phosphates precipitation, generates sludge characterized by good sedimenting properties. However, a part of the sludge floats through the surface of the settling tank. Lime added for phosphorus removal simultaneously removes also sulphates to a level of above 2000 mg/l. The liquid associated with floated sludge contains low sulfates concentration – about 370 mg/l. The aim of the research project was to examine the causes of such a low sulphates concentration.

Keywords: industrial wastewater, sludge, sulphate.

1. Introduction

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. The fatty substances are removed by means of fat traps. Phosphates can be removed by chemical precipitation. Phosphates precipitated by means of calcium hydroxide (lime) turn into calcium phosphates, usually in the form of hydroxyapatite (HAP), which together with an excessive amount of calcium hydroxide create a well-sedimented sludge. However, the industrial application of the method for the treatment of the analyzed effluent leads to the burdensome floating sludge.

Moreover, calcium hydroxide removes organic compounds, which become an integral part of the sludge. However, according to Ruffer’s [1] theory, it is possible to remove sulphates by means of lime to the level of above 2000 mg/dm³. The liquid associated with floated sludge contains low sulfates concentration - about 370 mg/l. This study was done to explain the decrease in sulfates concentration. It was assumed, that chemical or biological processes, which occur in the settling tank influenced the sulphates concentration. The latter can be reduced to sulfide or extracted in the dispersed oil membranes. This method has been applied for effluents remediation e.g. from zinc mine and plating plant and for removal of organic pollutants (phenol) from water [2], and for removal of chlorine and sulphur from used industrial oils [3]. In order to verify above assumptions, the sedimentation process was transferred into 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 into a fat trap. The wastewater is pumped 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 flocks are precipitated. The wastewater leaves the flocculation tank and is directed into a settling tank. The clarified samples are neutralized to lower pH (Fig. 1). The generated sludge is mechanically dewatered by means of a centrifuge and the sludge supernatant is recirculated into the reaction tank.

2. Experimental

Samples of wastewater (raw and after sedimentation process) as well as sludge samples collected from the settling tank were analyzed with the aim to identify their chemical content: sulphates, fatty substances, CODs, pH, oxidation - reduction potential (ORP). In case of the sludge, the concentration of sulphates as well as CODs measurements were conducted in the sludge supernatant after it had been centrifuged. Chemical analyses were carried out according to the methodology presented in Standard Methods for Examination of Water and Wastewater [4].

3. Results and Discussion

The research results show that the applied method removed phosphates – in over 99 % of all cases. The amount of COD decreases by about 50 %. Whist the recorded degree of fatty substrates – expressed as ether extract was established at a similar level (Table 1).

Next, sedimenting and floating sludge were investigated. In case of the sludge taken from the bottom of the settling tank, an ORP value fluctuated between -372 and -99 mV. The sludge floating through the surface of the settling tank, exhibited the ORP value at the level between -450 and -250 mV (reductive range), which allowed to conclude that the processes are anaerobic in nature (Table 1).

The recorded values of conductivity for the analyzed sludge are not clear. In case of the floating sludge (liquid phase), the values achieved for several series of tests were lower as compared to the values recorded for the sedimenting sludge. The above results correspond to lower sulphates concentration recorded in the floating sludge. The recorded concentration of sulphates at the level of 370 mg/dm³ was unexpected, mainly because of the fact that the raw wastewater, treated wastewater (after sedimentation process) as well as the sludge taken from the bottom part of the settling tank contained almost the same amount of sulphates. Moreover, the floating sludge contains fatty substances at the level of 20–70 g/dm³. Taking into account the above values, it was assumed that the extraction phenomenon in the dispersed oil membrane occurred.

Then, in order to transfer the sedimentation process into laboratory conditions and gain more information about processes in the settling tank, the sludge samples were mixed mechanically (15 days).

Furthermore, significant changes in organic (CODs) as well as inorganic (sulphates) compounds in the sedimented sludge were observed. The CODs and sulphates content increased when the samples were undergoing mechanical mixing (Fig. 2). It was probably caused by complex compounds (lime, fatty substances and sulphates) destruction as well as release of sulphates and easier – oxidated compounds, which are measured as CODs. The higher increase in sulphate concentration was associated with an increase in sludge conductivity.

In case of the floating sludge, the sulphates concentration measured in the liquid phase (of the sludge) decreased when sludge samples were mixed mechanically. Whilst, CODs concentration increased under such conditions (Fig. 3).
The floating sludge, due to its high content of easy accessible substrates (organic carbon, sulphates) and the ORP value, is considered as highly accessible to anaerobic digestion. Under such conditions, sulphides generation, as well as a hydrogen sulphide, may be one of the processes occurring in the settling tank. Simultaneously a significant decrease in sulphates concentration was observed. Strong reductive conditions (the ORP value at the level of about -430 mV) were favourable for sulphates conversion into the hydrogen sulphide and sulphides. The conversion was additionally proved by a specific odour (hydrogen sulphide).

4. Conclusions

Lime milk added to phosphates precipitation is usually used in excess. It leads to precipitation of sedimenting calcium phosphates. Simultaneously, due to high contents of fatty substances as well as a significant sulphates concentration, the addition of lime milk leads to surplus sludge generation containing excessive amounts of fatty substances, calcium and sulphates. As a result of secondary processes occurring in the settling tank, the sludge changed its physical and chemical properties, which was mainly shown in terms of COD and sulphates release. A proportion of the sludge floats through the surface of the settling tank. Taking into account strong anaerobic conditions in the settling tank, it was established that the main occurring process is the sulphates conversion into sulphides and the hydrogen sulphide.

References
