# CHEMICAL AND BIOLOGICAL SULFATES REMOVAL

J. Suschka and L. Przywara

University of Bielsko-Biała
43-309 Bielsko-Biała, ul Willowa 2, Poland

**ABSTRACT**
Experiments aiming at effective sulfates removal form industrial waste waters are presented. Laboratory scale experiments have demonstrated the possible to obtain relatively good effects of chemical precipitation with lime. The limit concentration which is possible to get is rather high in the order of 1500 mg $SO_4$/l. Biological anaerobic processes are effective and much lower concentration of sulfates are possible to be obtained. The effluent concentration can be as low as about 50 mg $SO_4$/l. There is an evident loss of sulfur based on sulfur mass-balance. That problem is so far not sufficiently explained also in recent publication of the subject.

**KEYWORDS**
Sulfates removal, sulfides, anaerobic treatment

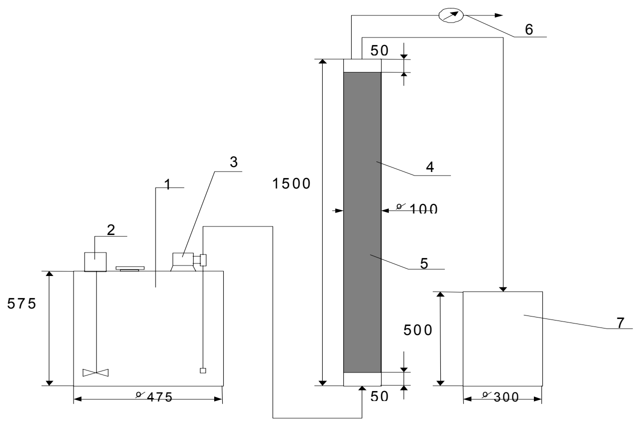
## INTRODUCTION

Industrial waste waters could contain high concentration of sulfates which should be removed before discharge to receiving waters or municipal sewerage. An example are wastewaters from margarine production. As much as several thousand of mg $SO_4$//l can be present in such wastewaters. Chemical precipitation can be effectively executed with the use of $Ba(OH)_2$. In practice because of the toxicity of barium salts that technique is not used. Most often lime is used with however, limited effects and large quantities of sludge produced.

Biological process under anaerobic conditions convert sulfates into sulfides which in addition can be removed (precipitated) as ferrous sulfide. In spite of long experience in the application of the biological sulfate reduction process, also in full technical scale, not all aspects are sufficiently explained. The main issue is the fate of sulfides which is also addressed in this paper.

## MATERIALS AND METHODS.

The experiment were carried out in a laboratory scale anaerobic filter of a diameter of 10 cm and high of 1.5 m. The model of the anaerobic filter was shown in Fig. 1.The anaerobic reactor was constructed as a PVC tube filled in with propylene rings. The active volume of the reactor was 12 liters. The wastewater were obtained twice - weekly from a margarine factory. The wastewater was continuously injected into the reactor using a pump at a flow of 0.69 l/h. Three series of investigations have been carried out. The anaerobic reactor was installed in a temperature-controlled chamber, where a constant temperature of 30˚C was maintained. Different retention time and loading rates as well as initial sulfate concentration were investigated.




1. Supply tank 60 l
2. Mixer
3. Dozing pomp
4. Anaerobic filter
5. Plastic rings
6. Manometer
7. Receiving tank

**Fig.1.** Anaerobic filter model

Samples of influents and effluents were analyses daily for: pH, temperature, redox (ORP) potential and routinely for: chemical oxygen demand (COD), sulfates and sulfides. Samples for COD determination were digested in glass vials of a HACH DR 4000, COD reactor. Sulfates were determined by the turbidimetric method. The total dissolved sulfides analysis was carried out by the procedures described in Standard Methods for the Examination of Water and Wastewater.

## RESULTS AND DISCUSSION

Precipitation of sulfates with lime results in production of gypsum according to the reactions given below.

$$SO_4^{--} + Ca^{++} \leftrightarrow CaSO_4$$

$$H_2SO_4 + Ca(OH)_2 \leftrightarrow CaSO_4 + 2\,H_2O$$

Calcium sulfate is however, relatively well soluble. The solubility is 1990 mg /l, what means 1404 mg $SO_4$/l at 20 $^oC$. In practice due to the presence of other impurities (other ions) the amount of remaining sulfates is even higher.

Usually the pH should be above 8, and relatively long reaction time is required. Below an example from our experiments is given. Only after 60 hours of reaction time the results are close to the theoretical limit.

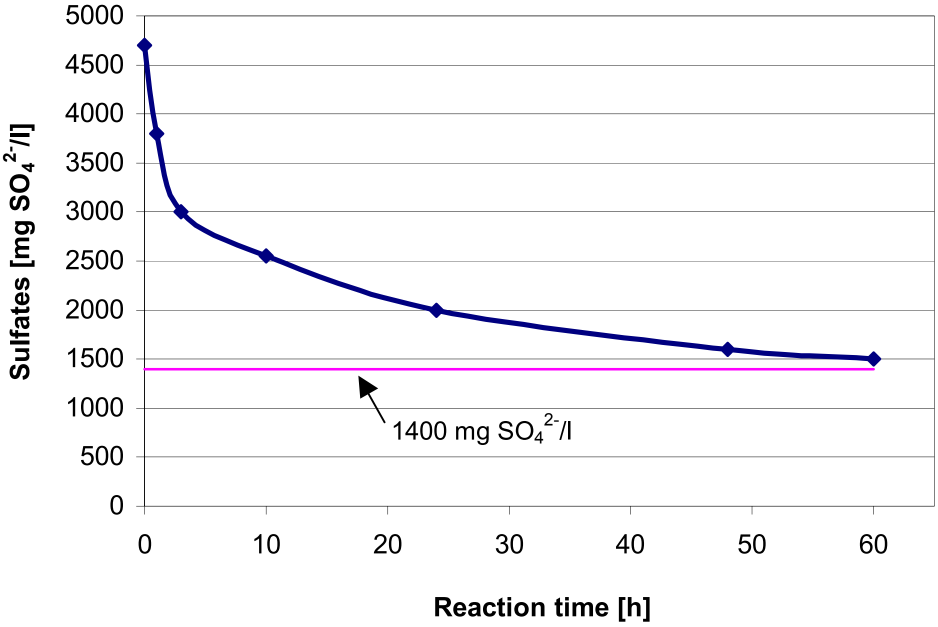



**Fig. 2.** Sulfates precipitation with lime

Addition of calcium chloride allows achievement of better effects of gypsum precipitation. The increase is in the order of 10 %, and thus has no practical application. Heave metals present affects adversely the effects of gypsum precipitation.

Biological processes of sulfates are based on anaerobic reduction to sulfides and hydrogen sulfide. The bacteria active in sulfates reduction are *Desulfovibrio* or *Desulfobacterium.* Also *Thioploca* lub *Thiotrix* could be present. The sulfate reducing bacteria SRB, are utilising hydrogen and organic substances as electron donors and sulfates as acceptors. There is a competition between sulfate reducing bacteria **SRB** and methane reducing bacteria **MPB,** and an appropriate balance is required. Even more important seems the concentration of sulfides which could be toxic to the micro-organisms active in the reduction process. There are contradictory data given in the literature. The toxic effect is claimed to commence with 50 mg $S^-$/l. Our results of investigation do not confirm the aforementioned limiting value. The process of sulfates reduction was found to be effective even at sulfides concentration as high as 150 mg $S^-$/l. In Fig. 3 a correlation between oxidation reduction potential and sulfides concentration was given. Independently of the sulfides concentration in the effluent the effects of sulfate removal are above 90 %. An example of sulfates concentration, before and after the anaerobic filter are shown in Fig. 4.

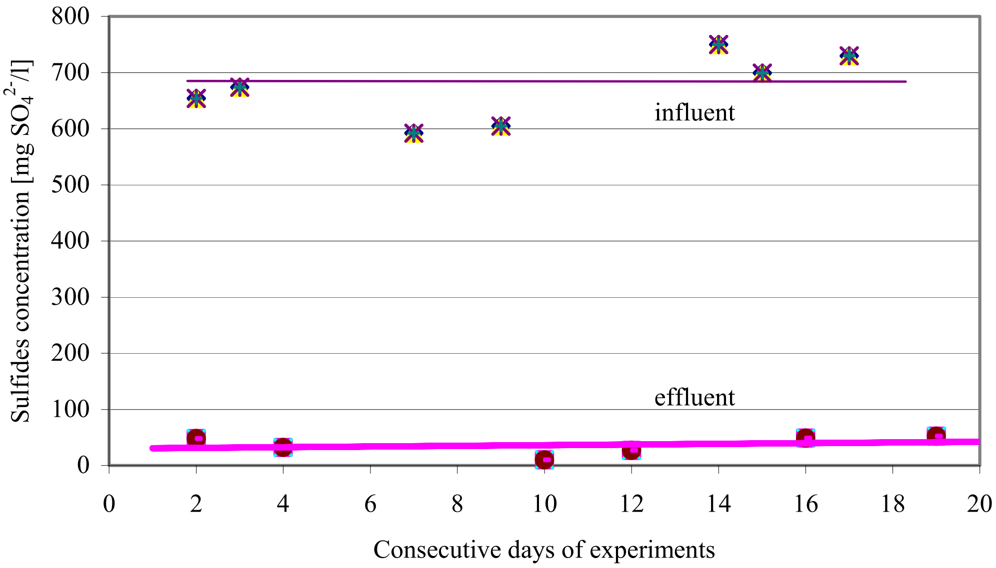



**Fig. 3.** Effects of biological sulfates removal

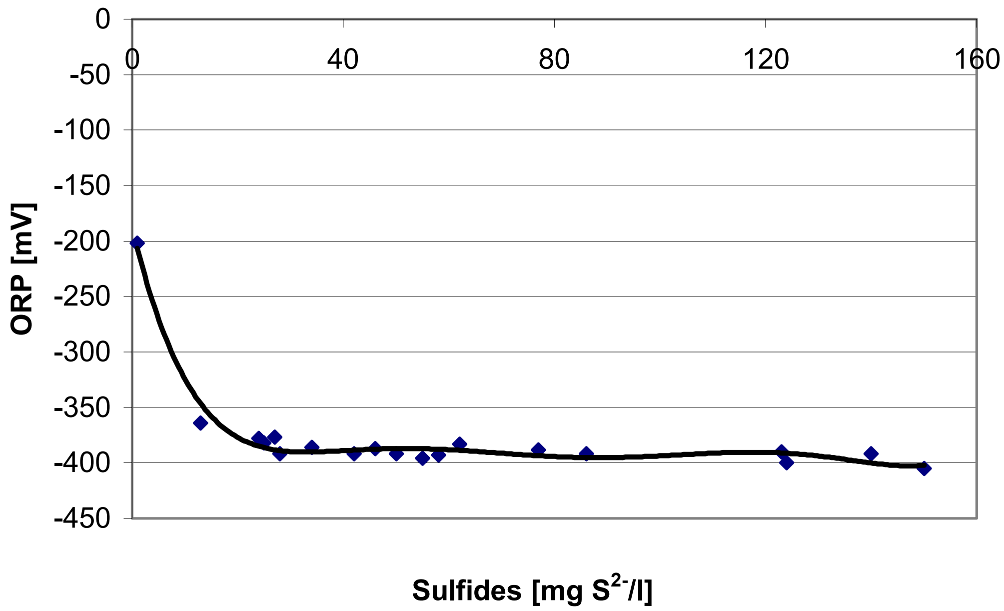



**Fig. 4.** Effluent sulfides concentration in correlation to ORP

The open question, which is the main subject of this paper, is the sulfur mass-balance. In the case presented above in average 660 mg $SO_4$/l , what means 220 mg S/l are removed and only about 100 mg S/l are present in the effluent as sulfides. A much higher discrepancy was presented by Jong and Parry (2003). With a nominal sulfur concentration of 761 mg S/l introduced into the treatment system, only 124 mg S/l was detected in the effluent. Although the difference is partly due to the formation of heavy metals sulfide precipitates, they constitute only 3.5 % of the total sulfur budget.

The explanation given by Jong and Parry (2003), that sulfide measurements are not accurate and also that there is a possibility of diffusion of $H_2S$ into the anaerobic filter column wall, is not satisfactory.

Experiments presented by Khanal and Huang (2003) with sulfates concentration in the influent of 1000, 3000 and 5000 mg $SO_4$/l have shown a disappearance of 84, 984 and 1340 mg S/l respectively. The comment given by Khanal and Huang (2003) is that the significantly low dissolved sulfide detected has "unknown reason" !

Evidently more experiments are required to explain the fate of sulfides.

In our experiments in which the raw wastewater was in admixture with wastewater chemically treated with lime, and in which $Ca(OH)_2$ was present the effluent sulfides concentration was as low as 1.2 mg S/l at maximum. These carried out experiments however, does not explain the main issue the disappearance of sulfides in the biological anaerobic sulfate reduction process.

## CONCLUSIONS

Biological sulfate removal process has a high potential for practical application. The fate of produced sulfides are an open question, and more research is required.

## REFERENCES

Khanal S.K. and Huang J. (2003), ORP-based oxygenation for sulfide control in anaerobic treatment of high-sulfate wastewater. Wat. Res. **37**, 9, 2053-2062

Jong T. and Parry D.L. (2003), Removal of sulfate and heavy metals by sulfate reducing bacteria in short-term bench scale upflow anaerobic packed bed reactor runs. Wat.Res. **37,** 14, 3379-3389