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VARIATION OF ANIONIC AND NONIONIC SURFACTANTS PRESENCE IN WASTEWATERS

Daniel Mitru, Elena Stanescu, Alina Roxana Banciu, Mihai Nita-Lazar

Research and Development Institute for Industrial Ecology-ECOIND, 71-73 Drumul Podu
Dambovitei, district 6, 060652, Bucharest, Romania, daniel.mitru@incdecoind.ro

Abstract

It has been known the surfactants have been used to remove stains from leather, clothes and household items, particularly from kitchens and bathrooms.

Our studies were carried out during eight months in order to include all the seasons (July, August 2016 – Summer; September, October 2016 – Autumn; January, February 2017 – Winter and March, April 2017 – Spring) to detect the variation of anionic and nonionic surfactants concentration from industrial wastewaters. The wastewater samples were taken from three sampling points belonging to a subway maintenance company: Berceni, Militari and Pantelimon.

The total concentration of anionic surfactants in wastewaters was analyzed by Methylene Blue Active Substances Method (MBAS), and the total concentration of nonionic surfactants was detected by the method with Dragendorff reagent.

The results showed that anionic and nonionic surfactants concentrations detected in wastewater samples were less than 0.1 mg/L (under the quantification limit) up to 2.03 mg/L for anionic surfactants and the nonionic surfactants had less than 0.15mg/L (under the quantification limit) up to 1.72 mg/L. According to the national legislation (HG 352/2005, NTPA 002, Annex 2/2005), the accepted value of surfactants (as sum of anionic and nonionic) is less than 25 mg/L.

The results of the study revealed the highest concentration of both anionic and nonionic surfactants during March, one of the possibilities of this variations could be the lower level of maintenance in February than the other months. Furthermore, this change of concentration may be the result of switching the type of organic compound (detergent) using for the subways cleaning.

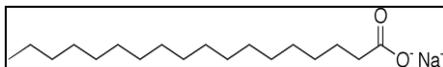
Keywords: *anionic surfactants, Dragendorff reagent, MBAS, nonionic surfactants, subways, wastewater*

Introduction

A detergent is an effective cleaning product because it contains one or more surfactants (American Cleaning Institute, 2017) that could be engineered to perform well under a variety of conditions (Figure 1). Sodium stearate is the most common component of most soap, which comprises about 50% of commercial surfactants and B, 4-(5-Dodecyl) benzenesulfonate is a linear dodecyl benzenesulfonate, one of the most common surfactants (Rosen & Kunjappu 2012).

The application of surfactants is various such as industrial use (oil recovery), domestic use (laundry detergent), food processing and pharmaceuticals synthesis (Schramm, Stasiukb & Marangonic 2003).

A



B

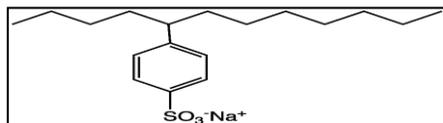


Figure 1. Structures of surfactants. A: Sodium stearate; B: 4-(5-Dodecyl) benzenesulfonate

The most wide-spread usage of surfactants was related to the domestic area. They have been used to remove stains from clothes, leather and household items, but also to clean kitchens and bathrooms.

Surfactants operate by breaking down the interface between water and oils and/or stains. They are able to act in this way, because they contain both a hydrophilic group, such as an acid anion, (-CO₂⁻ or SO₃⁻) and a group, such as an alkyl chain. As we can see in Fig. 2, the head is hydrophilic and the tail is hydrophobic. After the action of cleaning, the surfactant surrounds the stain in order to prevent its redepositing (Figure 2).

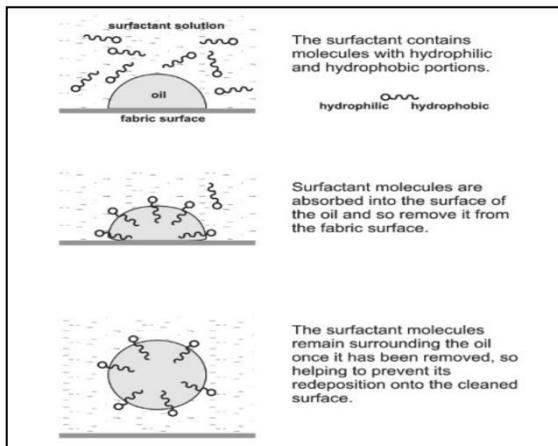


Figure 2. Action of a surfactant (The Essential chemical industry 2013)

Depending on the nature of the hydrophilic group, surfactants are classified as:

- Anionic surfactants*, a surfactant in which the hydrophilic part carries a negative charge such as soaps, RCOO⁻, alkyl sulphates, ROSO₃⁻;
- Nonionic surfactants*, a surfactant in which the hydrophilic part carries a uncharged, such as acyl diethanolamides, RCON(C₂H₄OH)₂, ethoxylated fatty alcohols R(OC₂H₄)_nOH;

iii) *Cationic surfactants*, a surfactant in which the hydrophilic part carries a positive charge, such as alkyltrimethylammonium salts $\text{RN}^+(\text{CH}_3)_3$, alkildimethylbenzylammonium salts $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{C}_5\text{H}_6$;

iv) *Amphoteric surfactants*, a surfactant in which the hydrophilic part contains both positive and negative charges such as alkylaminopropionates $\text{RNH}_2^+(\text{CH}_2)_2\text{COO}^-$ alkyl betaines, $\text{RN}^+(\text{CH}_3)_2\text{CH}_2\text{COO}^-$. It is possible for amphoteric surfactants to have more than one charge of either sign, or to lose one charge by addition or removal of a proton (Cullum 1994).

A large number of surfactants from wastewaters have been discharged into the environment, harming aquatic life, polluting the water and endangering human health. All these environmental issues could be addressed starting by the control of surfactants dispersion in wastewater (Yuan et al. 2014).

This study aimed to monitor the variation of anionic and nonionic surfactants of industrial wastewaters from a subway maintenance company, during July to October 2016 and February to April 2017. Anionic and non-ionic surfactants were chosen taking into account the frequency with which they are used as raw materials in the detergent composition and also, they are the most widely used type of surfactants because of their excellent cleaning and high foaming potential.

Experimental

Reagents

The Methyl ester of dodecyl benzene sulfonic acid ($\text{C}_{19}\text{H}_{32}\text{O}_3\text{S}$, MDS, 99% purity, $M = 340.53 \text{ g/mole}$) purchased from Merck was used as a reference for methylene blue active substances (MBAS).

Phenolphthalein indicator solution was prepared according to the standard method (SR EN 903). Moreover, 0.1 mole/L NaOH and 0.5 mole/L H_2SO_4 solutions were prepared for pH controlling. Chloroform (99% purity) was purchased from Chimreactiv (Bucharest, Romania) and was used in the separation process between water matrix and organic matrix. Methylene Blue reagent was prepared according to the standard method (SR EN 903). Glass wool was pre-washed with CHCl_3 to remove impurities. De-ionized water was used. Tampon solution used to sustain a constant pH ($\text{pH} = 10$) was obtained by dissolving the sodium bicarbonate (NaHCO_3) and sodium carbonate (Na_2CO_3).

Nonylphenol polyethylene glycol ether ($\text{C}_9\text{H}_{19}\text{C}_6\text{H}_4(\text{OCH}_2\text{CH}_2)_9\text{OH}$, 99% purity, $M = 616.82 \text{ g/mole}$) (Sigma Aldrich, USA) was used as a control reference for nonionic surfactants determination. For the precipitation agent, two solutions were used. Solution A was a mixture between bismuth oxynitrate and potassium. Solution B was barium chloride dissolved in water. Precipitation agent was based on two-thirds of solution A and one-third of solution B.

Equipment

Specord BU 205 spectrophotometer (Analytic Jena, Germany) was used for both anionic and nonionic detection by absorbance reading. The wavelength for detection of anionic surfactants was at 650 nm and the optical cell length path was of 10 mm. Detection of nonionic surfactants was carried out at 263.5 nm and an optical cell length path of 20 mm (Analytik Jena AG 2005).

Detection of anionic surfactants was performed by using a calibration curve based on reference material (RM) solutions of six different concentrations. The RM was methyl ester of dodecylbenzene sulfonic acid (C₁₉H₃₂O₃S) and the calibration curve was constructed according to the standard method (SR EN 903) using 6 standards with concentrations between 15 µg to 200 µg. The linearity range of the calibration curve was between 17.5 µg - 200µg (Figure 3).

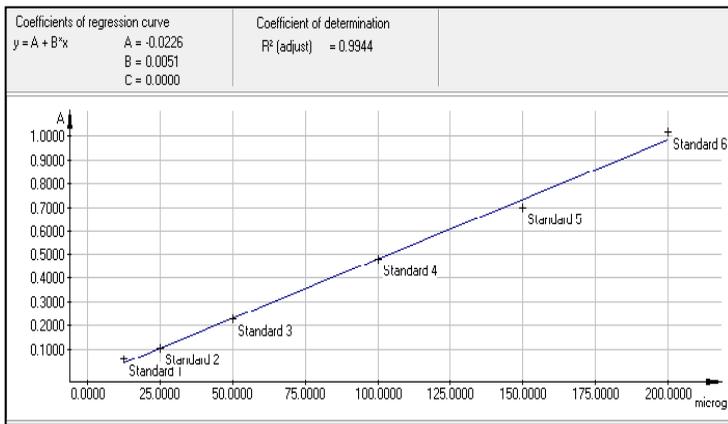


Figure 3. Calibration curve of anionic surfactants

A calibration curve with five standards was used for determination of nonionic surfactants concentration.

The standards were prepared by adding 200 µg, 400 µg, 600 µg, 800 µg and 1000µg of Nonylphenol polyethylene glycol ether and then dissolved in 5 mL methanol and 400 mL of water according to the standard ISO 7875-2:1984.

The linearity range of the calibration curve was between 200 µg and 1000 µg (Figure 4).

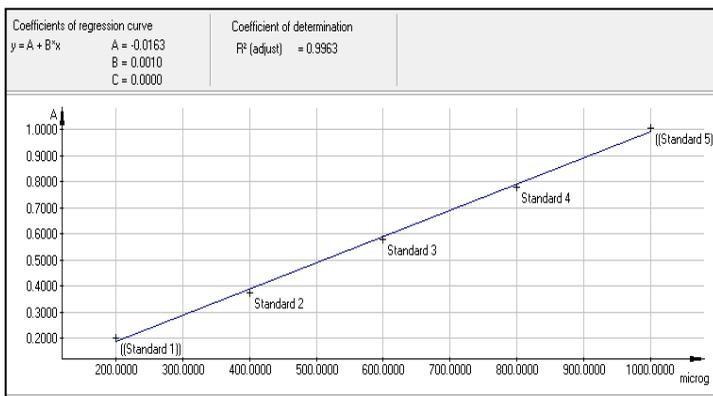


Figure 4. Calibration curve of nonionic surfactants

As is presented below (Table 1), for both spectrometric methods, the following method performance criteria were investigated: linearity domain, detection limit, quantification limit, precision evaluated by repeatability (n = 10) and interim precision/reproducibility (6 replicates measured in 3 different days) (ISO 8466-1:1990). Sources of uncertainties were identified and extended standard uncertainty was estimated for each spectrometric method using measurements on wastewater samples.

Table 1. Performance parameters

Type of parameter	MBAS method	Nonionic determination
Detection limit	0.05 mg/L	0.05 mg/L
Quantification limit	0.10 mg/L	0.15mg/L
Repeatability (RSDr)	2.48%	4.75%
Reproducibility(RSDr)	4.18 %	6%
Measurement uncertainty	8%	11%

Formulas and calculation

The concentration of MBAS was detected by the formula:

$$p_y = \frac{(A_1 - A_0) f_2}{V_0} \quad (1)$$

where, p_y is masic concentration of MBAS;

A_1 is the absorption of sample;

A_0 is the absorption of control sample;

f_2 is the calibration factor which was the amount of anionic surfactant represented in milligrams (it was calculated as sodium salt of dodecyl benzenesulfonate acid);

V_0 is the volume was represented in milliliters.

The concentration of nonionic surfactant was detected by the formula:

$$p_y = \frac{(c_1 - c_0) * 100}{V_0} \quad (2)$$

where, p_y is masic concentration of nonionic surfactant ($\mu\text{g/mL}$);

c_1 is the concentration of sample red with calibration curve ($\mu\text{g/mL}$);

c_0 is the concentration of control sample red with calibration curve ($\mu\text{g/mL}$);

V_0 is the volume was represented in milliliters.

Results and Discussion

An increase of anionic surfactants was recorded in August, 2016 and March 2017 in all the places (Berceni, Pantelimon and Militari). Thus, the highest concentration of anionic surfactants (2.03 mg/L) was observed in Pantelimon Station. The concentrations of surfactants were below the detection limit in all stations during the month of February 2017 (Figure 5).

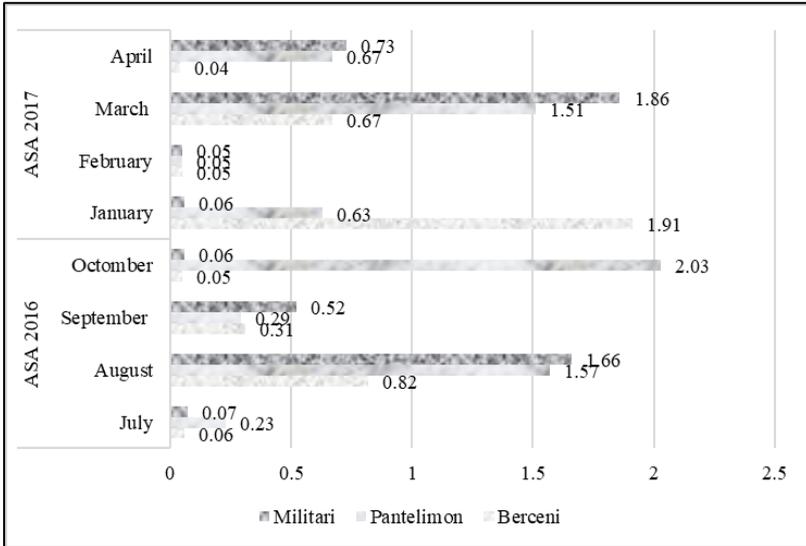


Figure 5. Concentration of anionic surfactants during eight months

The same situation was in case of nonionic surfactants, so in August 2016 and March 2017 it was recorded an increase of nonionic surfactants at the same places). Moreover, the highest concentration of nonionic surfactants was observed in Pantelimon Station (1.72 mg/L) and also, the lowest concentration was in February (below the detection limit) for all the Stations (Figure 6). Thus, the limit of concentration according to the national legislation was 25 mg/L (HG 352/2005, NTPA 002, and Annex 2/2005). It means that the results for the combined concentration of anionic surfactants and nonionic surfactants have to be less than 25 mg/L.

Low concentrations of surfactants recorded in February may be explained by a lower level of subway maintenance compared to the other months of investigation, was due to the fact that the cross between winter and spring, the possibilities of maintenance were lower than other periods of the year. Starting from March, more activities were performed (washing, oil changing, cleaning) so more surfactants were used. The other possibility could be the snow retention of the especially since February (month with the snow time) and it could lead to a small amount of surfactant in sewage. Moreover, another explanation could be the change of detergent type (it supposed that was used a different class of surfactant (cationic/amphoteric) and that it meant different concentration of surfactants).

Overall, it was observed that the sampling location could play a role in surfactants variation. This fact was confirmed during February 2017 in all the places the concentration of surfactants where under the limit of detection, but in January 2017 we had an increase of concentration only in Berceni Station. That could be meaning that in every season a station is doing maintenance for all the others stations.

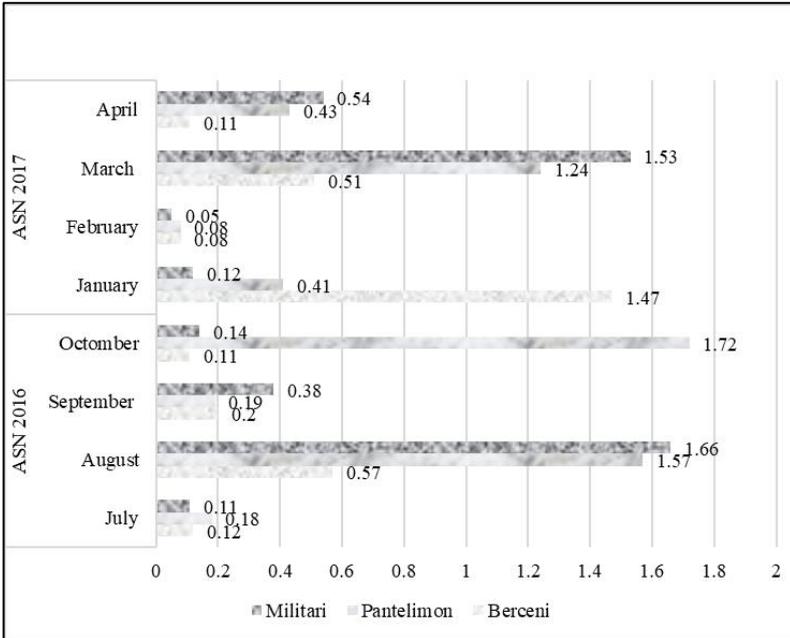


Figure 6. Concentration of nonionic surfactants during eight months

Conclusions

According to the legislation for wastewaters the concentration of surfactants detected were not so high.

The activity of the subway maintenance company was depending on the time of the year and the place (winter – less, except January 2017 – Berceni station; spring, summer, autumn – more).

The surfactants concentration has varied between sampling points. The results could be more comprehensive if the monitoring period would be more extensive (at least one year or above).

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