Pol. J. Environ. Stud. Vol. 24, No. 1 (2015), 83-91
DOI: *10.15244/pjoes/28640*

Original Research

The Effect of Anionic Surfactant Concentration on Activated Sludge Condition and Phosphate Release in Biological Treatment Plant

Alina Dereszewska[1]*, Stanisław Cytawa[2], Renata Tomczak-Wandzel[3], Krystyna Medrzycka[4]

[1]Department of Chemistry and Industrial Commodity Science, Gdynia Maritime University, Morska 83, 81-225 Gdynia, Poland
[2]'Swarzewo' Wastewater Treatment Plant, Władysławowska 84, 84-120 Władysławowo, Poland
[3]Aquateam COWI AS, Hasleveien Str. 10, 0571 Oslo, Norway
[4]Chemical Faculty, Gdansk University of Technology (GUT), Narutowicza 11/12, 80-233 Gdańsk, Poland

Received: 28 May 2014
Accepted: 3 August 2014

Abstract

This paper discusses the influence of a wide range of anionic surfactant concentrations on activated sludge. Linear alkylbenzene sulphonate (LAS) was chosen as an example of a commonly used anionic surfactant. The fate of the surfactant during biological treatment of wastewater was tested. The effect of surfactant on glucose and starch removal was studied. It has been found that in the case of glucose the removal was independent of LAS concentration, while in the case of starch it was incomplete at high surfactant loads (above 15 $mg\cdot(g\cdot dss)^{-1}$). The study established that surfactants can activate or inhibit microorganism activity, depending on surfactant concentration. LAS loads up to 3 $mg\cdot(g\cdot dss)^{-1}$ positively stimulate the removal of COD, phosphorus release and the respirometric activity of the sludge. LAS loads higher than 15 $mg\cdot(g\cdot dss)^{-1}$ inhibit respiration of activated sludge bacteria and decrease phosphorus removal. It also affects the morphology of activated sludge flocs, causing their fragmentation and lysis of protozoa cells.

Keywords: activated sludge, anionic surfactant, phosphorous release, respirometric activity

Introduction

Synthetic surfactants are used as principal constituents of commercial detergents. The average surfactant concentration in municipal wastewater varies from 10 to 20 mg/dm^3, whereas in some industrial wastewater it may reach 300 mg/dm^3, even after the coagulation process [1, 2]. Examples are wastewater from the textile, cosmetic, and detergent industries, and laundry and car washing services [3]. Among anionic surfactants, linear alkylbenzene sulphonates (LAS) are most widely used for domestic and industrial purposes. Due to the linear structure of the alkyl group, LAS have been proposed as being biodegradable under aerobic conditions and thus environmentally friendly surfactants [4]. Even though LAS are reasonably aerobically degradable and not particularly toxic at low concentrations [5, 6], high concentrations of this surfactant are harmful for the environment [2, 7]. In a risk assessment study it was noted that the risk posed to the aquatic environment by anionic surfactants depends on the applied treatment scheme prior to the discharge of wastewaters [8]. Therefore, the fate of surfactants, and particularly their decomposition in activated sludge processes, plays an important role in minimizing environmental impact.

*e-mail: a.dereszewska@wpit.am.gdynia.pl

The purification of municipal wastewater is performed via wastewater treatment plants (WWTPs), where it is subjected to biological treatment. Surfactant-rich industrial sewage is often pretreated by different physicochemical processes, but the biological treatment is the important part of its purification [3, 9]. During wastewater treatment, and especially in the biological process of activated sludge, surfactants are partially aerobically broken down and partially adsorbed on sewage sludge flocs. It has been reported that high concentrations of the surfactant have a negative influence on sludge flock properties [1] and can lead to microorganism cell degradation [10]. The adsorption of anionic surfactants can modify the characteristics of activated sludge and inhibit some types of enzymes [11]. Furthermore, surfactants supplied to the sludge interact with carbohydrates and peptides [12]. This may reduce the degradation pattern of these compounds.

Relatively little is known about the impact of surfactants on the biological removal of nutrients. Bacteria responsible for biological nitrification, denitrification and dephosphatation processes are very sensitive to external environmental factors. The inhibitory effect of LAS against nitrifying bacteria has been described in some works [13, 14]. The LAS concentration causing a 50% inhibition (IC_{50}) against nitrifying bacteria has been set at about 2 mg/dm^3. These results indicate that surfactants, even at low concentrations, may strongly affect wastewater treatment efficiency. Unfortunately, there are no experimental data on surfactant effects on biological phosphorus removal. Some papers deal with surfactant effects on the fermentation of sludge from wastewater treatment plants [15, 16]. Authors have reported that LAS promoted sludge hydrolysis in the anaerobic fermentation and, thus, enhanced phosphorus release. However, those results relate to sludge processing and not wastewater treatment.

The main goal of the present studies was to investigate the influence of LAS concentration on activated sludge activity and sewage purification effectiveness, including the phosphorous removal process. Considering that the effectiveness of wastewater treatment is based mostly on COD removal, the study includes the impact of LAS concentration on the biological removal of simple organic pollutants. Glucose and starch were used as models of substances representing rapid biodegradable COD (RBCOD) and slowly biodegradable COD (SBCOD), respectively. Laboratory experiments were carried out under conditions similar to those pertaining in a full-scale SBR-type bioreactor (sequencing batch reactor). The effectiveness of sewage purification was evaluated in terms of COD and nutrient concentration reduction. The condition of activated sludge was evaluated based on OUR value, granulometric measurements, and microscopic observations.

Materials and Methods

Analytical Methods

The research included investigations of the effect of LAS on glucose and starch removal. These carbohydrates were selected as examples of simple organic compounds present in sewage. Glucose concentration in the supernatant was determined via the Glucose RTU – BioMerieux test [17] commonly used to determine glucose levels in urine and blood with the enzymatic method. The method is based on colorimetric measuring of absorption at 500 nm.

The concentration of starch in the supernatant was determined via the iodometric method [18]. After the addition of an iodine excess, the absorbance of the blue complex formed between the iodine and the starch was measured using a spectrophotometer at 569 nm. The starch concentration was found from a previously prepared calibration curve.

The filtered sludge supernatant was analyzed for anionic surfactant concentration in accordance with the methylene blue method (MBAS) [19].

The concentrations of phosphates were measured using commercial Merck tests (Spectroquant® 114752, 114542, and 114543, respectively). The chemical oxygen demand (COD) analyses were also conducted using tests from Merck (Spectroquant® 114541 and 114540). All colorimetric analyses were performed using a Spectroquant Vega 400 spectrophotometer (Merck).

Suspended solids of the activated sludge samples were determined according to Standard Methods [20], and this was between 3.4 and 5.1 g·dss/dm^3 (dss – dry suspended solids).

Verification of the possible inhibitory effect of the surfactant on activated sludge was performed via the measurement of the respiratory activity of microorganisms with the application of the oxygen uptake rate (OUR) test [21]. The sludge was aerated in a 1 dm^3 vessel, keeping the dissolved oxygen level above 5 mg/dm^3. The OUR was expressed as the decrease in dissolved oxygen content (mg·O_2) per time unit (h) per 1 gram of dry mass of activated sludge (g dss).

The measurement of sludge flock size distribution was performed using a laser granulometer (Mastersizer 2000, Malvern Instruments Ltd, UK), with a size measuring range from 0.02 to 2000 μm. This device calculates the particle size based on light dispersion.

Other experimental parameters, such as dissolved oxygen concentration, pH, and temperature were monitored by ELMETRON sensors.

Materials

The activated sludge used in experiments was taken from the municipal wastewater treatment plant in Swarzewo. The biological unit of this treatment plant is an anaerobic/aerobic sequencing bath reactor (SBR) with biological nutrient removal. The plant treats about 10,000 m^3 of wastewater daily (97% domestic sewage). The composition of wastewater is generally constant, with a mean anionic surfactant concentration of about 10 mg/dm^3. The activated sludge for experiments was taken directly from the SBR aeration chamber during the sedimentation phase.

Synthetic wastewater used in the experiments consisted of: commercial soap, 50 mg/dm^3; beef extract, 150 mg/dm^3; $MgSO_4 \cdot 7H_2O$, 7 mg/dm^3 NaCl, 30 mg/dm^3; KCl, 7 mg/dm^3; sodium acetate, 10 mg/dm^3; $CaCl_2$, 7 mg/dm^3; and urea, 20

mg/dm^3. The additional carbon source in the synthetic sewage was glucose or starch. Their initial concentrations were 200 mg/dm^3 (glucose) and 800 mg/ dm^3 (starch).

It was assumed that in all experiments even the reference sample should be present in the source of easy biodegradable carbon, therefore synthetic wastewater contained sodium acetate. It is essential for the proper activated sludge operation, especially for correct evaluation of the phosphorus release or immobilization processes in activated sludge. The soap, is an no toxic and biodegradable anionic surfactant, was added to the composition of synthetic wastewater to assure that those observed in experimental changes are related only to LAS interaction

Commercial sodium salt of dodecylbenzene sulphonate with a purity of 80% (Sigma Chemical Company Ltd) was used as a model of linear anionic surfactant (LAS). The LAS concentrations applied in the experiments varied from 10 to 200 mg/dm^3, which related to sludge loading with LAS from 2.3 to 40.4 mg·(g·dss)$^{-1}$.

Methods

The experiments were conducted in a 20 dm^3 model reactor provided with a stirrer, aeration system, and sensors (O_2, pH, temperature).

To minimize pollutant levels the 15 dm^3 of activated sludge taken from the SBR chamber was aerobically conditioned for 24 hours (aerated to keep oxygen levels at 3 mg/dm^3). After the conditioning process the relevant amount of surfactant solution was added and mixed with activated sludge for 15 min. Afterward, 5 dm^3 of synthetic wastewater enriched with a carbohydrate (glucose or starch) was added. The mixture was stirred constantly to ensure steady conditions in the bioreactor. First, a 3-hour period in anaerobic conditions was provided; next, aerobic conditions (with an oxygen concentration of about 3 mg/dm^3) were applied by continuous aeration. The whole experimental process lasted 24 hours, analogous to the real purification cycle at Swarzewo WWTP.

During the first 6 hours of the experiment the concentration of glucose or starch was determined in the filtrated supernatant every half an hour and then after 24 hours of the process. In addition, as surfactants may affect dephosphatation processes, the concentrations of phosphates were determined in the samples of supernatant taken during experiments with synthetic wastewater enriched with starch.

Results and Discussion

The Effect of LAS Concentration on Glucose and Starch Removal

These studies examined the effect of surfactant adsorbed on the sludge on the decomposition of simple organic compounds. Glucose and starch were chosen as RBCOD and SBCOD, respectively.

The previous investigations carried out at the wide range of LAS concentrations showed that the activated sludge demonstrates a high sorption capacity (about 70 mg of LAS per 1 g of sludge dry mass.) [22]. The majority of surfactant mass flowing to the treatment plant adsorbs on the sludge flocs and, under favorable conditions (aeration, composting), undergoes biodegradation. The elimination of the LAS solutions (at concentrations used in experiment) in sludge enriched with a synthetic wastewater was investigated. The majority of the LAS elimination from sewage appears during the first minutes of the process. It can be assumed that surfactant concentration decreases mainly due to strong sorption to the sludge. When the LAS concentration in the influent is lower than 25 mg/dm^3, surfactant is rapidly eliminated from the solution, and after 15 minutes remains constant at a level of about 0.1 mg/dm^3. When the LAS concentration in the influent is higher than 70 mg/dm^3 and up to 200 mg/dm^3 (LAS load > 25 mg·(g·dss)$^{-1}$), a significant quantity of LAS remains in the supernatant and is not removed (even up to 23 mg/dm^3), despite the long time of aeration. The residual amount of LAS was neither degraded nor adsorbed on the sludge, although the sorption capacity has not yet been depleted in the experiments

The process of glucose removal in the presence of LAS is presented in Fig. 1.

The addition of LAS did not affect the process of glucose removal. The degradation of glucose is quick and it disappears from the solution within the first 3 hours or even faster, depending on the initial glucose concentration. The calculated rate of glucose decomposition varies from 0.20 to 0.27 mg of glucose/dm^3·min.

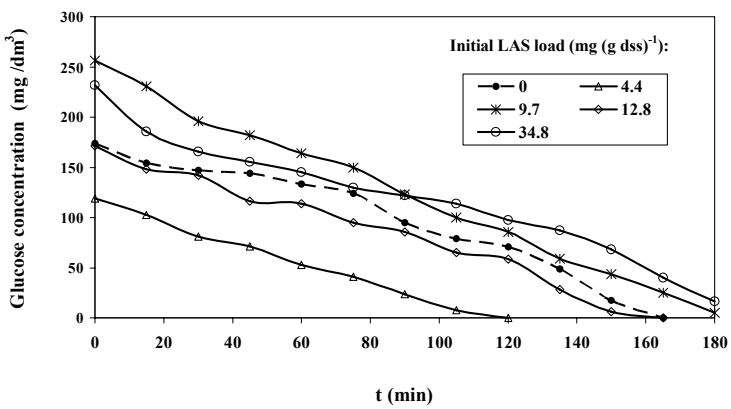

Fig. 1. Changes in glucose concentration vs. period of sewage treatment.

Interesting results were obtained in measuring the respirometric activity of activated sludge (oxygen uptake rate, OUR). When the sludge was taken from the process in which the influent contained only glucose (no surfactant), its respirometric activity rose from an initial OUR value equal to 2.4 $mg \cdot O_2 \cdot h^{-1} \cdot (g \cdot dss)^{-1}$ at the beginning of the experiment to a maximal value of about 8 $mg \cdot O_2 \cdot h^{-1} \cdot (g \cdot dss)^{-1}$ after 30 min. In the presence of surfactant, the oxygen consumption was higher (maximal values of about 12-14 $mg \cdot O_2 \cdot h^{-1} \cdot (g \cdot dss)^{-1}$), for all LAS concentrations. The results show that in the investigated range of surfactant concentrations the inhibition of microorganism respiration does not occur. Moreover, the surfactant, even at the highest concentration, improved sludge respiration.

The increase in microorganisms respiration in the presence of a surfactant could be assigned to an increase in the availability of organic substances associated with sludge. Activated sludge consists of microorganisms, as well as organic and inorganic matter, held together in a matrix formed by extracellular polymeric substances (EPS). The majority of these biopolymers are tightly bounded with sludge flocs (TB-EPS), but a more loosely bound part (LB-EPS) remains unattached in solution as biocolloids [23]. The anionic surfactant causing a breakdown of sludge flock agglomerations [1] releases part of the biocolloids, making them available for biodegradation and, thus, increases oxygen consumption by microorganisms.

These studies also examined the effect of adsorbed surfactant on the decomposition of starch, as an example of SBCOD compounds. Fig. 2 shows the changes of starch concentration in the supernatant that occurred during the full 24-hour purification cycles.

Removal of starch was observed in the activated sludge process both without and with surfactant adsorbed by the sludge. However, there were certain differences in the runs of the processes, depending on LAS concentration.

The rapid decrease in the concentration of starch in the first 15-30 minutes of the experiment can be attributed to two parallel phenomena: adsorption of starch to biomass [24, 25] and surfactant-starch interactions. It is known that surfactants can create complexes with both components of starch: amylase and amylopectin [26, 27]. Hydrophobic groups of surfactant complex with the amylase and linear chains of amylopectin by becoming inserted into the hydrophobic inner area of the helical structures. The saturation of starch helices by a surfactant can cause the faster loss of starch observed in the experiments with the surfactant. However, the magnitudes of starch concentration loss differ greatly. In the case of a control sample (without surfactants), adsorption on activated starch was very small and was about 20% of the initial concentration and for LAS load 2.3 $mg \cdot (g \cdot dss)^{-1}$ it accounted for 14%. In comparison, for high concentrations the interaction of starch with a surfactant was observed to have a significant effect, as the starch concentration decreased by half in 15 minutes.

The concentration of surfactant also affects the degree of removal of starch from the sewage in the full treatment cycle. When the system was free of surfactant, or the LAS load did not exceed the value of 2.3 $mg \cdot (g \cdot dss)^{-1}$, the starch was removed almost completely within a period of three hours (Fig. 2). However, at an initial LAS load higher than 15 $mg \cdot (g \cdot dss)^{-1}$, the reduction of starch is not complete, and after 2-3 hours (the time depends on LAS concentration) the level of residual starch remains unchanged for at least 24 hours.

The negative impact of high LAS concentrations on activated sludge metabolism was confirmed by respirometric measurements (Fig. 3). The rate of oxygen uptake (OUR) by sludge microorganisms depends on sludge conditions and also on the availability of organic substrates. The initial OUR value for sludge used in the experiments was about 3 $mg \cdot O_2 \cdot h^{-1} \cdot (g \cdot dss)^{-1}$.

High starch content in the inflowing sewage results in an increase in oxygen consumption by sludge in the control process (no added LAS) from 3 to 7 $mg \cdot O_2 \cdot h^{-1} \cdot (g \cdot dss)^{-1}$. When sludge was mixed with low concentrated LAS solution, the oxygen consumption increased much more – up to 14.4 and 11.5 $mg \cdot O_2 \cdot h^{-1} \cdot (g \cdot dss)^{-1}$ at LAS load 2.3 and 15 $mg \cdot O_2 \cdot h^{-1} \cdot (g \cdot dss)^{-1}$, respectively. As the process progressed, and when the starch has been exhausted, the OUR values

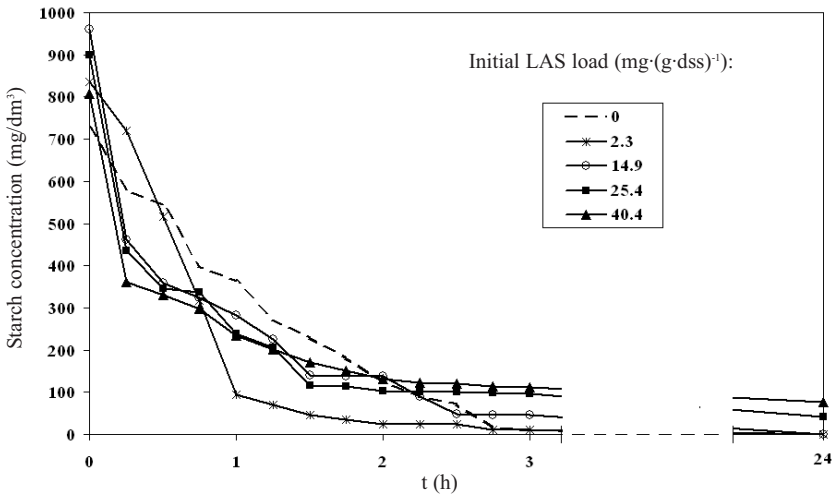

Fig. 2. Changes in starch concentration vs. duration of sewage purification.

Table 1. COD values (mg·O_2·(g·dss)$^{-1}$) for different LAS concentrations measured at different times during the experiment.

Process	Time (h)	LAS load [mg·(g·dss)$^{-1}$]					
		0	2.3	4.2	14.9	25.6	40.4
Anaerobic	0	300.8	304.5	304.7	302.4	300.6	301.7
	0.25	276.2	272	291.0	272.7	269.8	275.2
	3	229.7	168.1	248.7	281.7	280.7	276.8
Aerobic	7	163.9	80.5	111.1	257.7	277.0	274.2
	24	35.1	25.5	35.6	64.8	91.5	139.8

decreased, reaching at the end of the experiment a level identical to that in the control process. In contrast, a high LAS load has revealed a definitely negative impact on activated sludge. The respiration process was inhibited at LAS loads 25.6 and 40.4 mg·(g·dss)$^{-1}$. The oxygen consumption remains at a low, almost constant level (2-3 mg mg·O_2·h^{-1}·(g·dss)$^{-1}$), despite the presence of nutrients in the sewage (Fig. 3).

In practice, the effectiveness of wastewater treatment is based mostly on COD removal. The initial COD of sewage enriched with starch and LAS was approximately 300 mg·O_2·(g·dss)$^{-1}$. Within the first three hours (anaerobic conditions) a rapid decrease in COD was observed only in the case of the lowest LAS content (2.3 mg·(g·dss)$^{-1}$). When LAS loads are higher than 4.2 mg·(g·dss)$^{-1}$, the COD value practically does not change during the first seven hours of the process. After a full 24-hour sewage treatment, in experiments with LAS loads up to 15 mg·(g·dss)$^{-1}$, the attained final COD values were similar to or lower than those in the control process (Table 1).

These results and the increased oxygen consumption indicate that LAS, at its low concentration, slightly stimulates the degradation of pollutants in an activated sludge treatment system. For sewage with high LAS loads a COD reduction was only achieved after long-term aeration. However, this was not satisfactory, as the COD reductions were about 80%, 70% and 55% at LAS loads of 14.9, 25.6 and 40.4 mg·(g·dss)$^{-1}$, respectively. As was shown, the reduction of such high loads of COD requires a long period of aeration, much longer than the retention time in the SBR bioreactors. Unfortunately, at high LAS loads and prolonged aeration, the breakdown of sludge flocs was observed and tiny (fine) particles can be flushed out from the sludge. This may result in a deterioration of effluent parameters or may require an extended period of wastewater purification. In both cases the cost of wastewater treatment increases.

In summary, one can state that in the case of high surfactant loads (up to 14 mg·(g·dss)$^{-1}$) the respiratory activity of activated sludge bacteria is inhibited, resulting in a limited reduction of pollutants in sewage. It is probable that at such elevated surfactant concentrations the interactions between LAS and starch are strong and may reduce the bioavailability of starch (the carbon source) to activated sludge bacteria.

Surfactant content in typical municipal sewage usually does not exceed 14 mg/dm^3; thus it does not negatively affect the activated sludge process. However, some industrial wastewater with high surfactant concentrations [1, 28] could have a destructive impact on activated sludge. Negative impacts of LAS on the sludge influence economic factors such as the cost of wastewater treatment (high COD in the outlet) limit the proper functioning of the bio-

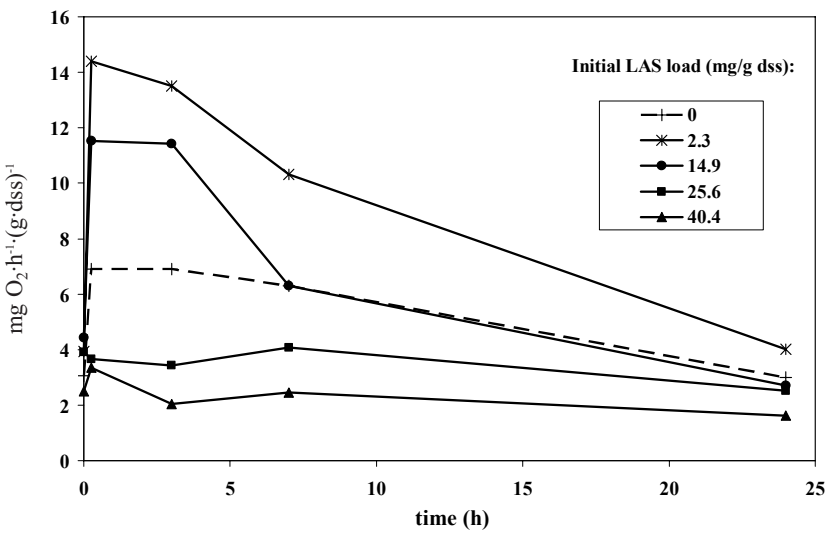

Fig. 3. OUR of activated sludge in sewage enriched with starch and LAS vs. duration of treatment.

logical wastewater treatment (lack of nitrification and dephosphatation) and can even lead to the degradation of activated sludge. Therefore, before biological treatment such sewage should be pretreated to decrease surfactant content and for this purpose such methods as foaming, adsorption, or coagulation are suggested.

The process of biological phosphorous removal occurs in two steps: in anaerobic conditions phosphorous is released from sludge to solution (supernatant); next, in the aerobic phase phosphorous is absorbed from solution and cumulated in the sludge bacteria cells. When significant amounts of LAS are present in sewage the phosphorus release and uptake are dependent on surfactant concentration (Fig. 4).

In sludge not containing surfactant, and with an LAS load less than 15 mg LAS/g dss, typical changes in phosphorous concentration in the supernatant were observed. Within the first three hours of the experiment, under anaerobic conditions, the phosphorus content rises from about 5 mg/dm^3 to about 68 mg/dm^3. Under aerobic conditions the concentration of phosphorus decreases to the initial concentration due to the absorption of phosphorus by polyphosphate accumulating organisms (PAO). Phosphorous release decreases when the LAS load exceeds 15 mg·(g·dss)$^{-1}$ (Fig. 4). Moreover, the intense leaching of phosphorus by activated sludge in anaerobic conditions is not followed by intense absorption of phosphorus in aerobic conditions. As can be seen from Fig. 4, the uptake of phosphorus is relatively slow and after 24 hours the final P concentration in the supernatant is about 25-40 mg/dm^3. Such a high LAS load can lead to disintegration of the bacteria cells. The amount of destroyed cells is rather high, so the viable cell number is decreased to such extent that their multiplication is less intensive than in the experiments without LAS addition (or even those with low surfactant concentrations), and this results in lower absorption of phosphorus.

In each experiment different sludge samples were used, and these differed in terms of activity, especially in their ability for phosphorus release and uptake. In order to evaluate the effect of LAS concentration on phosphorus removal the difference between phosphorus content in the control experiment and the experiment with LAS addition (ΔP) was calculated (equation 1):

$$\Delta P = (P)_{LAS} - (P)_{contr} \quad (1)$$

...where:

$(P)_{LAS}$ – phosphorus concentration in the supernatant in the process with LAS added,

$(P)_{contr}$ – phosphorus concentration in the supernatant in the control process (no LAS added).

A positive value for ΔP for the anaerobic phase (first 3 hours) indicates that LAS improved the release of phosphorus, while a positive ΔP value for the aerobic phase indicates that phosphorus uptake is hindered by LAS. The results are presented in Fig. 5.

As can be seen from Fig. 5, the positive influence of LAS on P release is observed only at low levels (2.3 mg·(g·dss)$^{-1}$). However, in the presence of low doses of LAS enhanced biological phosphorous release is observed, but its absorption during the aerobic phase proceeds more slowly than in the control process. At higher LAS concentrations the release of phosphorus is lower than in control experiments. Phosphorus uptake was hindered by LAS presence at each concentration. The introduction to the wastewater of a large dose of surfactant resulted in significant changes in the biochemical transformations of the phosphorus. Phosphates were released to a lesser extent, but over a longer time. Their absorption by the activated sludge was very low. Release of phosphate during the aerobic phase indicates a disruption of the process of the synthesizing and incorporation of polyphosphates into bacteria cells. Abnormal phosphorus metabolism may suggest a toxic effect of LAS toward the phosphate-accumulating bacteria.

However, there are some advantages to the presence of surfactants at high loads. Surfactants may enhance perma-

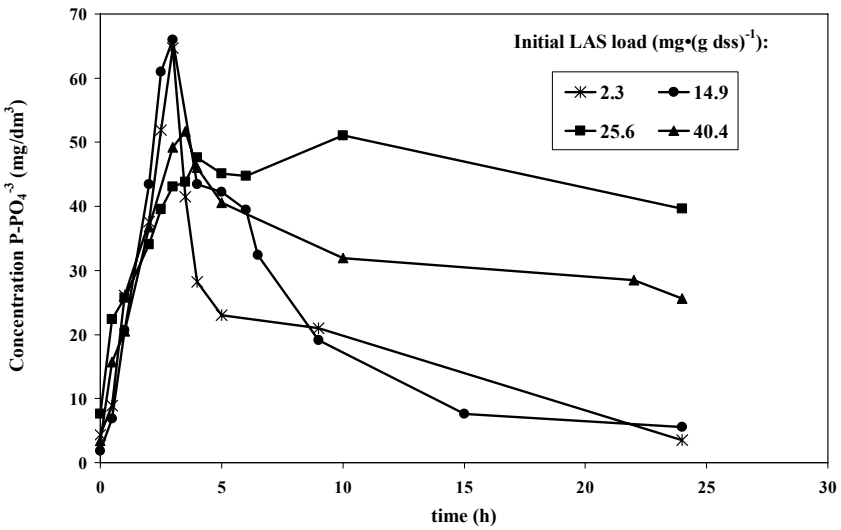

Fig. 4. Changes in phosphorus concentration in supernatant during the anaerobic and aerobic periods of the activated sludge process in the presence of LAS.

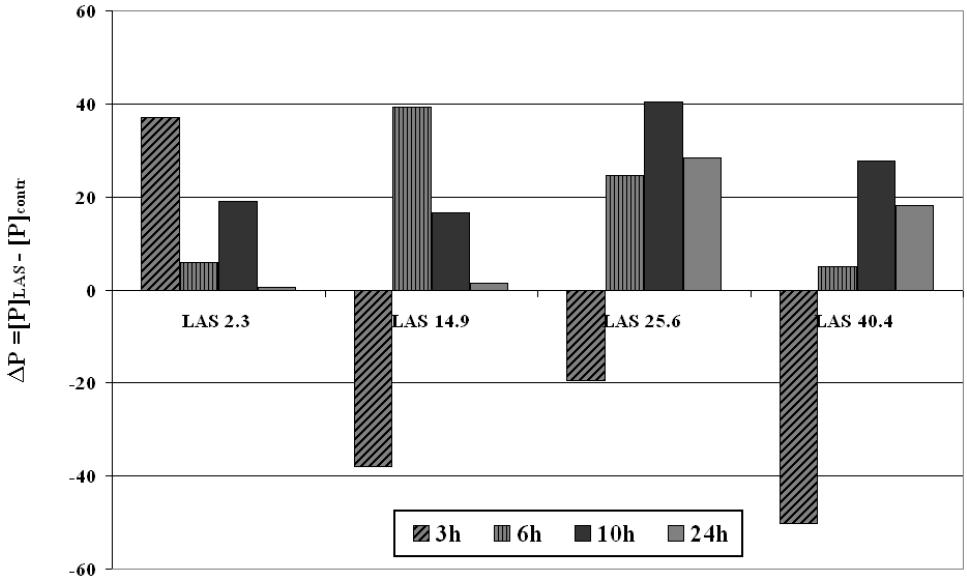

Fig. 5. Phosphorus content changes (ΔP) caused by LAS addition to activated sludge, observed at different times of the anaerobic and aerobic process.

nent phosphorus release from bacteria cells, which may be useful when considering phosphorus recovery from excessive sludge (waste-activated sludge). Such a trend has recently been observed in research and this concept has already been implemented on a full scale.

The Effect of LAS on Activated Sludge Flock Morphology

The effect of LAS on the morphology of activated sludge was analyzed via a microscopic study. Microscopic examination confirms changes in the morphology of activated sludge caused by the addition of high loads (25.6 $mg\cdot(g\cdot dss)^{-1}$) of LAS (Fig. 6). Such high concentrations (typical only for industrial wastewater) were used in the experiment because it allows the effect of surfactants to be observed within a very short period.

The presence of surfactant in the sewage influences the vitality of protozoa, causing substantial changes in their morphology. Upon strong superficial impact of LAS changes of protozoa morphology occur and the formation of cysts is observed (Fig. 6b). Formation of cysts is a type of a defensive response by protozoa to hazardous environmental conditions, in order to survive. However, lysis of cellular walls and total cell damage is also observed (Fig. 6c).

The microscopic observation of sludge flocs shows that bacteria cells are also strongly affected by surfactants. Surfactant alters the shape and size of sludge flocs. Microscopic observation shows that, after the addition of LAS, the sludge flocs disintegrated, became smaller, and some of the cells were damaged. This observation is in agreement with phosphate release observed during the experiment (Fig. 4), which was explained partly as a result of microbial cell lysis.

The effect of LAS on activated sludge flock size was assessed using granulometric measurement. Particle size analyses were carried out using the laser diffraction method. This device calculates the particle size distribution based on analysis of light dispersion. For irregular particles the equivalent spherical diameter was calculated.

The granulometric analysis shows that the activated sludge was composed of particles with sizes from 2.9 μm to 1.4 mm. The mean volume-number diameter (d_{30}) of sludge flocs (defined by the equation (2) [29]), and calculated for dispersion of activated sludge flocs, was equal to 377 μm.

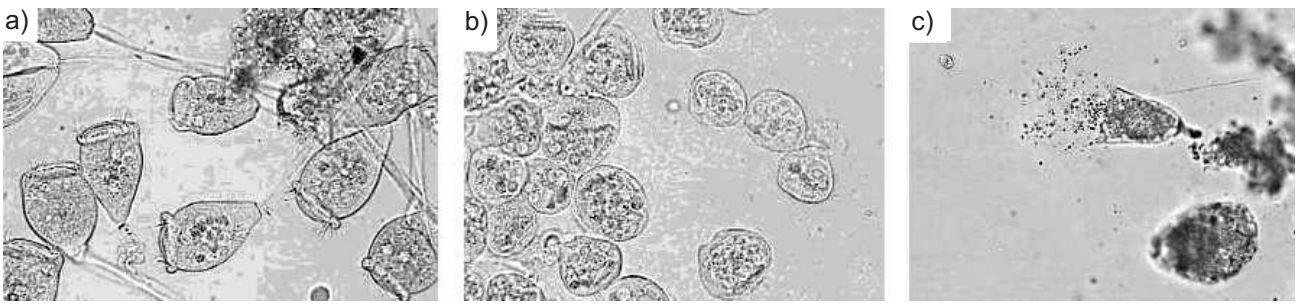

Fig. 6. Microscopic images of activated sludge protozoa (magnification 400×): a) control sample, b) and c) sludge with LAS load 25.6 $mg\cdot(g\cdot dss)^{-1}$.

$$d_{30} = \sqrt[3]{\frac{\sum n_i d_i^3}{n_i}} \quad (2)$$

…where n_i is the number of particles with diameter d_i.

After LAS addition to activated sludge, the particle size distribution curve has been shifted to a region of smaller sizes of particles. The flocs with a diameter above 800 µm have disappeared. The dimensions of dominating particles have decreased from about 300 µm to about 200 µm and the mean volume-number diameter of sludge flocs has decreased from 377 to 255 µm. The detailed description of changes in flocs sizes of activated sludge affected by LAS is the subject of another publication [30].

The appearance of fine sludge flocs and released intercellular mucus has resulted in a more than 20 times higher sludge filtration time through filter paper in laboratory conditions. Furthermore, the changes of sludge flocs morphology may negatively affect some indirect parameters of sewage treatment, such as secondary clarification time, excess sludge thickening time, and the effectiveness of sludge dewatering. The worsening of the clarification caused by surfactants results from the change in the sludge sedimentation rate after its disintegration and the appearance of fine flock particles in the supernatant.

Conclusions

The sewage with LAS loads not exceeding 3 $mg\cdot(g\cdot dss)^{-1}$ has no negative influence on the functioning of the treatment plant-, moreover, it can improve the biological activity of the sludge. When surfactant loads exceed 15 mg LAS/g dss, negative biochemical processes, such as decreasing microorganism respiration and a disruption of phosphorus uptake, are observed. LAS also affects the morphology of activated sludge, causing fragmentation of flocs and lysis of protozoa cells. The presence of surfactants at high loads in sludge may enhance permanent phosphorus release from bacteria cells, which may be useful when considering phosphorus recovery from excessive sludge.

Acknowledgements

We would like to thank A. Tuszyńska (GUT) for her technical support with the laser granulometer.

References

1. LIWARSKA-BIZUKOJC E., BIZUKOJC M. Digital image analysis to estimate the influence of sodium dodecyl sulphate on activated sludge flocs. Process Biochem. **40**, 2067, **2005**.
2. ALOUI F., KCHAOU S., SAYADI S. Physicochemical treatments of anionic surfactants wastewater: Effect on aerobic biodegradability. J. Hazard. Mater. **164**, 353, **2009**.
3. YÜKSEL E., SENGILI. A., ÖZACAR M. The removal of sodium dodecyl sulfate in synthetic wastewater by peroxi-electrocoagulation method Chem. Eng. J. **152**, 347, **2009**.
4. HERA. Human & Environmental Risk Assessment on ingredients of European household cleaning products. Report for LAS, http://www.heraproject.com. **2007**.
5. MÖSHE M., MEYER U. Toxicity of linear alkylbenzene sulfonate in anaerobic digestion: influence of exposure time. Water Res. **36**, 3253, **2002**.
6. PASTEWSKI S., MĘDRZYCKA K. Monitoring Surfactant Concentrations in Surface Waters in Tricity Agglomeration. Pol. J. Environ. Stud. **12**, (5), 643, **2003**.
7. KARAHAN O. Inhibition effect of linear alkylbenzene sulphonates on the biodegradation mechanism of activated sludge, Bioresource Technol. **101**, 92, **2010**.
8. GONZÁLES S., PETROVIC M., BARCELÓ D. Removal of a broad range of surfactants from municipal wastewater – Comparison between membrane bioreactor and conventional activated sludge treatment. Chemosphere, **67**, 335, **2007**.
9. YAPIJAKIS C., WANG L.K. Waste treatment in the process industries: Treatment of Soap and Detergent Industry Wastes, Taylor & Francis Group, New York, pp. 307-363. **2006**.
10. PANG Z., AL-MAHROUKI A., BEREZOVSKI M., KRYLOV S.N. Selection of surfactants for cell lysis in chemical cytometry to study protein-DNA interactions, Electrophoresis, **27**, 1489, **2006**.
11. CSERHÁTI T., FORGAÁCS E., OROS G. Biological activity and environmental impact of anionic surfactants,. Environ. Int. **28**, 337, **2002**.
12. FEITKENHAUER H. Anaerobic digestion of desiring wastewater : influence of pretreatment and anionic surfactant on degradation and intermediate accumulation. Enzyme and Microbial Technol. **33**, 250, **2003**.
13. DOIANAKIS N., KORNAROS M., LYBERATORS G. Impact of five selected xenobiotics on isolated ammonium oxidizers and on nitrifying activated sludge. Environ. Toxicol. **21**, 310, **2006**.
14. OTHMAN M.Z., DING L, JIAO Y. Effect of Anionic and Non-ionic Surfactants on Activated Sludge Oxygen Uptake Rate and Nitrification. Int. J. Civil Environ. Eng. **2**, (4), 196, **2010**.
15. JI Z., CHEN G., CHEN Y. Effects of waste activated sludge and surfactant addition on primary sludge hydrolysis and short-chain fatty acids accumulation. Bioresource Technol. **101**, 3457, **2010**.
16. JIANG S., CHEN Y., ZHOU O., GU G. Biological short-chain fatty acids (SCFAs) production from waste-activated sludge affected by surfactant. Water Res. **41**, 3112, **2007**.
17. HAMZA N., BERKE B., CHEZE C., AGLI A.N., ROBINSON P., GINC H., MOORE N. Prevention of type 2 diabetes induced by high fat diet in the C57BL/6J mouse by two medicinal plants used in traditional treatment of diabetes in the east of Algeria. J. Ethnopharmacol. **128**, 513, **2010**.
18. MINO T., SAN PEDRO D. C., MATSUO T. Estimation of the rate of slowly biodegradable COD (SBCOD) hydrolysis under anaerobic, anoxic and aerobic conditions by experiments using starch as model substrate. Water Sci. Technol. **31**, 95 **1995**.
19. ISO 7875-1 Water Quality. Determination of Surfactants. Part1: Determination of Anionic Surfactants By Measurement of the Methylene Blue Index (MBAS) ISO/TC 147. **1996**.
20. APHA, Standard Methods for the Examination of Water and

Wastewater, 20th Edition, Method 2540D, Washington, **1998**.
21. ORUPÕLD K., HELLAT K., TENNO T., Estimation of treatability of different industrial wastewaters by activated sludge oxygen uptake measurements, Water Sci. Tech. **40**, 31, **1999**.
22. DERESZEWSKA A. Sorption of anionic surfactants on activated sludge from biological wastewater plant, Jt Proc. – Hochschule Bremerhaven – Gdynia Maritime University, **23**, 35, **2010**.
23. YU G.H., HE P.J., SHAO L.M. Characteristic of extracellular polymeric substances (EPS) fractions from excess sludges and their effects on bioflocculability. Bioresour. Technol. **100**, 3193, **2009**.
24. PURSELL MR, MENDES M.A., STUCKEY D.C. Interactions between surfactants and biomass during liquid-liquid extraction, Biotech. Progress. **25**, (6), 1686, **2009**.
25. SEN T.K., THI M.T., SHARMEEN AFROZE S., PHAN Ch., ANG M. Removal of anionic surfactant sodium dodecyl sulphate from aqueous solution by adsorption onto pine cone biomass of Pinus Radiate: equilibrium, thermodynamic, kinetics, mechanism and process design. Desalination Water Treat. **45**, 263, **2012**.
26. SVENSSON E., GUDMUNDSSON M., ELIASSON A.C. Binding of sodium dodecylsulphate to starch polysaccharides quantified by surface tension measurements. Colloids Surf. B: Biointerfaces. **6**, 227, **1996**.
27. MIRA I. Interactions between surfactants and starch: From starch granules to amylose solutions. Doctoral Thesis, Royal Institute of Technology, Stockholm. **2006**.
28. SULEJ A., POLKOWSKA Ż., NAMIESNIK J. Contaminants in Airport Runoff Water in the Vicinities of Two International Airports in Poland. Pol. J. Environ. Stud. **21**, (3), 725, **2012**.
29. BECHER P. Encyclopedia of emulsion technology: Basic Theory, Dekker, New York. **1983**.
30. DERESZEWSKA A., TUSZYNSKA A., CYTAWA S. Application of the laser diffraction particle size analyser to the study of the changes of activated sludge structure in the presence of surfactant. Ecol. Chem. Eng. ser. A [In press].