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MONITORING OF ANIONIC AND NON-IONIC SURFACTANTS IN ACTIVATED SLUDGE SAMPLES

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Introduction

The surfactants are one of the most commonly used class of chemicals (15billions tons per year) in various applications: household cleaning, personal care products and industry. Anionic surfactants represent the major class of surfactants used in detergents, the predominant groups being linear alkylbenzene sulphonates (LAS) and linear alkyl suphates (AS). Non-ionic surfactants are used in large quantities in domestic and commercial products, e.g. cleaning solutions. The most widely used non-ionic surfactants are alkylphenol ethoxylates (APEs) and the most used commercial APEs are octylphenol ethoxylates (OPEs) and nonylphenol ethoxylates (NPEs). Because of the large utilization of surfactants, they can accumulate in the domestic and industrial wastewaters, affecting treatment plants (WWTP) due the inhibition off activated sludge. As a result, surfactants could affect the water bodies quality through discharge of WWTPs' effluents or soil quality through various modes of sludge disposal.
Due to large quantities of sludge resulting from urban wastewater treatment process, methods for the recovery / storage / disposal of sludge must be identified, depending on sludge composition and the concentrations of pollutants in them.
This paper represent a monitoring study to investigate the surfactants concentration (LAS and NPE) from different influents to WWTPs and sludge samples collected during 1 year (from March 2018 until March 2019).

Material and methods

Samples were collected from different wastewater treatment plants (WWTPs), during one year in the months: March 2018, August 2018, November 2018, January 2019, March 2019. The composite water samples were collected from influent to WWTPs and sludge samples were taken from drying beds of WWTPs. The analysis of surfactants was performed on the same day of sample collection.
The analytical methods used to determine the surfactants concentrations were: the MBAS (methylene blue active substances) method – standard method SR EN 903:2003 for anionic surfactants and BIAS method (bismuth active substances) – standard method ISO 7875-2:1984 for non-ionic surfactants.

Sodium dodecylbenzene sulphonate (SDBS), as LAS surfactant (linear alkylbenzene suphonate) forms ion pairs with methylene blue that is extracted by chloroform and determined spectophotometrically at 650 nm.
The BiAS procedure consists of gas-stripping of non-ionic surfactants from liquid sample to an ethyl acetate layer, evaporation of ethyl acetate, dissolution of the residue in a water/methanol mixture, precipitation of ethoxylates with Dragendorff reagent, filtration and washing of the precipitate with glacial acetic acid, dissolution of the precipitate in sodium tartrate solution and determination of bismuth UV spectophotometrically at 263.5 nm.
The pretreatment of solid samples includes the extraction of surfactants before analysis by several steps. The first step is to dry and grind the collected sludge samples and then to extract the surfactants using small amounts of methanol. The second step is the filtration and diluted with methanol. The third step supposed to take a small amount of filtrated and putting in a separation fuel, then adding water, methylene blue reagent and chloroform for anionic surfactant determination. After shaking the entire matrix, the absorbance of chloroform extract is read at 650 nm. Similar pretreatment of sludge samples is applied for the NPEs extraction, but the last step is different. In this case the filtrated is mixed with water and treated like in the procedure of Dragendorff reagent.
The spectrophotometer Specord BU 205 (Analytic Jena, Germany) was used for the surfactants quantification by spectrometric absorbance.

Results and Conclusions
The first phase of this study involved monitoring of concentration of anionic and non-ionic surfactants in the different influents to urban / industrial WWTPs, during the period March 2018 – March 2019. The time period when the samples were taken, the type of WWTPs and the surfactants concentrations are presented in Table 1.

Table 1. Concentration of anionic and non-ionic surfactants in influents of WWTPs

Day of Monitoring	Type of WWTP	Anionic surfactants (mg/L)	Non-ionic surfactants (mg/L)
14.03.2018	Local urban WWTP	3.04	0.59
21.03.2018	Local urban WWTP	3.95	0.53
28.03.2018	Municipal WWTP	7.09	1.46
10.08.2018	Local urban WWTP	2.63	0.18
24.08.2018	Municipal WWTP	5.23	0.32
31.08.2018	Local industrial WWTP	6.05	3.56
14.11.2018	Municipal WWTP	9.85	2.46
22.11.2018	Municipal WWTP	10.79	4.96
30.11.2018	Municipal WWTP	9.54	3.85
10.01.2019	Municipal WWTP	7.32	2.15
21.01.2019	Local urban WWTP	5.04	2.59
31.01.2019	Local urban WWTP	7.09	1.58
11.03.2019	Municipal WWTP	3.87	0.46
21.03.2019	Local industrial WWTP	3.52	0.15
29.03.2019	Municipal WWTP	5.28	1.83

The concentration of anionic surfactants ranged from 2.63 to 10.79 mg/L, with an average of 6 mg/L and non-ionic surfactants showed a range varying from a minimum of 0.15 mg/L to 4.96 mg/L, with an average of 1.78 mg/L (figure 1).

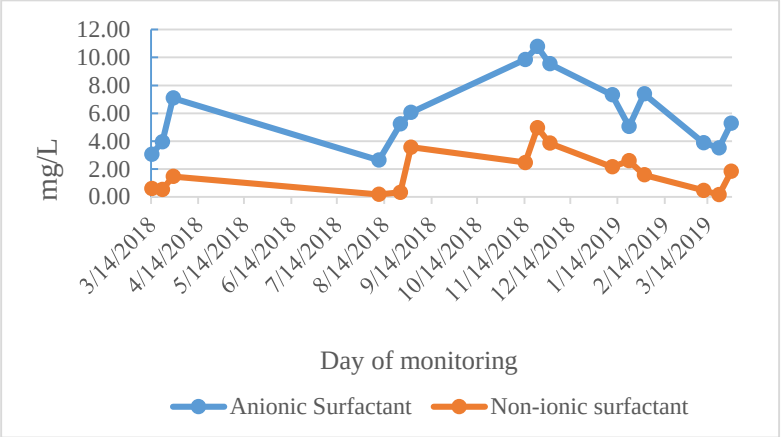

Figure 1. Concentration of anionic and non-ionic surfactants in the influent to WWTPS

The concentration of both surfactants were measured in 5 different sludge samples collected from drayed beds of municipal WWTPs, in the months: March 2018, August 2018, November 2018, January 2019, March 2019. The date and WWTPs from which the sludge samples were collected are greyed out in Table 1. The results were expressed in milligrams/kilograms drayed substance (mg SDBS and NPE / kg DS).
The results revealed the presence of both SDBS and NPE surfactants in sludge samples (table 2), in concentrations higher than those determined in the influent to WWTPs.

Table 2. Concentration of anionic and non-ionic surfactants in sludge samples

Time of the Year	mg SDBS / kg DS	mg NPE / kg DS
March 2018	238.41	223.89
August 2018	201.68	187.50
November 2018	238.42	194.13
January 2019	161.73	152.48
March 2019	133.91	115.59

It has been found that the highest concetrations of surfactants found in the influets of WWTPs in March 2018 and November 2018 are well correlated with those determined in the sludge samples. The anionic surfactant (SDBS) concentrations were higher than non-ionic surfactant (NPEs) concentration, both in the influent water to WWTPs and in the sludge deposited on the drying beds.
Our study will be continued to highlight the effect of anionic and non-ionic surfactant concentrations on the biological activated sludge.