THE APPLICATION OF OIL EMULSION FOR REMOVAL OF SULPHATE

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Abstract: Wastewaters from the production of edible oils contain high concentration of phosphates, sulphates and organic compounds. Treatment of such waste water is difficult. 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 settles well. However, a part of sludge is floating on the settling tank surface. Lime which used for phosphorus removal from waste waters permits a partial simultaneous removal of sulphates. The remaining concentration was about 3000 mg/l. Surprisingly the liquid associated with the floated sludge contained definitely lower concentrations of sulfates, only of about 300 mg/l. The aim of the carried out experiments was to explain of phenomenon of sulfates concentration decrease. Preliminary experiments have been carried out to explain the mechanism and chemistry of sludge flotation i.e. probable the extraction of sulphates in dispersed oil membranes.

Keywords: liquid-liquid extraction, sulphate, industrial wastewater.

INTRODUCTION

Wastewaters from edible oil production contain high concentration of organic pollutants, as well as high concentrations of phosphates and sulphates. In order to meet quality standards set by sewage treatment plants and avoid high penalties, edible fat and oils companies are forced to pre-treat the wastewaters. Therefore a pre-treatment step is necessary.

Lipids are one of the major components of organic matter in wastewaters. Wastewaters may contain emulsified and dissolved vegetable oils. The most common fatty acids in the wastewaters from a sunflower oil factory were linoleic (52.4%), oleic (29.3%), and other compounds like stearic and palmitic acids (Saatci et al., 2003).

Apart from fatty substances mentioned above as well as lipids, the wastewaters contain total phosphorus in the range of between 216 and 556 mgP/dm^3. The wastewaters are additionally polluted with COD – between 5600 and 15300 mg O_2 / dm^3. The process of colza oil production also generates wastewaters polluted with COD (between 940 and 6364 mg O_2/dm^3), total phosphorus (between 67 and 354 mgP/dm^3), as well as sulphates - (between 911 and 4210 mg SO_2/dm^3) **(**Przywara, 2006).

The fatty substances are removed during floating. Phosphorus can be removed by chemical precipitation with lime. Calcium and phosphate ions easily form complexes together with various molecules. The precipitation is always preceded by the formation of an amorphous tricalcium phosphate, hydroxyapatite (HAP), or less frequently in the form of tetracalcium (octacalcium) phosphate. The formation and transformation may be influenced by supersaturation, pH value (Bever, 1997), Ca/P ratio (Song at al., 2001), temperature, as well as solution composition and presence of other substances (carbonate or organic ligands) (Matynia at al., 2002).

Usually, the pretreatment of industrial wastewater based on precipitation of calcium phosphates generate well sedimenting sludge. However, a part of sludge is floating on the settling tank surface.

Moreover, calcium hydroxide removed organic compounds, which become an integral part of the sludge. The lime milk added removes sulphates, which according to the Ruffer's (Ruffer et al., 1998) theory, permit sulphates precipitation by means of lime to a level above 2000 mg SO_4/dm^3. Surprisingly the floated sludge contained definitely lower concentrations of sulfates of about 300 mg SO_4/l.

This study was done to explanation the decrease of sulfates concentration. The reason of such low sulphates concentration in the liquid associated to the floated sludge is probable sulphates extraction in the dispersed oil membranes or formation of emulsion liquid membrane.

Liquid -liquid extraction is a useful method to separate components of mixtures. The success of this method depends upon the differences in solubility of a compound in various solvents. This method has been applied for effluents remediation e.g. from zinc mine and plating plant (Schwuger, 2001). Lopez, (2005) used liquid -liquid extraction for removal of organic pollutants (phenol) from water, and Moralez – Munoz (2004) for the removal of chlorine, sulphur and fluorine from used industrial oils.

MATERIALS AND METHODS

The carried out investigations concerned treatment of wastewater and sludge stemming from a pretreatment plant aiming at phosphates precipitation by means of lime milk. The sludge was collected from the bottom of the settling tank as well as from the surface of the wastewater. Samples of wastewaters as well as sludge collected in the settling tank were analyzed with a view to identify their chemical content. The investigations were based on the methodology used at the laboratory of the Institute of Environmental Engineering in University of Bielsko-Biała, which are according to those given in Standard Methods for the Examination of Water and Wastewater.

Sulphates were determined by the turbidimetric method. Samples for COD determination were digested in glass vials of HACH DR 4000 for rapid photometric analysis.

Fatty substances concentration measurement was conducted by means of petroleum ether method in compliance with Soxhlets. The equipment – DBAS Soxtherm, was used.

In case of sludge, the concentrations of sulphates as well as COD measurements were conducted in the supernatant after it has been centrifuged.

The pH and oxidation – reduction potential (ORP) in the liquid associated with sludge ware measured using a glass electrodes.

RESULTS

Qualitative analysis of wastewaters, treated wastewaters and sedimented sludge – collected from the bottom of the settling tank as well as from the surface is presented below. Moreover, with the view to investigate the technological process, the sludge was stored and mixed mechanically in laboratory conditions. It was assumed that chemical reactions and biological processes might have changed the chemical content of the sludge and causes it to float on the surface of the settling tank.

Wastewaters qualitative analysis
The application of lime for precipitation (removal) of phosphate was very successful. The applied method guarantied an almost complete removal of phosphates – in above 90% of cases, the average amount of phosphates does not exceed 2 mg PO_4 /dm^3.

What is more, the analyzed wastewaters contain large amounts of COD between 2000 and 8500 mg O_2/dm^3, on average about 5000 mg O_2/l. Figure 1 presents the results of treating wastewaters with lime milk. The latter reduces the value of COD by about 65%.

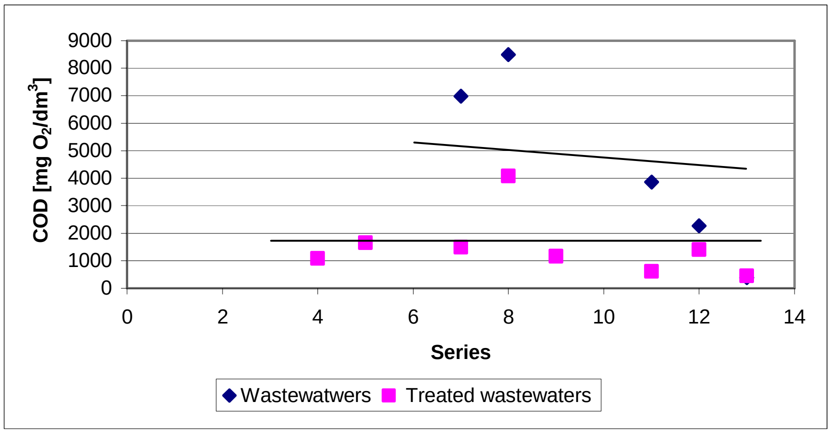

Figure 1. COD value in industrial wastewaters and treated wastewaters

The concentration of sulphates in wastewaters fluctuated between 1300 and 3300 mg SO_4 /dm^3, whereas in treated wastewaters between 500 and 2100 mg SO_4 /dm^3. The relatively high sulphates content in treated wastewaters proves that lime treatment does not permit complete removal sulphates, what confirms Ruffer's (Ruffer et al., 1998) theory, according to which sulphates precipitation by means of lime reduces the content of sulphates to no less than 2000 mg SO_4/dm^3.

Since fatty substances might have been retained in sludge, the level of fats measured as ether extract in both wastewaters and treated wastewaters was monitored. Figure 2 presents data conforming the removal of fatty substances from wastewaters.

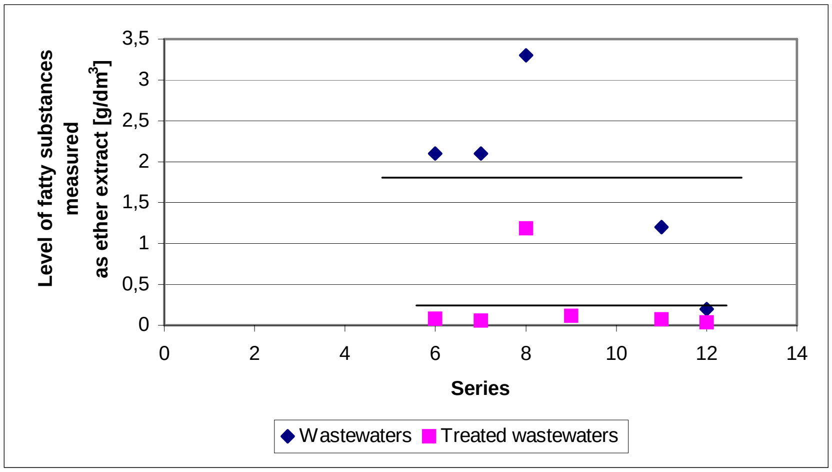

Figure 2. Level of fatty substances measured as ether extract in wastewaters and treated wastewaters

Sludge qualitative analysis

Sludge from the bottom of the settling tank as well as from the surface was investigated. Moreover, with the view to gain more information about processes in the settling tank, the sludge samples were stored and mixed mechanically in laboratory conditions. The sludge from the bottom of the settling tank exhibits an ORP value at the level of between –210 and –500 mV, while the surface sludge shows ORP at the level of between –390 and – 450 mV. In case of the surface sludge, the presented ORP values above allow to conclude that the processes involved are exclusively anaerobic in nature. Next, it was establish that there are significant differences between the sludge from the surface and the bottom of the settling tank in terms of conductivity – the supernatant of the surface sludge on average exhibited conductivity which was higher by about 1000 µS/cm (Fig. 3).

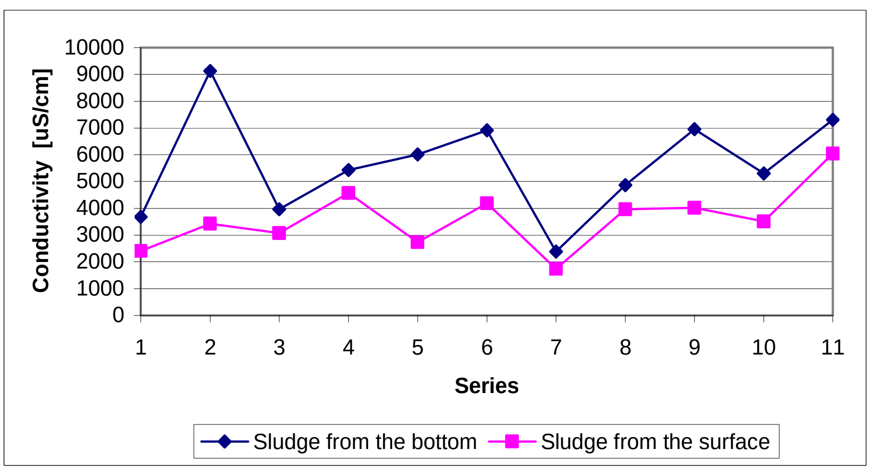

Figure 3. Conductivity of the sludge from the bottom and from the surface of the settling tank

The difference may be traced to the low content of sulphates in the surface sludge susupernatant. (Fig. 4).

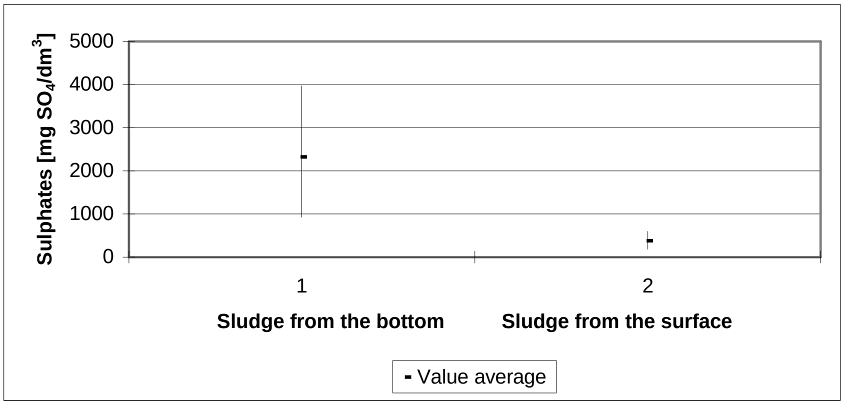

Figure 4. Sulphates concentrations in sludges

The average level of sulphates in the surface sludge at 350 mg SO_4 /dm^3 was rather unexpected. It cannot be convincingly explain because the wastewaters, treated wastewaters as well as sludge from the bottom of the settling tank 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 a hydrogen sulfide.

Mentioned removal of COD and fatty substances from the sewage by means of lime treatment, influences the chemistry of sludge. The sludge from the bottom of the settling tank contains between 10 and 20 g/l of fatty substances, while the sludge from the surface contains at least three times as much of these compounds – between 20 and 60 g/l (Fig. 5).

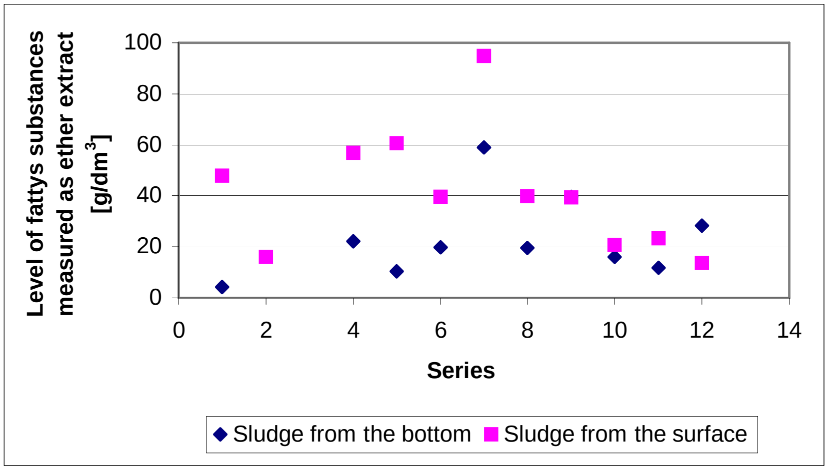

Figure 5. Level of fatty substances measured as ether extract in sludge of the settling tank

Figure 6 presents the amount of fatty substances in sludge in a different way, i.e. as a percentage of sludge solids.

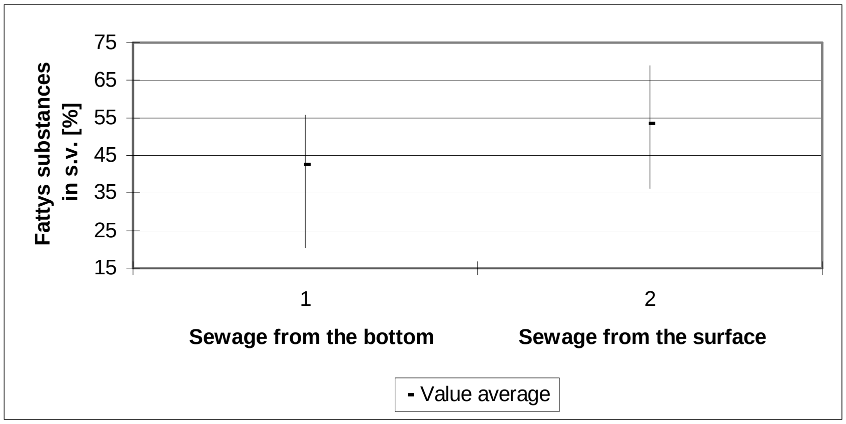

Figure 6. Level of fatty substances (s.v. %) in sludge of the settling tank

Wastewater and sludge sample were mixed mechanically and aerated in laboratory. The process was accompanied by change physic-chemical parameters, including concentrations of organic matters measured as COD, fatty substances, sulphates. It was established in a series of measurements that pH value decreased slightly and conductivity value increased. The latter may be associated with an increase in the concentration of sulphates (Fig.7).

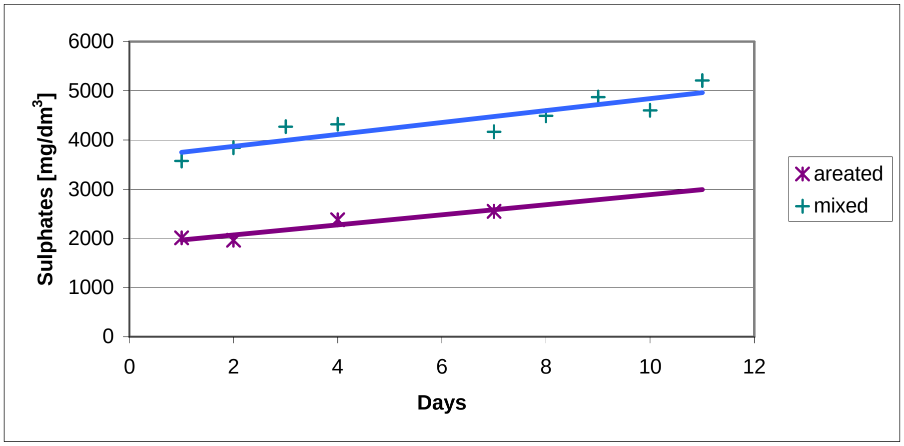

Figure 7. Release of sulphate

The concentration of COD increased significiently – Figure 8. It is likely that fatty substances are decomposed during mixing and aeration into easier oxidable compounds which are also measured as COD, e.g. fatty acids. In these processes the sulphate are released into the supernatant.

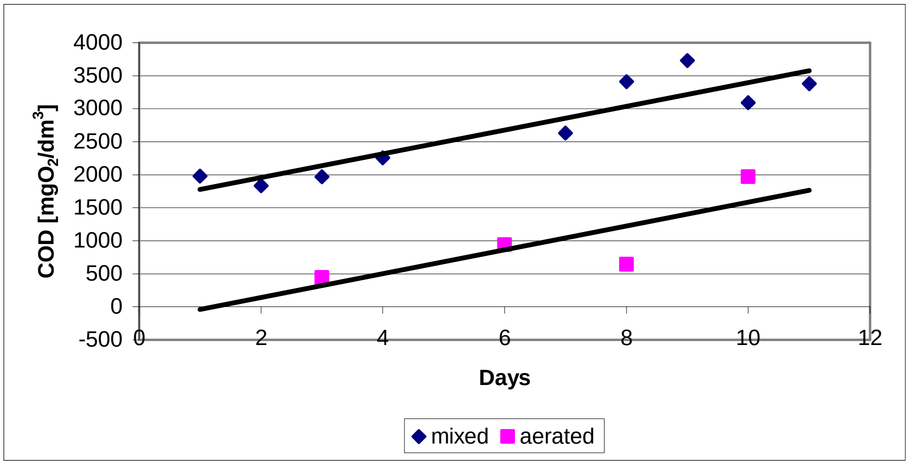

Figure 8. Release of COD

SUMMARY

The aim of the research project was to establish of the decrease of sulfates concentration in surface sludge. The surface sludge is a side effect of wastewatwers being treated with lime milk which is used to precipitate phosphates.

Flotation may be caused by an increase level of fatty substances in the sludge from the surface of the settling tank, which was confirmed by the results of conducted chemical analyses. What is more, greater level of fatty substances in the sludge may be connected with higher content of calcium ions. Due to coagulative properties, lime can generate compounds with fatty substances, which may be further modified and floated on the surface of the settling tank.

Moreover, with the view to investigate the technological process, the sludge was mixed mechanically and aerated in laboratory conditions. The research results confirmed that the sludge changed its chemical properties in the following way: pH value decreased slightly; conductivity value increased; concentration of sulphates increased. It is highly probable that sulphates ions are separated by oil membranes and released during destruction of sludge. It has also been proved that the concentration of COD increased throughout the experiment - it may be the result of organic substances decomposition into easier oxidable compounds which are also measured as COD. The latter also include fatty substances. However, the research results presented above should be further verified. Separations of salt ions using oil membranes seem to be a new method to solve the problem of sulphates removal from industrial wastewaters.

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