Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1157038

57 (2016) 25677–25685
November

Taylor & Francis
Taylor & Francis Group

Determination of anionic surfactants in wastewater treatment plant in Algiers City

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Received 16 February 2014; Accepted 16 February 2016

ABSTRACT

A spectrophotometric method was adapted for the determination of anionic surfactants (AnS) using the Crystal Violet. Anionic surfactant gives an ion pair with the dye, which is extracted with an organic solvent. The developed method has been studied and optimized for various parameters, such as the effect of the buffer solution on the extraction of the ion pair (pH 8.1) and the volume of solvent extraction (15 mL). Determination of AnS in distilled water gives good precision and a significant detection limit up to 2.5×10^{-6} M. Interferences have been eliminated by determining AnS in seawater. An application part for this method was carried out in the determination of AnS in an estuary treatment plant in Algiers city. Many results have been obtained and some interesting observations are made. For this, the optimized method for anionic surfactant determination gives significant and reproducible results.

Keywords: Anionic surfactant; Spectrophotometry; Wastewater treatment plant

1. Introduction

The importance of water pollution has increased significantly since the early 60s worldwide. In industrialized countries, large programs have slowed the progression of contamination of fresh- and seawater. This contamination is due to the discharge of domestic and industrial effluents containing organic materials.

Among these organic compounds, AnS are used in daily life through commercial detergents, cosmetics, and many industrial applications. It should be noted that their high consumption or use has unfortunately negative consequences on the environment [1,2]. Indeed, direct impacts on different areas are proven as the pollution from various industrial and urban waste draining large amounts of these compounds to marine and freshwaters [3,4].

Several techniques have been developed [5–11] in order to analyze anionic surfactants (AnS) in industrial and urban waste [12–20]. Generally, different levels of AnS are determined by UV–visible spectrophotometry, based on the principle of extracting AnS as an ion pair in a suitable organic solvent using a cationic organic dye [21–24]. AnS concentration is deduced by measuring the absorbance of the organic phase to the maximum wavelength of absorption of the dye.

The ethyl violet offers a wide opportunity for AnS extraction with different organic solvent, such as benzene and toluene. It is one among the dyes that gives a steady ion pair extracted in a single step, and it has been used for the determination of AnS levels in marine

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waters [25]. Introduction of Methyl Violet in this technique proves that this dye [26,27] offers a wide possibility of determining AnS in marine waters. Methyl Violet (Crystal Violet (CV)) was used with toluene as a solvent for the determination of AnS in Algiers Bay with a very low detection limit and less interferences [28].

Giving importance to the research carried out in our laboratory [28] and literature reports on the extraction of AnS with CV [29], we were interested to develop and use methods for the determination of AnS in industrial and urban wastes. The technique was applied to determine different levels of AnS and follow their evolution before, during, and after treatment of wastewater in a treatment plant in Algiers city.

2. Materials and methods

2.1. Materials

1. (1) UV–visible spectrophotometer: for the study, we used a UV–visible spectrophotometer JASCO.V Type 530 with quartz cells of 1 cm optical path.
2. (2) pH-meter: A TACUSSEL pH meter with calomel electrode was used for pH adjustment.

2.1.1. Chemicals

CV ($C_{25}H_{37}N_3Cl$) is the cationic dye used for this study.

Sodium Dioctyl sulfosuccinate “Manoxol OT” ($C_{20}H_{37}NaO_7S$).

Buffer solution: Ammoniacal buffer (NH_4Cl/NH_3) was used, this was prepared by dissolving 26.75 g of NH_4Cl in one liter of distilled water and adding 3.6 ml of aqueous NH_3 to adjusted pH between 8 and 8.2.

Sodium Sulfate solution: In order to accelerate phase separation, 0.5 M of sodium sulfate solution is added to the extraction system.

Toluene is used as solvent extraction.

2.2. Analytical procedure

Transfer 100 mL of a sample solution containing anionic surfactant into an Erlenmeyer flask; add 5 mL of the sodium sulfate solution, 5 mL of ammoniacal buffer, and 2.5 mL of CV solution. Shake for 15 min with 10 mL of toluene. After phase separation in a separator funnel, recover the organic layer and wash with 10 mL of distilled water. Measure the absorbance of the organic phase at the maximum wavelength absorbance of CV against Toluene as reference.

3. Results and discussion

3.1. Validation/optimization of the method

3.1.1 The cationic dye

The absorption spectra of cationic dye present a characteristic absorption band at 589 nm (Fig. 1).

3.1.2. Standard anionic surfactant

Sodium Dioctyl Sulfosuccinate “Manoxol OT” ($C_{20}H_{37}NaO_7S$) was used as standard anionic surfactant reference, for its significant response compared to other commonly used AnS, such as sodium dodecyl sulfate (SDS). Fig. 2 shows the absorption spectra of the ion pair obtained with both Manoxol OT and SDS.

3.1.3. Extraction of the ion pair

The ion pair formed between the anionic surfactant (Manoxol OT) and the cationic dye (CV) shows absorption spectra in Fig. 3. Maximum absorption of the ion pair appears in toluene at 589 nm. It should be noted that the initial amount of CV decreases because of its association with the anionic surfactant in a molar ratio of 1/1 with a different absorption band for the ion pair.

3.1.4. Influence of buffer media

The ion pair [(AnS) (CV)] is extracted in the presence of a basic buffer to prevent the formation of degradation products of CV, and the elimination of some interferences. As shown in Fig. 4, the maximum absorbance is obtained for pH 8.1. For this, the extraction of AnS with CV will be performed at this pH (using ammoniacal buffer).

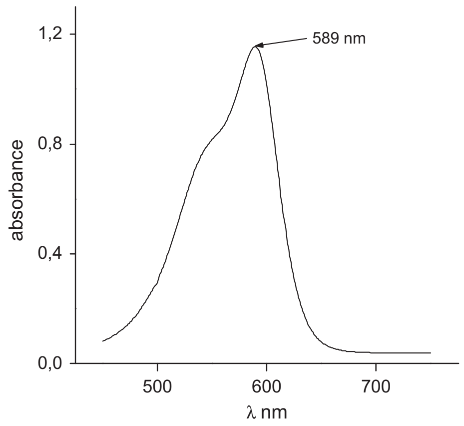

Fig. 1. Absorption spectra of a solution of Crystal Violet (5×10^{-4} M; $\varepsilon_{max} = 2.99 \times 10^3$ m^2 mol^{-1}).

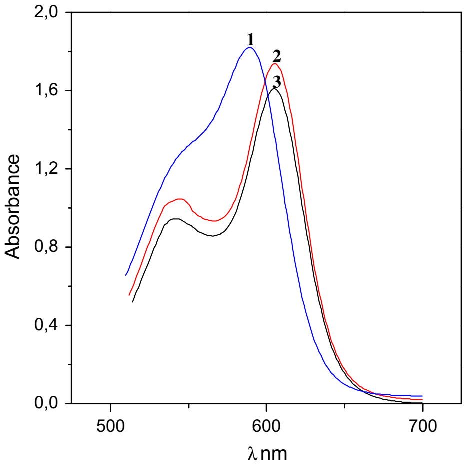

Fig. 2. UV–visible absorption spectra of: (1) Aqueous solution of CV ([CV] = 10^{-3} M; ε_{max} = 1.8 × 10^3 m^2 mol^{-1}), (2) Ion pair (CV) (SDS) ([CV] = 10^{-3} M, [SDS] = 8 × 10^{-4} M; ε_{max} = 2.1 × 10^3 m^2 mol^{-1}), and (3) Ion pair (CV) (Manoxol OT) [CV] = 10^{-3} M, [Manoxol OT] = 8 × 10^{-4} M; ε_{max} = 2.1 × 10^3 m^2 × mol^{-1}).

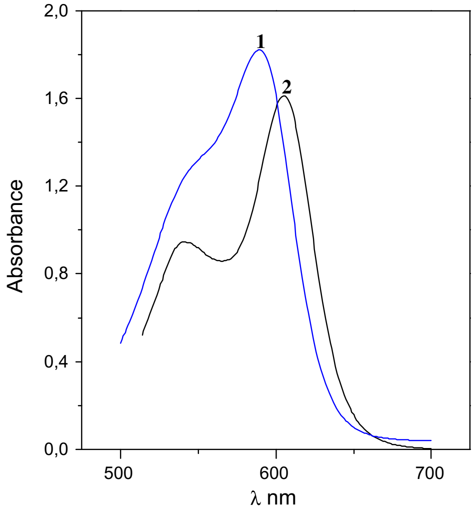

Fig. 3. Absorption spectra of: (1) Aqueous solution of Crystal Violet (10^{-3} M; ε_{max} = 1.8 × 10^3 m^2 mol^{-1}) and (2) Ion pair in Toluene ([Manoxol OT] = 5 × 10^{-4} M, [CV] = 10^{-3} M; ε_{max} = 2.29 × 10^3 m^2 mol^{-1}).

3.1.5. *The volume of solvent extraction*

All extraction steps were carried out with Toluene. The volume of Toluene was varied according to the initial conditions ([Manoxol OT] = 5 × 10^{-4} M, [CV] = 10^{-3} M). As shown in Fig. 5, we note that the maximum extraction is obtained for 15 mL of Toluene.

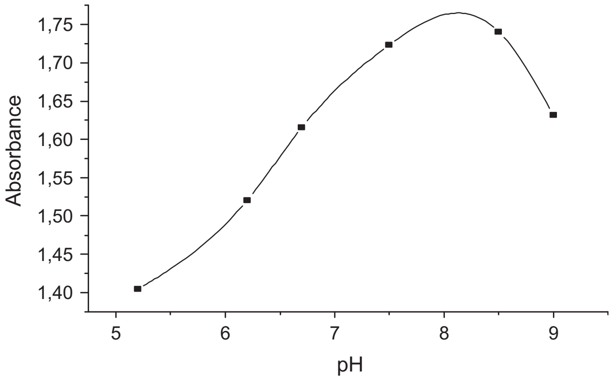

Fig. 4. Effect of pH on the extraction of the ion pair ([CV] = 10^{-3} M, [Manoxol OT] = 5 × 10^{-4} M).

3.1.6. *Calibration curve in distilled water, precision and limit of detection*

The calibration curve (Fig. 6) obtained for a series of AnS standard solutions is linear in the range 0–10^{-6} M of Manoxol OT with a following linear regression equation:

$$A = 2.042 \times 10^3 C + 0.999,$$

with a coefficient of correlation $r = 0.0997$.

The precision is obtained by determining the relative standard deviation (RSD %). The results obtained show that the RSD is less than 14.37% for 5 × 10^{-4} M and about 5.64% for 10^{-3} M of Manoxol OT. The limit of detection obtained for 10 replicate of the blank reagent is found to be 2.5 × 10^{-6} M.

The effects of the presence of various species present in a sample of seawater, which may interfere with the extraction of the ion pair [AnS-CV], was examined using the optimized procedure, taking into account that a maximum error of ± 5% is tolerable. The results obtained show that species like Ca^{2+} (0.003 M), Mg^{2+} (0.014 M), SO_4^{2-} (0.02 M) and chlorides from a level of 0.5 M causes real interferences. In order to remove interferences, we have established a calibration curve with seawater aqueous standard solutions of Manoxol OT; samples of seawater were collected in Algiers bay.

3.1.7. *Calibration curve in seawater, precision*

The procedure was rigorously applied to get a calibration curve in seawater. The curve is also linear in the range 0–10^{-5} M of Manoxol OT (Fig. 7), the

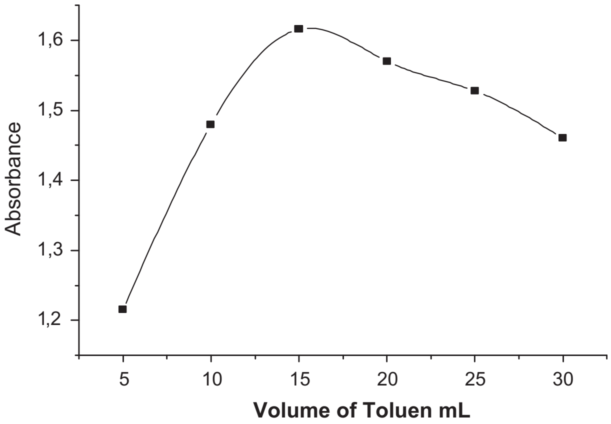

Fig. 5. Variation of the volume of solvent extraction ([CV] = 10^{-3} M, [Manoxol OT] = 5×10^{-4} M).

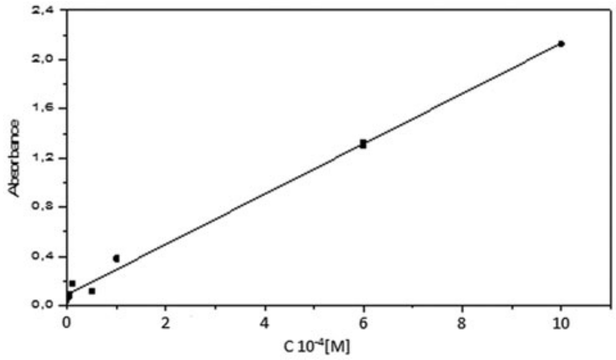

Fig. 6. Calibration curve in distilled water.

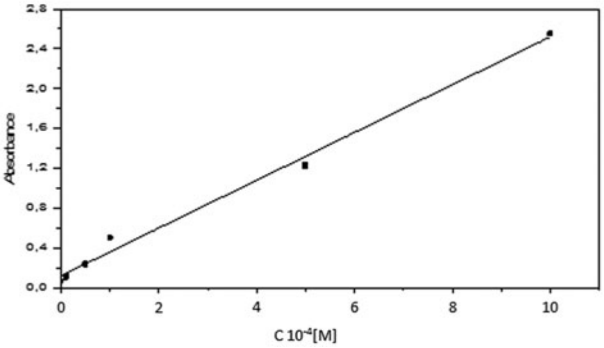

Fig. 7. Calibration curve in seawater.

regression equation is: $A = 2.39 \times 10^3\ C + 0.123$, with a coefficient of correlation $r = 0.996$. The results obtained show that the RSD is less than 17.42% for 2×10^{-5} M and about 5.44% for 8×10^{-4} M of Manoxol OT.

Finally, all optimization parameters lead us to get a significant and complete method compared to those used in the same way [2,27].

3.2. Applications to wastewater

Once the method was optimized with different parameters, we carried out real applications. In order to complete the establishment of pollution maps of Algiers bay, the application concerns a treatment plant of wastewaters in Algiers city. The choice is comforted by a significant amount of wastewater drained to the treatment plant and its specific location (Algiers city center).

A lot of interest is made to follow the changes in AnS levels in wastewater before, during, and after treatment in the sewage treatment plant, and later to be discharged in Oued El Harrach estuary. Most detergents used (domestic or industrial) are discharged directly through the sewers to the station.

A sampling methodology was adopted in order to determine different amounts of AnS in all samples collected.

Treatment plant description: The wastewater treatment plant (WWTP) of BARAKI was conducted under the general scheme of reorganization of Algiers city, which provided for the creation of the main collectors along Oued El Harrach estuary.

The catchment of Oued El Harrach estuary with 1,126,000 inhabitants is represented by 20 municipalities. It includes:

(1) Industrial area of Oued Smar (210 industrial units).
(2) Industrial area of El Harrach (53 industrial units).
(3) Industrial area of Gué de Constantine.
(4) Industrial areas of Dar el Beida, Eucalyptus, Birtouta, Ouled Chebel.
(5) In total, nearly 300 industrial units discharge effluents in the estuary without any treatment.

The WWTP sized to receive a quantity of wastewater estimated at 114,000 m^3/d [30].

Fig. 8 shows the location of the treatment plant of BARAKI in Algiers city.

3.2.1. Sampling

A systematic sampling was conducted with three (3) sampling points, chosen in order to follow the variation of the concentration of AnS before, during, and after treatment of wastewater in the treatment plant. The samples collected must be filtered through a

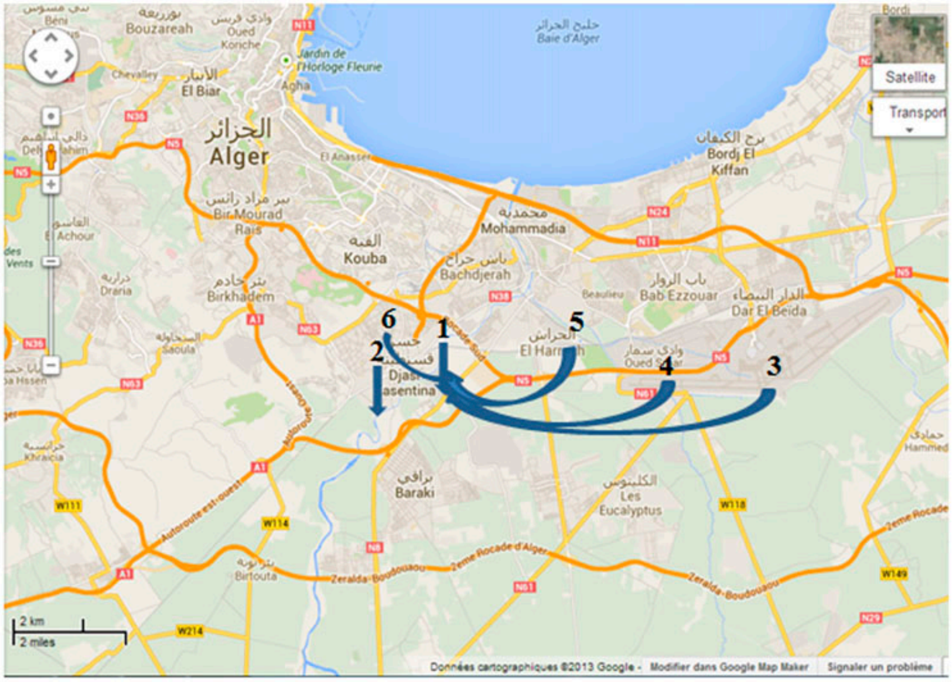

Fig. 8. Location of the WWTP in Algiers city. (1) The wastewater treatment plant (WWTP) of BARAKI, (2) Oued El-Harrach, (3) Industrial areas of Dar el Beida, (4) Industrial area of Oued Smar, (5) Industrial area of El Harrach, and (6) Industrial area of Gué de Constantine.

membrane (0.45 μm) to eliminate suspender matters and treated with a hydrogen peroxide solution H_2O_2 (30%), in order to eliminate organic matters and proteins. The recommended procedure was rigorously applied without modification for all samples, which lead us to determine all AnS amounts with three (3) replicate for all samples. Deduced levels are determined by using calibration curve in distilled water. Before the treatment of the results, we first verified the presence of AnS in the combined form with the dye in collected samples. The absorption spectra (Fig. 9) show the same characteristic band of the ion pair.

3.2.2. Results

All results obtained in this campaign lead us to establish some interesting variations of the AnS concentrations vs. some parameters such as: the sampling time, the day of sampling, and the kind of sampling point and the period of sampling.

The first interesting variation considered was the variation of [AnS] vs. the sampling time during the same day. To give sense to this variation, the graph has been divided into three curves for each time sampling point (Figs. 10–12).

We noticed that the amounts of AnS gradually increased throughout the day (8 am–12 pm). For all the contents, the lowest level deduced during this sampling campaign was found to be 6.02×10^{-4} M at the tenth day.

Fig. 12 shows that the lowest concentrations are deduced at point C both at 8 am and at 12 pm, with the same trend observed on all days, with an increase

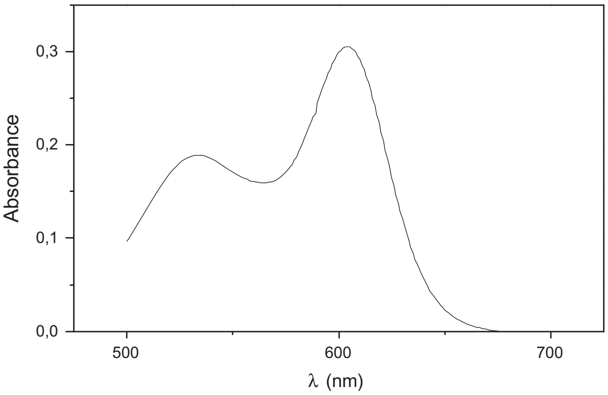

Fig. 9. Absorption spectra of the pair of ions extracted from a sample.

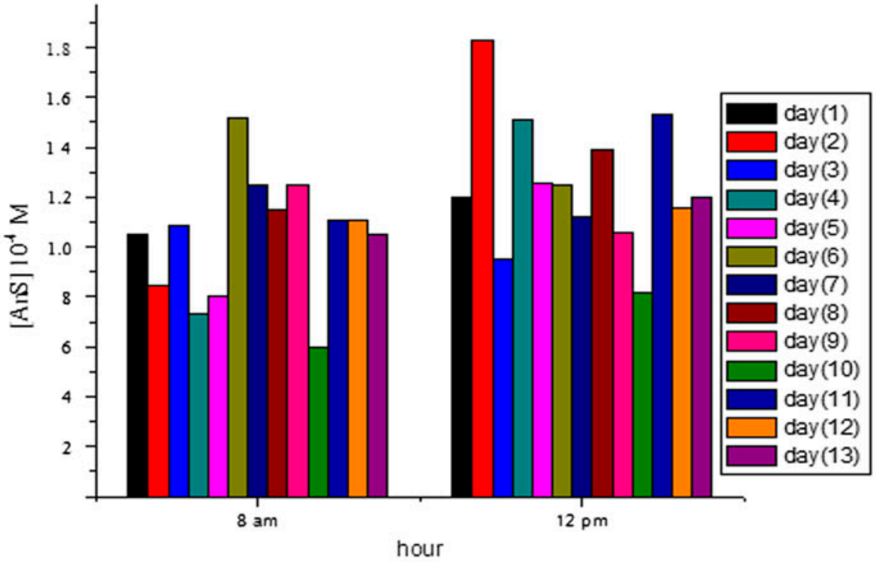

Fig. 10. Variation of [AnS] with the time of sampling at point A.

in the content of AnS from 8 am to 12 pm. We also noticed that different levels of AnS decreases from A to B and C during all the campaign.

The second considered variation concerns the variation of [AnS] vs. the day of sampling (Figs. 13 and 14). We have noticed a particular day (the sixth day) corresponding to the maximal level of AnS deduced at point A (1.52×10^{-3} M); this is due to fact that the sixth day corresponds to a week end day, where great amounts of sewage from industrial discharges are carried to the treatment plant. The lowest [AnS] was deduced at the 10th day (3.25×10^{-4} M), corresponding to a national holiday, industrial units did not generate wastewater.

The third variation of [AnS] with the kind of sampling point shows a significant decrease of anionic surfactant concentration from point A–C for all days, from 10^{-3} to 10^{-4} M corresponding to the removal of about 10% AnS (Fig. 15). The biological treatment of the sewage (in point B) is carried to ensure AnS degradation.

The different amounts of AnS deduced in this campaign lead us to confirm the sensitivity of the method. Predictable low values of AnS concentrations

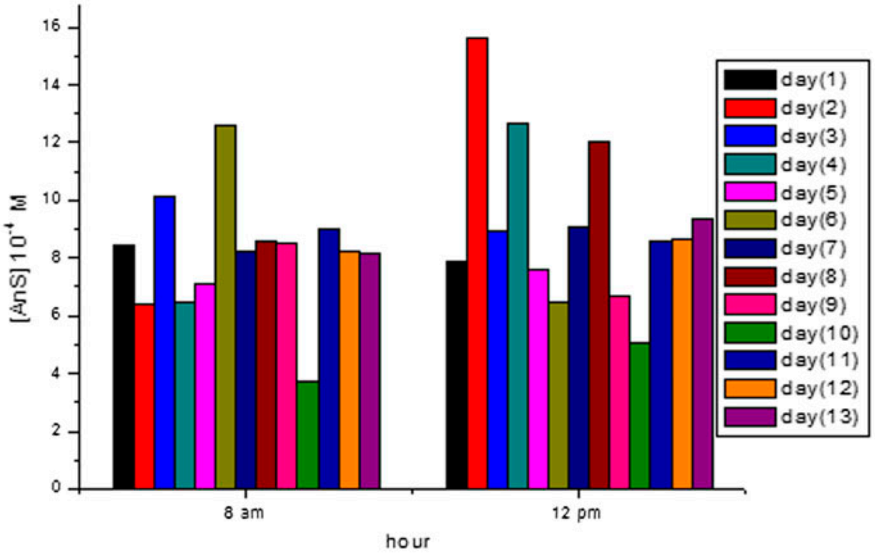

Fig. 11. Variation of [AnS] with the time of sampling at point B.

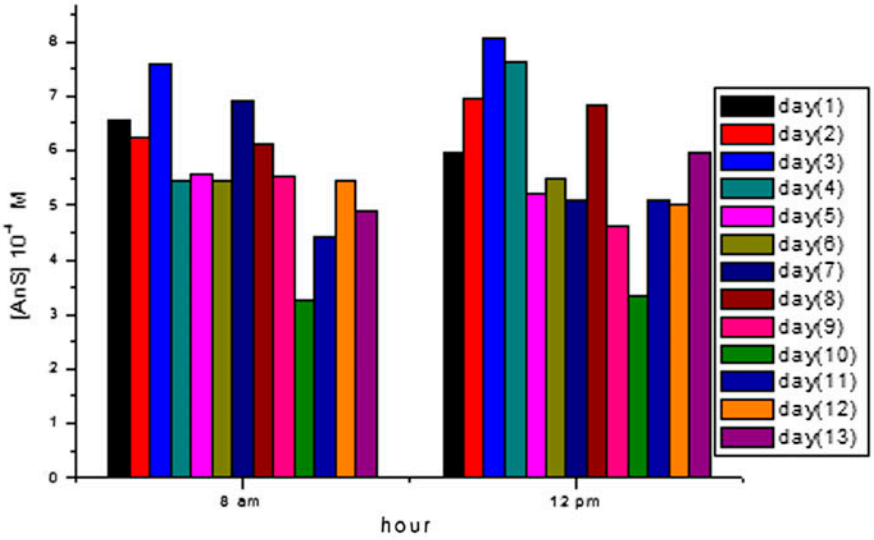

Fig. 12. Variation of [AnS] with the time of sampling at point C.

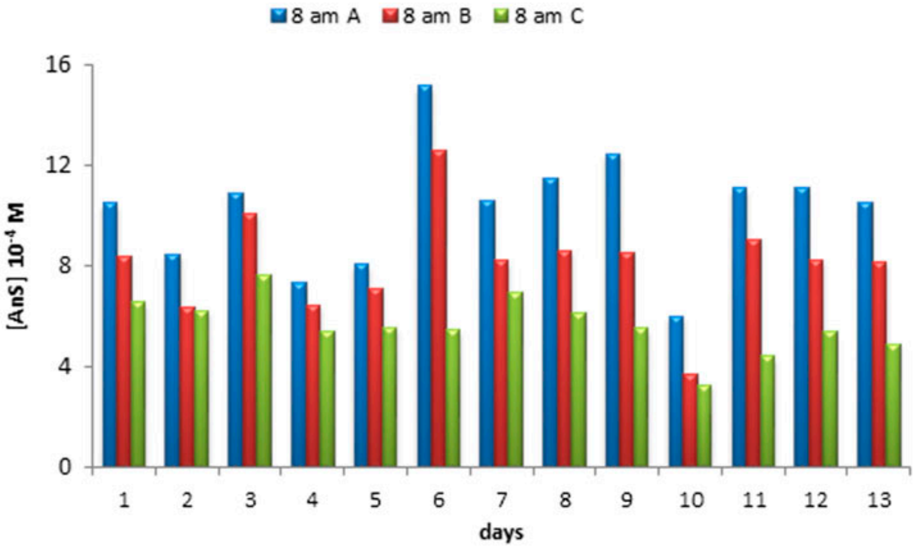

Fig. 13. Variation of [AnS] with the day of sampling at 8 am.

are present after treatment, which can be routed to marine waters.

In comparison with the different results also obtained in previous sampling campaigns, we can confirm that the adopted method gives more satisfaction for its application [28]. Also, in comparison with most research done in the same field in literature reports [2,27], we can also confirm the strength and the sensitivity of our technique.

Used techniques for the determination of AnS reported in the literature [26–28] did not show more applications or few [21,22]. Therefore, this permits us to conclude that the present work shows more applications in a large concentration range.

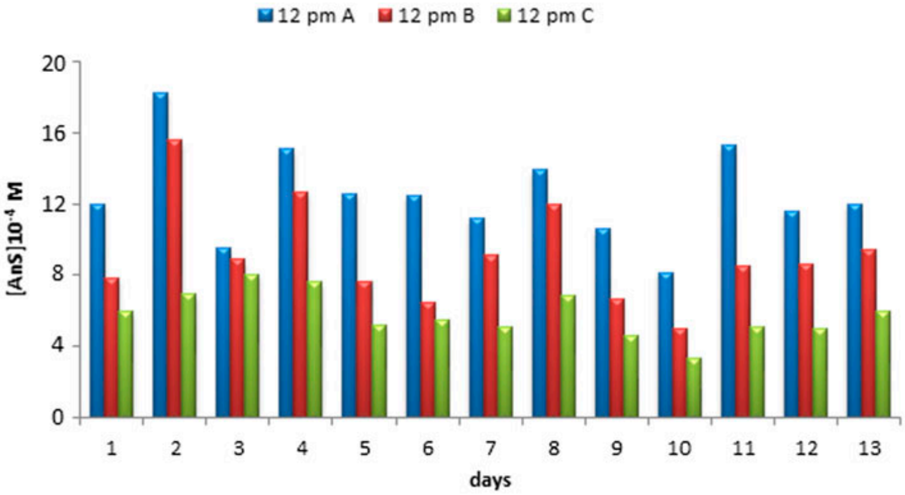

Fig. 14. Variation of [AnS] with the day of sampling at 12 pm.

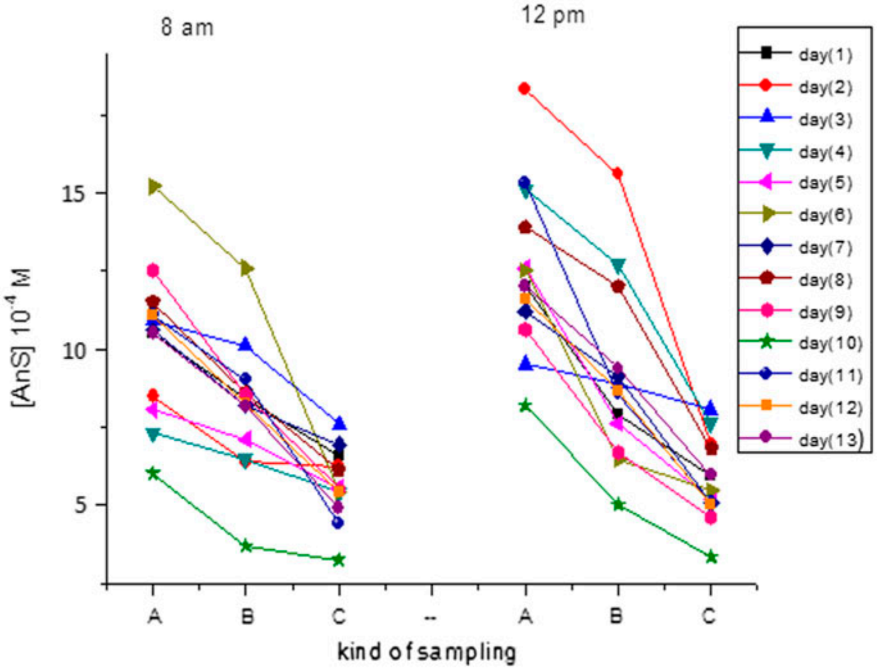

Fig. 15. Variation of [AnS] with the kind of sampling point.

4. Conclusion

According to the purpose on the use of the spectrophotometric determination of anionic surfactants, the optimized technique leads us to a direct application on real samples from a sampling done in a treatment plant located in Algiers center city. The results obtained on real samples lead us to make some interesting observations.

Before treatment (point A), high concentrations of about 10^{-3} M are deduced on the sampling period; this is due to the high daily sewage flow (about 149,040 m^3/d), divided in 2/3 of urban wastewater and 1/3 from industrial wastewater and with the high consumption of detergent.

After treatment (point C), low levels are deduced for about 10^{-4} M, this is due to the biological treatment efficiency suffered by the surfactant molecules falling on the treatment phase (B).

Final amounts of AnS present in the treatment process effective will be carried to be discharged in Oued

El Harrach estuary and in last flows into marine waters with concentration of 10^{-6} M [7].

From the results, we can conclude that the method gives great satisfaction in the determination of different amounts of anionic surfactants.

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