FATE OF LAS SURFACTANTS IN WWTPs BASED ON MEASURED CONCENTRATIONS IN WASTEWATER AND SLUDGE

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ABSTRACT

Surfactants are widely used in household and industrial products. After use, surfactants as well as their products are mainly discharged into sewage treatment plants and then dispersed into the environment through effluent discharge into surface waters and sludge disposal on lands. Surfactants have different behavior and fate in the environment. Non-ionic and cationic surfactants had much higher sorption on soil and sediment than anionic surfactants such as LAS. Most surfactants can be degraded by microbes in the environment although some surfactants such as LAS and alkylphenols may be persistent under anaerobic conditions. These pass into the sewage treatment plants where they are partially aerobically degraded and partially adsorbed to sewage sludge that is applied to land.

The fate of the surfactant LAS in the two different types of Waste Water Treatment Plants has been reviewed: the small "Swarzewo" WWTP (45 000 PE), and large WWTP "Wschód" (760 000 PE). The elimination of LAS from the water stream in Swarzewo (98,7%), is better than that found in Gdańsk (97,6%). In the sludge treatment course, the reduction of LAS in Swarzewo is greater than that in Gdańsk due to the greater biodegradation of LAS surfactant in composting treatment that take place in Swarzewo WWTP.

KEYWORDS: Surfactant, LAS, sewage sludge, wastewater, WWTP.

INTRODUCTION

Surfactants form a unique class of chemical compounds. They generally consist of a polar head group (either charged or uncharged), which is well solvated in water, and a nonpolar hydrocarbon tail, which is not easily dissolved in water. Hence, surfactants combine hydrophobic and hydrophilic properties in one molecule. They have the ability to radically alter surface and interfacial properties and to self-associate themselves into aggregates called micelles. These properties allow to apply surfactants in wettability modification, detergency, and the displacement of liquid phases through porous media on one hand, and to stabilize dispersions (including foams, froths and emulsions) on the other. Synthetic surfactants are economically important chemicals. They are widely used in household cleaning detergents, personal care products, textiles, paints, polymers, pesticide formulations, pharmaceuticals, mining, oil recovery and pulp and paper industries. The world production of synthetic surfactants in 2003 amounted to 18.2 million tons (Brackmann and Hager, 2004). Surfactants are divided mainly into three types: anionic, non-ionic and cationic. Linear alkylbenzene sulphonates (LAS), branch alkylbenzene sulphonates (BABS), alkyl ethoxy sulphates (AES), alkylsulphates (AS), alkylphenol ethoxylates (APE), alkylethoxylates (AE), and quaternary ammonium compounds (QAC) are the commonly used commercial surfactants (Figure 1) (CESIO statistics, 2009).

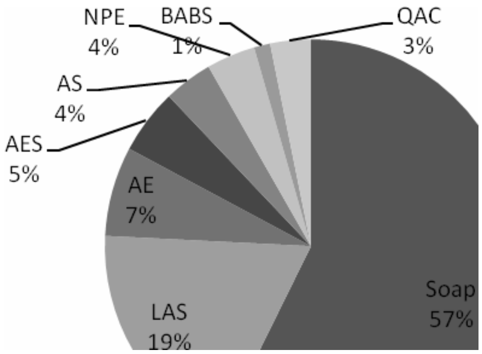

Figure 1. World surfactant production in 2003 (Brackmann and Hager, 2004 czy CESIO).

Linear alkylbenzene sulphonates (LAS) are the most popularly used synthetic anionic surfactants (Figure 2). It has been extensively used for over 30 years with an estimated global consumption of 3.9 million tons in 2007 (CESIO, 2009). Commercially available products are very complex mixtures containing homologues with alkyl chains ranging from 10 to 14 carbon units (C10-14 LAS). Furthermore, since the phenyl group may be attached to any internal carbon atom of the alkyl chain, each homologue contains 5–7 positional isomers. Excluding soap, LAS represent more than 50% of all surfactants used (Figure 1). Thus, it is not surprising that a large part of the published papers are focussed on the environmental problems arising from LAS.

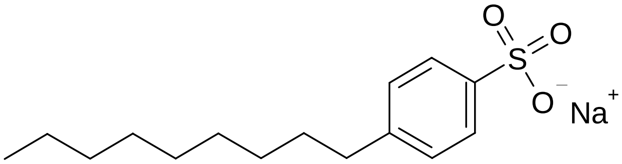

Figure 2. Structure of linear alkylbenzene sulphonates (LAS)

Concerning the negative impact of surfactants on the environment, research and legislation initiatives have been undertaken in many countries. In this regard, initiative that shows the seriousness of the problem of detergents in the environment is the making of the European law already in 1973 (Council Directive 73/404/EEC). Later, the European Commission improved the directive of the UE concerning the introduction of new detergents as well as their biodegradation (Council Directives, 1982, 1986). Each product newly introduced to the market should be tested for its biodegradability. According to EU Directives the detergent compositions may contain easily degraded surfactants, which means that within 28 days they can be degraded by at least 80% (Council Directive, 1982).

Balson and Felix (Balson and Felix, 1995) described biodegradation as the destruction of a chemical by the metabolic activity of microorganisms. When reviewing the literature concerning the degradation of surfactants it is apparent that the quoted data refer to primary and/or ultimate biodegradation. Primary degradation can be defined as to have occurred when the structure has changed sufficiently for a molecule to lose its surfactant properties. Ultimate degradation is said to have occurred when a surfactant molecule has been converted into CO_2, CH_4, water, mineral salts and new biomass.

Nevertheless, precision of criteria of biodegradability still arouses discussions because the required methods commonly determine the so-called preliminary biodegradation. This is not enough for the assessment of the effect of metabolites on the environment, which may significantly differ from the effects caused by non-decomposed surfactants. For example, restrictions on the use of APE have arisen since the discovery in 1984 that their breakdown products are more toxic to aquatic organisms than the APE themselves. Biodegradation of APE leads to the shortening of the ethoxylate chains to alkyl phenol carboxylates leading ultimately to nonyl and octyl phenols, which have low water solubility and adsorb to suspended solids and sediments. Nonyl phenol (NP) is approximately 10 times more toxic than its ethoxylate precursor and it is known to mimic the effect of the hormone estrogen (Renner, 1997).

The bulk of the materials reaching the environment (soil and natural waters) do so from consumer products by the use of sewage sludge on land, effluents from wastewater treatment plants (WWTP) and industrial discharges into freshwater and marine sites. Other sources of surfactant contamination are the use of surfactant dispersants for fuel oil spillages and surfactant-enhanced remediation of subsoil after spillage and contamination with non-aqueous liquids.

Different types of surfactants have been detected in sewage effluents with concentrations up to 1090 $\mu g/dm^3$ for LAS (Holt et al., 1998) and up to 332 $\mu g/dm^3$ for APEs (Snyder et al., 1999). These surfactants were also found in treated sludges at high concentrations of up to 30200 mg/kg dry weight for LAS (Berna et al., 1989), up to 81 mg/kg for APEs (Bruno et al., 2002). They have also been reported in surface waters at concentrations of up to 416 $\mu g/dm^3$ for LAS (Fox et al., 2000), and the degradation products of APE were widely detected in different environmental compartments (air, water, sediment).

LAS are generally regarded as biodegradable surfactants. Very high levels of biodegradation (97÷99%) have been found in some WWTP using aerobic processes (Brunner et al., 1988). It is well reported that LAS is readily degradable under aerobic conditions. The alkyl chain oxidation at the terminal methyl group (ω-oxidation) requires the presence of molecular oxygen. Subsequent degradation of the chain (β-oxidation) is followed by oxidative fission of the aromatic ring to give sulphonate substituted dicarboxylic acids. Finally, desulphonation of ring degradation products occurs (Schröder et al., 1999). In contrast, APE are less biodegradable and values of 0÷20% have been quoted (Swisher, 1987) based on oxygen uptake and 0÷9% based on spectroscopic techniques (Swisher, 1987).

Due to their amphiphilic nature, surfactants in raw sewage can adsorb to the surface of resident particulate matter. Anionic surfactants may also precipitate from solution in the presence of polyvalent metal ions (e.g. Ca^{2+}). Such behaviour may result in a significant proportion of the surfactant load of raw sewage being associated with the particulate fraction. A common initial step in a WWTP is the removal of particulate matter in primary settling tanks. Sediment removed from primary settling tanks is relatively rich in LAS, with concentrations ranging from 5000÷15 000 mg/dm^3 being reported (Brunner et al., 1988). The process of adsorption of LAS to particulate matter is primarily driven by the hydrophobic effect and specific or electrostatic interactions (Westall et al. 1999). The extent of adsorption has been shown to be dependent upon a number of factors. Prats (Prats et al., 1993) suggested that the type of LAS homologue present might be significant. Longer alkyl chains give greater hydrophobicity thus increase adsorptive tendency. Painter (Painter 1992) stated that for each carbon atom added to the alkyl chain a two- to three-fold increase in the Ka (association constant) for LAS was observed.

The concentrations of LAS in sewage sludge leaving the WWTP is dependent upon the type of treatment the sludge undergoes. Treatment of such sludge is commonly anaerobic digestion at elevated temperature. Many common surfactants used are easily biodegradable in aerobic conditions but due to restricted metabolic pathways the majority are not degradable under anaerobic conditions. Therefore, sludge treated anaerobically may still be relatively rich in surfactants post treatment.

At present no evidence exists for comparable degradation of LAS under anaerobic conditions (Brich 1992). Holt et al. (Holt 1989) stated that sewage sludge is generally digested under anaerobic conditions. Jensen (Jensen 1999) compiled results from ten studies of LAS in treated sewage sludge from various locations around the world. He found that sewage sludge that had been aerobically treated had LAS concentrations of 100÷500 mg/kg dry weight. This was considerably lower than levels found in anaerobically treated sludge (5000÷15000 mg/kg dry weight). Therefore, the extent of LAS contamination of sewage sludge is greatly dependent upon the individual WWTP and the method of sludge digestion it employs. The addition of anaerobically digested sewage sludge to agricultural land is a large potential source of LAS and other surfactants to the soil environment. The Central Statistical Office in Poland (CSO, 2010) reported data that in the year 2009, 0.56 M tons d.m of sewage sludge was produced in Poland. As a fertiliser to agricultural land 21% of sludge was used; up to 31% was landfilled only 4% was applied in cultivation of plants intended for compost production and the rest was disposed of by incineration or applied in land reclamentation.

Efficient treatment in WWPT will result in discharge of very low levels of surfactants into the environment. For LAS, secondary alkane sulphonates (SAS) and the cationic surfactant ditallowdimethylammonium chloride (DTDMAC) sorption to sewage sludge accounts for 26, 16 and 23 to 53%, of the influents materials respectively, while biodegradation removes 73, 43 and 36 to 43%, respectively. The effluent from the WWTP leaves only 1% LAS, < 1% SAS and 6÷41% DTDMAC (Ying, 2006). The surfactants will undergo further biodegradation in the environment that together with dilution will reduce their toxicological effects further. Wastewater effluent released into the environment appears to have its surfactant load reduced to an extent that lethal effects to aquatic organisms are negligible (Scott and Jensen, 2000).

Toxic effects of surfactants are also combined with adsorption tendencies of surfactant molecules. In the concentration range of 1 to 100 mg/dm^3, anionic and non-ionic surfactants are strongly toxic to fish, but cationic surfactants are even much more toxic (LC_{50}<1 mg/dm^3). In the research carried out by Japanese scientist (Tomiyama, 1975), it was proved that the toxic effect of surfactants results from their adsorption properties. He found that surfactants were not ingested in the alimentary track but they were strongly adsorbed on gills. The formed complex of surfactant and gill proteins disturbs the functioning of gills resulting in oxygen deficit.

The aim of the research was to investigate the fate of the surfactant LAS in the two different types of Waste Water Treatment Plants in northern Poland. The examined WWTPs were "Swarzewo" WWTP, a small treatment plant (45 000 PE), and "Wschód" in Gdańsk (760 000 PE). Different wastewater treatment system as well as sludge treatment can result in significant differences in surfactant elimination from wastewater and its content in sewage sludges.

EXPERIMENTAL

The amount of adsorbed anionic surfactant in different types of sewage sludge and surfactant migration in the process of wastewater treatment in two selected sewage treatment plants was examined. Sludge samples were collected at different times of the year to reflect the impact of temperature on the sorption process.

Seawage sluge samples

Samples of sewage sludge has been collected in Waste Water Treatment Plant in Swarzewo (SBR type WWTP) on Feb. 2, 2009 r. and June 22, 2009 r. Types of sewage sludge that have been taken:

- sand from vortex grit;
- activated sludge from the SBR reactor;
- excess sludge from sludge thickening station;
- dewatered sludge from mechanical dewatering station;

- compost from the compost pile.

Samples of sewage sludge has been collected in Waste Water Treatment Plant "WSCHÓD" in Gdańsk (flow reactor type WWTP) on Feb. 18, 2009 r. and June 3, 2009 r. Types of sewage sludge that have been taken:

- sand from grit chamber;
- raw sludge from the primary sedimentation tank;
- activated sludge from the biological reactor;
- excess sludge from sludge thickening station;
- sludge after anaerobic fermentation.

Wastewater samples

The wastewater samples were collected from WWTP Swarzewo and Wschód at the same time as sludge samples on February and June 2009 r. Following samples of wastewater were collected: raw, during biological treatment and purified.

Analytical procedures

The filtrated wastewater or methanol extract from the sludge sample was analyzed for anionic surfactants according to the procedure described earlier (Dereszewska et al., 2009). Concentration of anionic surfactants were calculated from calibration curve expressed as LAS concentration, absorbance was measured using spectrophotometer VARIAN at wavelength 652 nm. As a model of linear anionic surfactant for calibration curve, commercial sodium salt of dodecylbenzene sulfonate with a purity of 80% from Sigma Chemical company Ltd was used.

There are many different anionic surfactants in the wastewater flowing into WWTP, but most of them are linear alkyl sulphonates type. Therefore, in the following part of this paper, anionic surfactants extracted from the samples will be referred as LAS.

RESULT AND DISCUSSION

Investigations carried on the wide range of sludge samples showed that the sewage sludge demonstrates a high adsorption capability. The LAS concentration in the samples of sewage sludge from Swarzewo and Gdańsk are presented in Figure 3.

The initial concentration of LAS in raw wastewater were similar for WWTP in Swarzewo and in Gdańsk and were 687µg/dm^3 and 652µg/dm^3, respectively.

From the total LAS that enters the WWTP in Gdańsk (approximately 326 kg/day), a large percentage is physically separated during the primary settling step. The rest of the LAS leaves the primary settler in a dissolved form. Later, in the biological treatment stage, almost total elimination of the dissolved LAS takes place. The quantity of LAS present in the effluent from biological reactor represents 0.8% of the LAS which enters the WWTP in Gdańsk. Unlike treatment plant in Gdańsk, WWTP in Swarzewo has no preliminary sedimentation tank and all the LAS that enters the WWTP in Swarzewo (except small amount of LAS absorbed on the sand in the grit chamber) goes to the SBR reactor. The concentration of LAS in wastewater during biological treatment and in treated wastewater drops to 21.6 and 9.1 µg/dm^3, respectively.

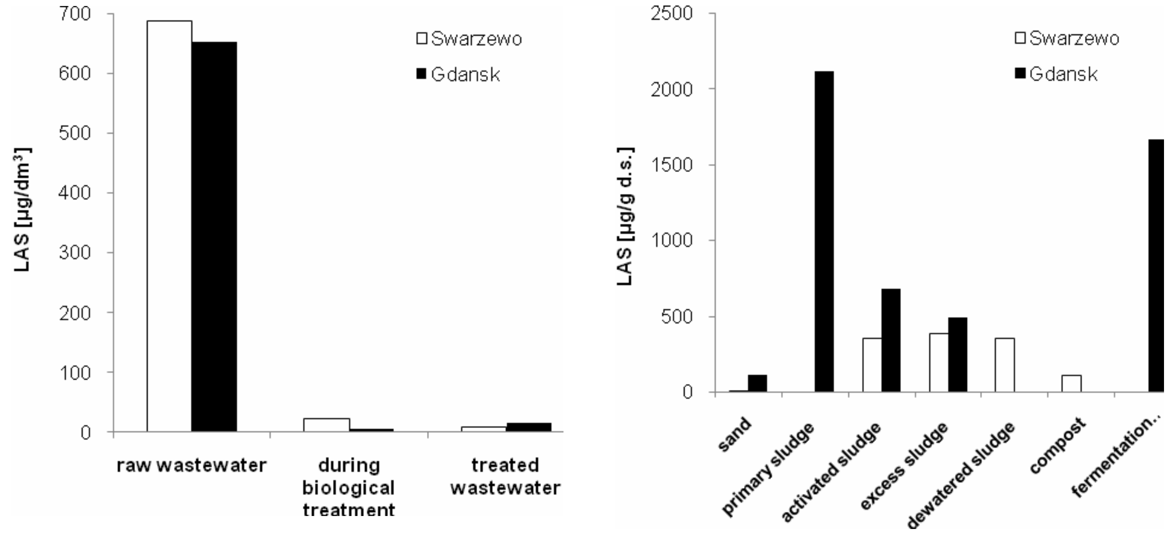

Figure 3. LAS concentration in samples of wastewater and sewage sludge taken from the WWTPs in Swarzewo and Gdańsk.

As was mentioned earlier large percentage of anionic surfactants are physically separated in the primary sedimentation tank due to strong adsorption of LAS on the primary sludge (the LAS concentration on the primary sludge 2114 µg/g d.s.). Therefore, the secondary settling tank allows the LAS concentration to be reduced to 680 µg/g d.s. The LAS concentration increases to 1664 µg/g d.s with the anaerobic treatment due to the degradation of organic material and not amended LAS concentration. The sludge treatment in Swarzewo is different than that in Gdańsk. The excess sludge is treated in three stages, gravity sludge thickening, mechanical dewatering and composting in piles as shown in Figure 3. The LAS concentration remains almost constant in activated sludge, excess sludge and dewatered sludge and is 622, 492, 576 µg/g d.s., respectively. Finally, the composting treatment causes the LAS concentration in sludge to reduce to 103 µg/g d.s..

The elimination of LAS from the water stream in Swarzewo (98,7%), is better than that found in Gdańsk (97,6%). In the sludge treatment course, the reduction of LAS in Swarzewo is greater than that in Gdańsk due to the greater biodegradation of LAS surfactant in composting treatment that take place in Swarzewo WWTP.

Sampling in Swarzewo were carried out also during two months representing two seasons, in February and June. The LAS concentration in the samples of sewage sludge from February and June is presented in Figure 4.

The temperature during collecting samples from Swarzewo WWTP in February and June differed noticeably and was 12.5ºC and 18.2ºC, respectively. The LAS concentration in sewage sludge samples and in wastewater is much higher in February than in June. Better elimination of surfactant from sludges and wastewater was observed during higher temperature in June, caused by higher activity of microorganisms. The smaller amount of LAS in the inlet to the wastewater can suggest that biodegradation processes of LAS proceeded before reaching the WWTP, but also it can be due to the greater amount of sewage that enters the WWTP.

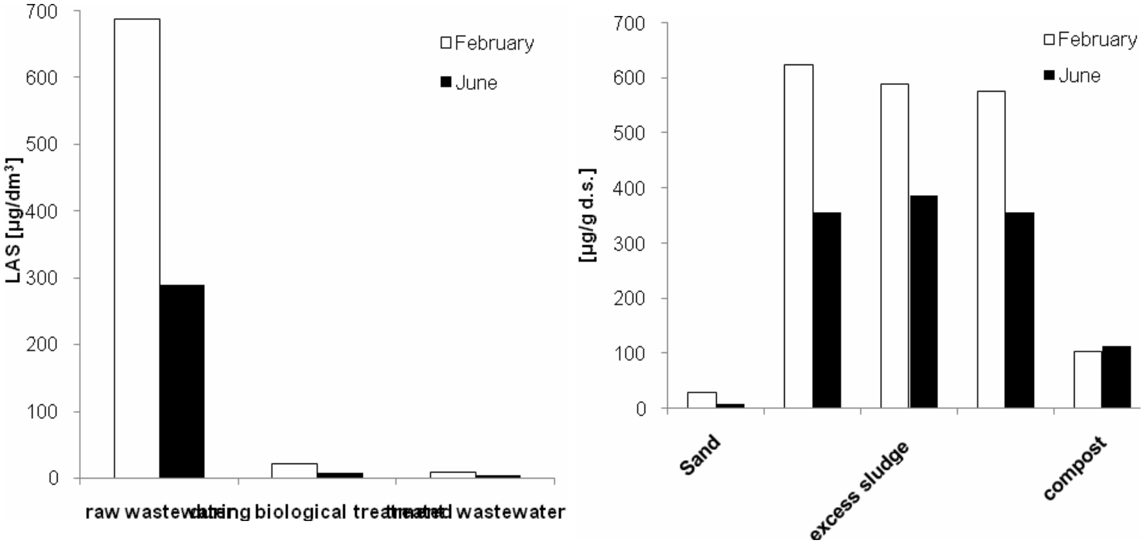

Figure 4. LAS concentration in samples of wastewater and sewage sludge taken from the WWTP in Swarzewo during two different seasons of 2009

CONCLUSIONS

The results of this paper show a higher degree of LAS surfactant distribution in a WWTP with aerobic digestion of sewage sludge. The amount of LAS present in the effluent represents 1÷2% of the LAS that enters the WWTP. At the same time, only one third of surfactant remains in the sludge after the composting stage compared to the amount of LAS in the dewatered sludge. While, in the sludge after anaerobic treatment the LAS concentration is high.

It is possible to confirm the environmental acceptability of LAS surfactant when the wastewater which contains them is treated in type of plant similar to that in Swarzewo WWTP. Research carried out by various authors show that the amounts which leave the treatment plant adsorbed in the sludge continue their biodegradation in sludge treated soils.

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