

The Loss of LAS during the Storage in Water and Seawater

LAS'ın Deniz Suyunda ve Suda Bekletme Esnasında kaybı

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Abstract

The loss of linear alkyl benzene sulfonate (LAS) was investigated in seawater of the Golden Horn, of the Black Sea and in distilled water. The loss of LAS found in the Golden Horn was 86.71 – 91.20 % after 20 days, in the Black Sea 58.21 – 89.93 % after 10 days and in distilled water 33.47 % after 15 days. According to these results LAS was degraded in seawater at 20 days 91.2 % and in distilled water at 15 days 33.5 %. The degradation of LAS changes according to the ecological conditions. The loss of LAS in the stations TRK (Samsun) was differed in the findings of 2006 and 2007. The difference between the results was depended on microbial pollution size and composition of the samples. Thus the LAS determination must be made immediately in seawater.

Keywords: LAS, seawater, distilled water

Introduction

A detergent is a mixture of various components. Surfactants (surface active substances, SAS) are the main components of detergents. Numerous surfactants exist and may be classified by the nature of their charge into anionic, cationic and nonionic surfactants. Nowadays, cationic and nonionic surfactants are relatively less used than the anionic ones.

The anionic surfactants constitute the most important class used in detergent. Among the anionic surfactants, alkyl benzene sulfonate (ABS) contains linear (linear alkyl benzene sulfonate, LAS) and branched alkyl benzene sulfonate (BAS). LAS is a cleaning agent generally used in detergent formulas for economic reasons. It was characterized by a lipophilic moiety with alkylaryl structure and a hydrophilic moiety as sulfonic group.

LAS was prepared from LAB (linear alkyl benzene). LAB is a mixture of aliphatic hydrocarbons. Carbon numbers vary depending on manufacturer as C8-C16. The chemical structure of LAS is shown in Figure 1.

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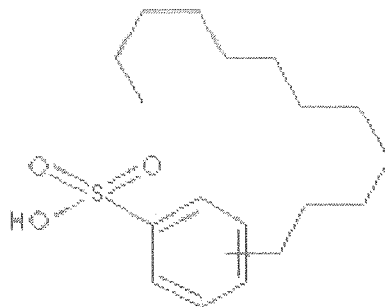


Figure 1. LAS structure

Benzene ring in LAB can be linked to different carbons of the linear chain from C2 to C6, consequently various isomers occurred. After sulphonation by Friedel-Craft reaction the final product is also complex mixture and contains many homologues with alkyl chain lengths usually depending on the source of LAB. During the process various products are obtained after oxidation, polymerization, and decomposition of the LAB molecules takes place.

Thus LAS contains many isomers depending on the number of carbon, the benzene link and sulphonation. Finally, the exact composition of commercial LAS is not clear.

LAS are responsible for many environmental problems. LAS are released into sea by mostly all waste systems. LAS are not stable in soil, streams and sea water and its concentration rapidly decreases in river and seawater depending on their microorganism content. LAS concentration decreases as a function of the distance from the discharge point. It is degraded approximately in 20 days. But because of the continuation of discharge to sea the concentration rises. The main factors influencing the stability of LAS are microorganisms, pH, temperature. LAS are biodegraded more rapidly than the branched type.

Various methods were proposed for the analysis of LAS. The colorimetric MBAS method (Standard Methods, 1995) was generally used for the LAS in water. Different substances interfere positively/ negatively in this method such as ions, chloride, thiocyanate, sulfate, organic sulfate, carboxylate, phosphate and phenol.

Other spectrophotometric methods are based on metachromatic reaction (Güven et al., 1994; Akıncı and Güven, 1997; Bektaş and Güven, 2004) and (bisethylenediamine) copper II with diethyldithiocarbamate (Percot et al., unpublished data). The other determination methods are IR (Hellman, 1978, 1979), GC/MS (Hon-Nami and Hanya, 1978; 1980, Raymundo and Preston, 1992), HPLC (Terzic et al., 1992; Terzic and Ahel, 1993; Marcomini and Giger, 1987; Koç et al., 2001; Sarrazin et al., 2005), and AAS (Crips et al., 1978; 1980).

LAS in seawater are not distributed uniformly. The distribution of detergent is strongly affected by wind conditions which enhances the velocity and changes the direction of surface currents. The distribution of LAS changes also along vertical profile on the water column due to sea current and surface active properties. The determination of LAS is difficult as affected by physical conditions and also the interfering substances on the determination method of MABS which usually used.

In this work the loss of LAS was investigated in Golden Horn seawater, the Black Sea water and distilled water as a function of storage time.

Material and Methods

The station seawater samples are:

1- Golden horn at surface water

Stations:

Valide Sultan

Adalar sonrası

Eyüp Sütlüce

2- The Black Sea

Stations:

Zonguldak (TRK13)

Bartın (TRK 18)

Samsun (TRK34, TRK35, TRK36)

3- Distilled water:

LAS solution was added to distilled water and the loss of LAS was measured with the same method as described later (using 700 ml sample).

LAS extraction in distilled water and sea water (Standard methods, 1995):

700 ml sample were transferred to a separatory funnel. The solution was alkalinized by addition drop wise of 1 N NaOH, using phenolphthalein indicator, then discharge the pink color by drop wise addition of 1 N H₂SO₄.

30 ml chloroform and 25 ml methylene blue reagent were added to the solution then separatory funnel was vigorously shaken for 30 sec and let the phases separate.

The chloroform layer was transferred into a second separatory funnel. The extraction was made three times.

All chloroform extracts were combined in the second separatory funnel. 50 ml wash solution was added and shaken vigorously for 30 sec. The chloroform phase was transferred into a 100 ml volumetric flask. The volume was adjusted to the mark with chloroform.

Measurement: The absorbance of the solution was measured at 652 nm against a blank of pure chloroform.

Calibration of LAS was performed in a concentration of range 10 µg/L to 100 µg/L. Its absorption graph was drawn using a spectrophotometer (Shimadzu, UV-1601) and standard curves were plotted at 652 again methylene blue.

Reference substances of LAS (97.7%) were obtained from Lever (Gebze, Turkey).

Chloroform (pro analysis, Merck) and all chemicals used were Merck products (Darmstad).

Reagents: Phenolphthalein solution was prepared with a concentration of 1/100 (v/v) in alcohol.

Base and acid solutions: 0.1N NaOH, 1N H₂SO₄ and 6N H₂SO₄ were prepared in distilled water.

Methylene blue (MB) solution: 30 mg of MB were dissolved in 50 ml of distilled water.

Washing solution: 50 g of Na₂HPO₄ H₂O were dissolved in 500 ml distilled water. 41 ml of 6N H₂SO₄ were added to this solution and the volume adjusted to 1000 ml.

Results and Discussion

The loss of LAS in Golden Horn water, the Black Sea water and distilled water are shown in Tables 1-3.

Table 1. The initial value (t_0) and loss of LAS in Golden Horn water ($\mu\text{g/L}$)

	t_0	12 days later	Losses %	22 days later	Losses %
Valide Sultan	113,23	37,24	67,11	9,96	91,20
Adalar Sonrası	91,6	42,24	53,89	14,90	83,73
Eyüp Sütlice	86,51	38,95	54,98	11,50	86,71

Table 2a. The initial value (t_0) and loss of LAS in the Black Sea water ($\mu\text{g/L}$) (15.20.2006)

	LAS amount			LAS amount	
	t_0	5 days later	Loss %	10 days later	Loss %
TRK13	103,51	40,39	60,98	-	
Bartın TRK18	91,13	63,18	30,67	-	
Samsun TRK 34	74,04	-		30,94	58,21
Samsun TRK 35	270,83	-		27,27	89,93

Table 2b. The initial value (t_0) and loss of LAS in the Black Sea water ($\mu\text{g/L}$)

	LAS amount		
	t_0	8 days later	Loss %
Samsun TRK 34	73.51	30.94	57.90
Samsun TRK 35	270.24	27.27	90.20
Samsun TRK 35	34.02	28.95	8

Table 3. The initial value (t_0) and loss of LAS in distilled water ($\mu\text{g/L}$)

LAS amount			LAS amount		LAS amount	
T_0	4 days later	Loss %	8 days later	Loss %	15 days later	Loss %
22,71	17,18	24,35	16,52	27,26	15,11	33,47

The graphical representations of LAS concentration as a function of time in different samples are shown in Figures 3 and 4.

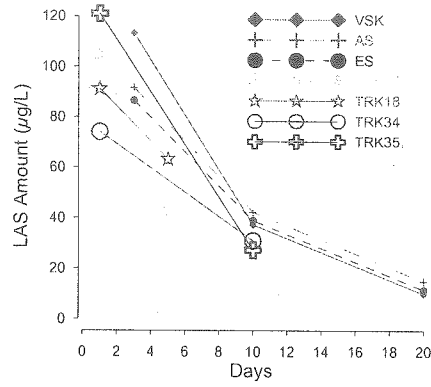


Figure 4. The graphical representation loss of LAS in examined seawater

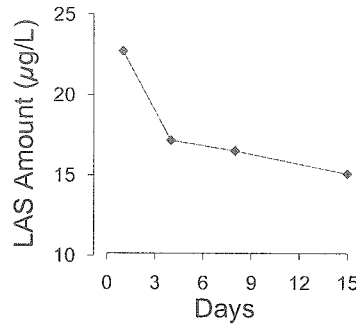


Figure 5. The graphical representation loss of LAS in distilled water

As can be seen in Table 2b the highest LAS concentration was found in TRK 35 and lower in TRK 36. The loss of LAS was found high in TRK 35.

Loss of LAS in Golden Horn samples varied from 53.89 to 67.11 % in 12th day and from 83.73 to 91.20 % after 22 days. In the Black Sea from 58.20 to 89.93 in 10 days and in distilled water the loss corresponds to 33.47 % in 15 days. The degradation of LAS was ranked as Golden Horn > The Black Sea > distilled water.

The degradation time of LAS in water was previously estimated to 22-29 days (Hon-Nami and Hanya, 1980), 20 days (Koç et al., 2002). The loss time of LAS was differed through the environment conditions.

The factors that influence biodegradation of LAS are pH, salinity, aeration, phenyl attachment to carbon chain, carbon number, time, type and number of microorganisms.

At the end of the this work we suggested that the variation of degradation time in the samples taken from Golden Horn and The Black Sea depended on the microorganisms population.

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Özet

Bu çalışmada LAS'ın deniz suyunda ve distile suda kaybı incelendi. Haliç deniz suyunda LAS kaybının 12 günde % 53,89 – 67,11, 22 günde % 83,76 – 91,20, Karadeniz suyunda Zonguldak'ta 5 günde % 60, 98, Bartın'da % 30,67, Samsun'da 2006'da 10 günde % 58,2 – 89,93, 2007'de 8 günde % 27,27 – 30,94

ve distile suda 4 günde % 24,35, 8 günde % 27,26, 15 günde %33,47 olduğu tespit edilmiştir. Aynı istasyonda (Samsun) 2006 ve 2007 yıllarında tesbit edilen farklılığın nedeninin mikroorganizma sayısı ve tipinden oluştuğu düşünülmüştür. Bu sonuçlara göre deniz suyunda LAS tayininin örneklemeyi takiben bekletmeden yapılması gerektiği sonucuna varılmıştır.

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