



Seasonal Variation and Distribution of Anionic Surfactants in and around Tirupati: A Famous Pilgrim Centre in South India

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This report presents the anionic surfactants concentration in water system collected in and around Tirupati, South India. The concentration of anionic surfactants such as sodium lauryl sulfate, sodium dodecyl sulfate, sodium hexadecyl sulfonate and sodium dodecyl benzene sulfonate were showed a rather homogeneous distribution (except sodium dodecyl benzene sulfonate) within the Tirupati, with high values of 80.0, 90.75, 46.90, 15.10 $\mu\text{g L}^{-1}$ in Tirupati and slightly less concentration values of 75.0, 60.55, 35.40, 10.0 $\mu\text{g L}^{-1}$ were found in samples collected from Renigunta Industrial Estate during pre-monsoon and monsoon seasons respectively. High concentration of these surfactants in open wells and open municipal wastewaters in Tirupati may be due to the huge discharge of domestic wastes into the drain system. The concentration of surfactants found in Renigunta Industrial Estate may be due to the direct discharge of industrial wastewater into the environment.

Keywords: Anionic surfactants, Seasonal variation, Pre-monsoon, Monsoon, Tirupati, Renigunta industrial estate.

INTRODUCTION

A surfactant molecule is composed of a hydrophilic head and a hydrophobic tail. The head can be an anionic, a cationic, a zwitter-ionic, or a nonionic group, while the tail is a non-polar hydrocarbon chain. These molecules are surface active as a result of the combination of the hydrophobic and hydrophilic properties. They have affinity for two immiscible phases, one of which is water. A zwitter-ionic surfactant has both a positive and negative charge in the head group. This charge separation causes a dipole moment to be present in the head group. Therefore, the head group is polar and soluble in water. In general soaps belongs to anionic surfactant group of molecules such as alkyl sulfates, alkyl sulfonates and alkyl benzene sulfonates. The structures of these surfactants are formed by interaction of aliphatic hydrocarbon chains (C10–C18) bound to carboxyl, sulfate or sulfonic groups, including benzene and naphthalene sulfonates¹. The most widely used anionic surfactants are sodium dodecylsulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS), which make part of various cleaning and personal hygiene products.

Due to the wide application of man-made detergent in day to day life, recently the determination of anionic surfactant in water has become a crucial research subject in the field of environmental sciences². Anionic surfactants were reported

as pollutants and their permissible limit in drinking water prescribed by the WHO³ is 1.0 ppm. The main sources of the commonly used anionic surfactants like sodium lauryl sulfate (SLS) and others, *viz.*, sodium dodecyl sulfonate (SDS), sodium hexadecyl sulfonate (SHDS) and sodium dodecyl benzene sulfonate (SDBS), in water bodies are household commodities and personal care products, *e.g.* detergents, soaps, shampoos and fabric and cosmetic materials. The level of surfactants in water bodies of densely populated countries such as India is increasing owing to the changes in lifestyle similar to western countries.

The development of novel methodologies for the sensitive determination of anionic surfactants has been identified as a challenge in recent reviews^{4,5}. A variety of analytical methods can be found in the literature for monitoring anionic surfactants. The standard method for the determination of total anionic surfactants in water samples is mainly based on ion pair formation and liquid-liquid extraction (LLE) followed by UV-visible spectrophotometry with various dyes^{3,5-8}. Other separation techniques include HPLC⁹⁻¹³, GC-MS¹⁴⁻¹⁶ and capillary electrophoresis¹⁷ for the determination and quantification of anionic surfactants in various samples of environmental importance.

Literature survey reveals that different preparation methodologies like liquid-liquid extraction¹⁶, solid phase

extraction¹⁸, solid-phase micro-extraction¹⁹, liquid-phase micro-extraction¹³ has been reported for the analysis of anionic surfactants. Recently, scientists developed various nano-materials for sample preparation to enhance the sensitivity and selectivity of the methods^{20,21}.

The present investigation highlights the knowledge of distribution and concentration of anionic surfactants in and around Tirupati, South India helps to detect the sources of pollutions in the different water systems and for this reason water should be included as one of the environmental parameters monitored in municipal pollution program. The present study is the first report in the literature that has been undertaken to understand the seasonal distribution pattern of anionic surfactants (sodium dodecyl sulfate, sodium lauryl sulfate, sodium hexadecyl sulfonate, sodium dodecyl benzene sulfonate) in and around Tirupati, an famous pilgrim centre in South India.

EXPERIMENTAL

Collection of samples: Open wells and open municipal wastewater samples from Tirupati, a famous pilgrim town in South India, situated on the longitude of 79°27' E' latitude of 13°40' N' and at a height of 500 ft above mean sea level. The city has a population of about 1,800, 000 and more than 10 million pilgrims visit annually this temple town. There are more than 1200 open wells which serve as secondary source of drinking water since the water from the municipal supply is inadequate. The sampling points for these samples were rural, urban, semi-urban and industrial areas. The samples were collected in 1 L polyethylene and filtered with Whatman No. 42 filter paper and stored in a refrigerator at 4 °C.

General procedure: Sample solution (100 mL) containing anionic surfactants with concentration (0.00003 M) was transfer into a separating funnel. Cationic dyes, Azure-A, Azure-B and 10 M HCl were added followed by 10 mL of chloroform and adjusting the whole solution pH 3.0 for Azure-A and 4.0 for Azure-B. The content was shaken for 3 min and allowed to settle for 5 min. The aqueous layer was separated and discarded. The organic layer was collected and 2.5 mL of this solution was directly used for absorption measurement in the range of wavelength (λ_{max}) 450 to 513 nm against reagent blank.

RESULTS AND DISCUSSION

The concentration of anionic surfactants such as sodium dodecylsulfate, sodium lauryl sulfate, sodium hexadecyl sulfonate and sodium dodecyl benzene sulfonate were measured in samples (open wells, open municipal wastewaters) collected from Tirupati and Renigunta Industrial Estate (25 Km around Tirupati). So far this is the first study to monitor the seasonal variations of anionic surfactants in and around Tirupati. But the concentration of sodium lauryl sulfate, sodium dodecylsulfate, sodium hexadecyl sulfonate and sodium dodecyl benzene sulfonate in the surface, ground and bore wells were within the ranges reported for the same areas in the literature⁶. Annual mean concentration of anionic surfactants like sodium dodecyl sulfate, sodium lauryl sulfate and sodium hexadecyl sulfonate were high in open wells and

open municipal wastewaters of Tirupati. The sodium dodecyl benzene sulfonate concentration was more or less equal at both open wells and open municipal wastewaters of Tirupati and Renigunta Industrial Estate. The data presented in Table-1 reveals the fact that the sodium dodecyl sulfate, sodium lauryl sulfate and sodium hexadecyl sulfonate concentrations were found to be 98.15, 110.10, 75.45 $\mu\text{g L}^{-1}$ and 98.43, 82.18, 64.90 $\mu\text{g L}^{-1}$ at Tirupati and Renigunta Industrial Estate respectively and concentrations were high during the pre-monsoon at both places. Sodium dodecyl benzene sulfonate concentrations were high in Renigunta Industrial Estate (15.10 and 12.25 $\mu\text{g L}^{-1}$) during pre-monsoon and post-monsoon seasons when compared to Tirupati (10.0 and 9.23 $\mu\text{g L}^{-1}$). In general, the order of abundance of these anionic surfactants was as follows:

Tirupati: SDS < SLS < SHDS > SDBS

Renigunta Industrial Estate: SDS > SLS < SHDS > SDBS

At both the places, concentrations of anionic surfactants in open wells and open municipal wastewaters were high during the pre-monsoon and post-monsoon seasons with the peak at the latter. Sodium lauryl sulfate concentration was high during the pre-monsoon season in November and December 2013 at Tirupati and Renigunta industrial estate respectively and low during the summer season in June (40.46 $\mu\text{g L}^{-1}$) at Tirupati and in April (35.12 $\mu\text{g L}^{-1}$) 2014 at Renigunta Industrial Estate as shown in Fig. 1. Such seasonal variations in different water systems were perhaps due to the major sources of domestic waste, municipal wastewaters and intensive human

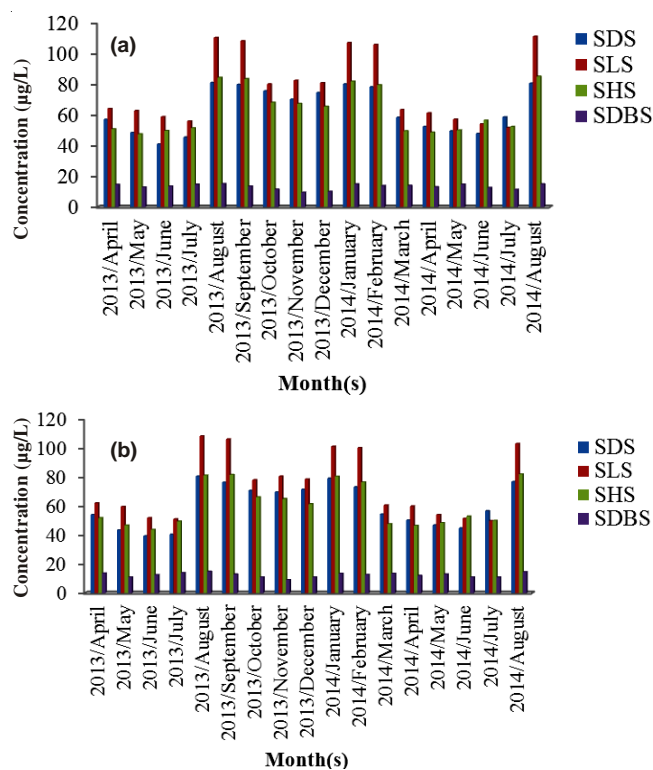


Fig. 1. (a) Graphical representation of seasonal distribution of anionic surfactants in samples collected from Tirupati (open wells and open municipal wastewaters) (b) Graphical representation of seasonal distribution of anionic surfactants in samples collected from Renigunta Industrial Estate (open wells and open municipal wastewaters)

TABLE-1
SEASONAL VARIATION, DISTRIBUTION AND MEAN CONCENTRATION OF ANIONIC SURFACTANTS IN
DIFFERENT WATERS ($\mu\text{g L}^{-1}$) AT TIRUPATI AND RENIGUNTA INDUSTRIAL ESTATE

Surfactant	Year	Summer	Pre-monsoon	Monsoon	Post-monsoon	Total mean
Tirupati						
Sodium dodecyl sulfate	2013-2014	67.03	98.0	75.25	96.50	84.19
Sodium lauryl sulfate	2013-2014	40.46	112.25	83.15	110.0	86.46
Sodium hexadecyl sulfonate	2013-2014	38.25	65.12	42.32	63.20	52.22
Sodium dodecyl benzene sulfonate	2013-2014	5.25	13.80	6.05	12.15	21.12
Renigunta Industrial Estate						
Sodium dodecyl sulfate	2013-2014	60.14	93.0	69.25	91.75	78.53
Sodium lauryl sulfate	2013-2014	35.12	106.12	80.25	104.40	81.47
Sodium hexadecyl sulfonate	2013-2014	32.26	59.06	39.15	57.88	47.08
Sodium dodecyl benzene sulfonate	2013-2014	4.75	16.25	5.50	14.10	10.15

activity (especially tourism) in Tirupati and high concentrations in Renigunta Industrial Estate is mainly due to land run-off, direct discharge of industrial effluents and sewage outlets. Further, less concentrations of sodium lauryl sulfate, sodium dodecyl sulfate, sodium hexadecyl sulfonate and sodium dodecyl benzene sulfonate during the monsoon season is due to the washing/dilution of pollution water systems.

Sodium lauryl sulfate concentration was high during the pre-monsoon reason ($92.17 \mu\text{g L}^{-1}$ and $89.29 \mu\text{g L}^{-1}$ in August 2014) at Tirupati and Renigunta industrial wastewaters respectively. High sodium lauryl sulfate concentration in open municipal wastewaters than open wells could have resulted due to the release of this surfactant from the domestic wastewater of Tirupati and industrial effluent discharge in Renigunta Industrial Estate. Further, sodium lauryl sulfate concentration was low during the summer season at both the places. This would have resulted due to the high temperature, evaporation of moisture and reduction in surface water levels. Enrichment ratios, used as the tool of quantification of contamination, were compared for water samples with respect of surface and ground water values separately. It was observed that for open wells and open municipal wastewaters the contamination was more in both places. Moreover, concentrations of the surfactants are increasing from year to year mainly due to increase of tourism in Tirupati town.

Conclusion

From the present study, it is concluded that the open wells and open municipal water systems of Tirupati and Renigunta Industrial Estate areas are rapidly polluted with these surfactants. Further, human activities in the form of tourism *etc.*, should be streamlined in order to minimize pollution. Hence, these results clearly indicate that local hydrography and seasonal variability are the factors which cannot be neglected in studies of the occurrence of anionic surfactants in open wells and municipal wastewaters. Thus Tirupati is relatively more polluted than Renigunta Industrial Estate. Therefore, strict enforcement of laws to prevent surfactant pollution in these areas should be made. Attention should be paid immediately to Tirupati especially the residential areas near to pilgrim centers and also industries must setup efficient wastewater treatment plants. Further, human activities in the form of

tourism *etc.*, should be streamlined in order to minimize pollution. Future work is going on for the identification of cationic surfactant from different samples collected in and around Tirupati, India.

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