# THE EFFECT OF SURFACTANTS ON ACTIVATED SLUDGE PROCESS

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#### Abstract

The effect of anionic surfactant sodium dodecylbenzene sulphonate (SDBS) on biological treatment of wastewater was investigated. The activated sludge method was applied. It was stated that SDBS concentration higher than 50 ppm affect strongly phosphorus and ammonium nitrogen transformations while nitrates and COD changes are not so sensitive to SDBS presence. The distribution of SDS between activated sludge and supernatant was also investigated and it was stated that some of 25-32% of SDBS was lost.

Keywords: activated sludge process, surfactant adsorption

## **INTRODUCTION**

Surfactants, due to their favorable physicochemical properties are widely applied in many sectors of technology i.e. in pharmacy, in cosmetics, detergent sector, textile industry, agriculture, biotechnology (Prats et al., 1997; Cserhati et al., 2002). After use large quantities of surfactants and their derivatives are released to aquatic and/or terrestrial environment. In the environment surfactants may reveal harmful effects to organisms living there, mainly due to their toxicity and also due to enhancement of solubility of other toxic organic compounds (e.g. pesticides).

The municipal wastewater streams reach wastewater treatment plants, where they are processed by mechanical, biological or chemical methods (Prats et al., 1997; Fauser et al., 2003). The most important, biological treatment of wastewater is usually performed using activated sludge method. Some of chemical pollutants may negatively affect microorganisms activity. Examples of such pollutants are surfactants, entering the system with laundry effluents. The average surfactant concentration in domestic wastewater is from 10 to 20 mg/dm<sup>3</sup>, whereas in some industrial wastewater may reach even 300 mg/dm<sup>3</sup> (Shcherbakowa et al., 1999; Scott and Jones, 2000). As surfactants reveal strong adsorbing properties, their molecules may adsorb at the activated sludge flocks. Due to adsorption as well, as toxicity, they affect biological activity of microorganisms, what results in decreasing of wastewater treatment efficiency (Liwarska-Bizukojć and Bizukojć, 2005). Thus, the interest in behavior of surfactants in activated sludge systems is in the scope of many researchers investigations.

The aim of current research was to investigate the effect of anionic surfactant concentration on wastewater purification and particularly on nitrogen, phosphorus and COD removal in biological process. However, due to adsorptive properties of surfactants it was necessary to examine the amount of surfactant adsorbed on activated sludge flocs, during wastewater treatment. In majority of papers the amount of surfactants adsorbed at various types of sludge was calculated as a difference between surfactant concentration in supernatant before and after contact with the sludge (Fytiankos et al., 1998; Szymański et al., 2003). Such method is reasonable in case of bottom, river or sea sludge, but not in case of activated sludge, where living microorganisms may degrade the organic compounds. Probably this was the reason of many discrepancies in the literature reports. So, in this research the amount of surfactants dissolved in solution as well, as adsorbed at the sludge were determined independently, and the mass balance have been calculated. As a model LAS surfactant (linear alkylbenzene sulphonate), sodium dodecylbenzene sulphonate (SDBS) was used.

# **METHODS**

SDBS concentration was determined according to a methylene blue method (MBAS). SDBS forms ion pairs with methylene blue that is extracted by chloroform and determined spectrophotometrically at 652 nm. Chemical oxygen demand (COD) was measured by a standard dichromate method using a HACH spectrophotmeter. Concentration of ammonia nitrogen was measured by Nessler method. Nitrate was measured by sodium salicylate method. Phosphate was determined by molybdate method. These parameters were determined according to Polish Norms and Standard Methods (Standard Methods, 1998). Starch was determined by reaction with iodine (Mastalerz, 2000).

The experimental part consisted of two parts: 1) development of analytical procedure for surfactant determination in the supernatant and in the sludge; 2) investigation of surfactants effect on wastewater treatment efficiency.

# **RESULTS AND DISCUSSION**

# Development of analytical procedure for surfactant determination in the supernatant and in the sludge

The experimental procedure (Fig. 1) consisted of mixing of activated sludge with surfactant solution and leaving them in contact for 15 min. Then, liquid was separated from sludge by sedimentation and decantation. In the liquid phase (supernatant) the surfactant concentration was directly determined using MBAS method. In order to determine the amount of SDBS adsorbed at the sludge, a special procedure has been developed (Fig. 1). It comprises centrifuging or filtration, then drying, milling and extraction of dried sludge using methanol. The extract was dissolved in water and MBAS procedure was applied to determine SDBS content. The results were expressed as a percentage of the total amount of surfactant introduced with solution to the system. The amount of SDBS used in experiments was 8 mg per 1 dm<sup>3</sup> of the sludge.

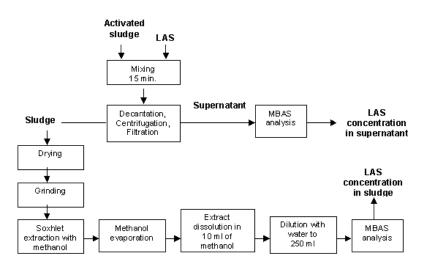


Fig. 1 Experimental procedure for LAS determination in activated sludge and supernatant

The experiments were performed for 6 different samples of activated sludge, taken from wastewater treatment plant in Swarzewo. In Fig. 2 the examples of the results obtained for one sample of the sludge are presented.

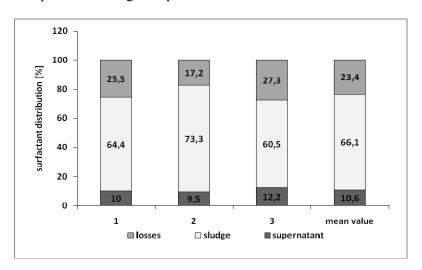


Fig. 2 Distribution of LAS between activated sludge and supernatant; 1, 2, 3 – experiment replications

It has been found that 6-12% of surfactant remains in supernatant, about 50-75% is adsorbed on sludge flocks and 25-32% is lost. The results for other sludge samples were similar and for 6 sludge samples the distribution of SDBS was as follows:  $60\div75\%$  in sludge,  $7\div12\%$  in supernatant and  $15\div30\%$  of losses. An additional experiments were performed to find the reasons of such great losses. It has been stated that adsorption in analytical vessels is only a small part of the total losses. The main reason of not balanced SDBS mass is probably its biodegradation, and this can not be stated when using MBAS method. Further research are needed.

## Investigation of surfactants effect on wastewater treatment efficiency

The batch experiments of activated sludge process were performed in a laboratory scale (in 20 l volume reactors). The activated sludge was taken from Wastewater Treatment Plant in Swarzewo and synthetic wastewater was prepared as presented in Table 1. The main source of carbon was starch. A defined amount of SDS was added to wastewater and initial concentration of SDBS was: 0, 10, 50, 100 and 200 mg/l. During the first three hours after filling the reactor was not aerated, so anoxic conditions were obtained. During the next 21 hours the mixture was aerated.

Component	Concentration [mg/l]
Broth/bullion	150
Soap	50
MgSO <sub>4</sub> ·7H <sub>2</sub> O	7
NaCl	30
KCl	7
Sodium acetate	10
CaCl <sub>2</sub>	7
Urea	20
Starch	800

Table.1 The composition of synthetic wastewater

Samples were taken in order to determine the concentration of ammonium and nitrate nitrogen, phosphorus, COD and starch. The selected results of these parameters changes during run of the processes are presented in Figs 3-9.

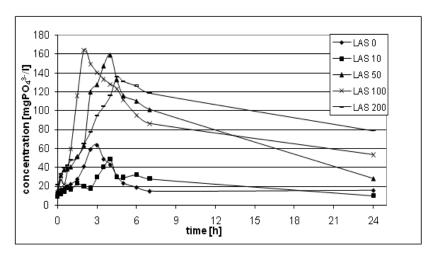


Fig. 3 Phosphates concentration changes during activated sludge process; the effect of surfactant concentration

As it can be seen in Fig. 3, the change of phosphorus concentration in all experiments is typical for biological process; during anoxic conditions (first 3 hours) its concentration rises and during aeration it decreases. However, the effect of SDBS concentration is clearly visible;

the higher the SDBS content, the more intensive release of P in anoxic period is observed. This could be positive, however unfortunately, phosphorus uptake in aerobic period is worse at higher SDBS content.

Changes of nitrogenous parameters are presented in Figs. 4-6.

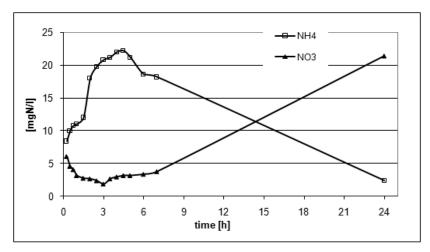


Fig. 4 Nitrogen concentration changes during activated sludge process; (SDBS concentration = 0)

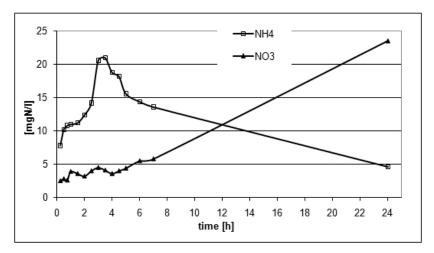


Fig. 5 Nitrogen concentration changes during activated sludge process; (SDBS concentration =10 mg/l)

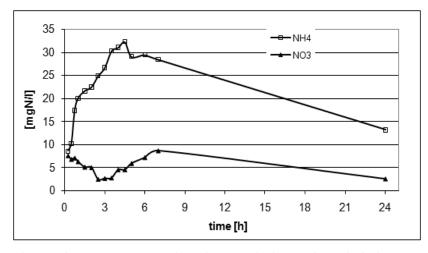


Fig. 6 Nitrogen concentration changes during activated sludge process; (SDBS concentration = 200 mg/l)

The ammonium nitrogen concentration in all experiments rises during anoxic conditions (first 3 hours), and during aeration it decreases (similarly as phosphorus concentration). The effect of SDBS concentration is also similar, the higher the SDBS content, the more intensive increase of  $NH_4$ -N in anoxic period is observed. In aerobic conditions the decrease of ammonium nitrogen is worse at higher SDBS content and after 24 hours of the run  $NH_4$ -N concentrations are about 2.0; 4.5 and 13 mg N/l in case of SDBS concentrations 0; 10 and 200 mg/l, respectively.

The changes of nitrates concentration is much less pronounced, and generally in anoxic conditions it slightly decreases and during aeration it increases. However, if the SDBS content do not exceed 100 mg/l, the effect of its concentration is practically not observed. At 200 mg/l the final NO<sub>3</sub>-N concentration (after 24 hours) equals only about 3 mg/l while at lower SDBS content it exceeded 20 mg/l.

In Figs. 7-9 the changes of COD and starch concentration are presented. It can be seen that the higher SDBS content the slower is COD decrease. On the other hand, there is no effect of surfactant concentration on starch concentration changes.

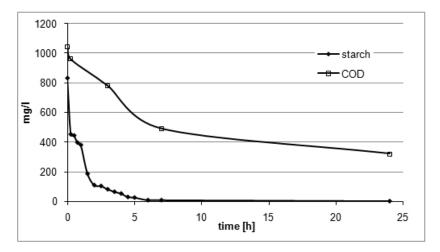


Fig. 7 Starch and COD concentration changes during activated sludge process; (SDBS concentration = 0)

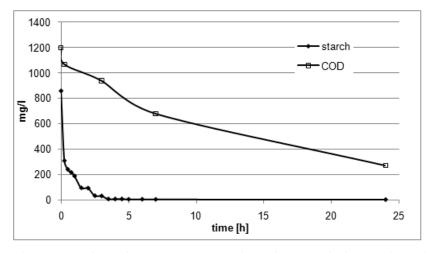


Fig. 8 Starch and COD concentration changes during activated sludge process; (SDBS concentration = 50 mg/l)

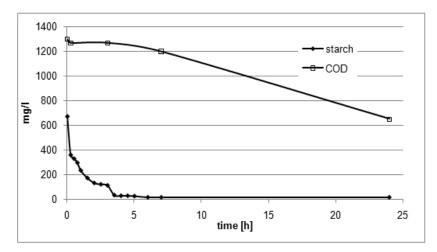


Fig. 9 Starch and COD concentration changes during activated sludge process; (SDBS concentration = 200 mg/l)

# CONCLUSIONS

It has been found that, anionic surfactant SDBS (sodium dodecylbenzene sulphonate) may influence the efficiency of activated sludge process. Especially strong effect was stated in phosphorus removal, where SDBS concentration higher than 50 mg/l enhanced phosphorus release in anaerobic conditions and slower its absorption in oxic conditions. Similar effect was observed in case of ammonium nitrogen concentration changes, however effects are not so strong. Removal of COD was the slower, the higher was SDBS concentration.

The procedure applied for surfactant determination in sludge and wastewater in activated sludge system gave no balanced results due to biodegradation and additional research should be undertaken.

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