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Linear Alkylbenzene Sulfonate Removal

AIS/CESIO environmental surfactant monitoring program; Pilot study of Linear Alkylbenzene Sulfonate (LAS) removal in Manresa sewage treatment plant and associated receiving treated water system

Within the scope of a European pilot program sponsored by AIS/CESIO to monitor the removal of different surfactants in sewage treatment plants as well as in the receiving waters, a study was carried out on the biodegradation of LAS in the sewage treatment plant of Manresa (Spain) and in the Cardener river receiving the treated water of this plant. The removal of LAS using specific analytical methods was > 98 %. Similar studies have been carried out in Germany, Holland, United Kingdom and Italy.

Im Rahmen eines europäischen Pilotprogramms, das – gesponsert durch AIS/CESIO – zum Ziel hatte, die Entfernung verschiedener Tenside aus Kläranlagen und Vorflutern zu beobachten, wurde eine Untersuchung über den Bioabbau von LAS in der Kläranlage von Manresa (Spanien) und dem Vorfluter dieser Anlage, dem Cardener, durchgeführt. LAS wurde zu mehr als 98 % entfernt, wie mit spezifischen Analysenmethoden festgestellt wurde. Ähnliche Untersuchungen wurden in Deutschland, den Niederlanden, England und Italien durchgeführt.

1 Introduction

A joint European Chemical Industry Task Force formed by the *Association Internationale de la Savonnerie et de la Détergence* (AIS) and the *Comité Européen des Agents de Surface et Intermédiaires Organiques* (CESIO) was set up to develop and apply specific analytical methods for the environmental monitoring of the most important surfactants. The use of specific analytical methods is considered as the most definitive means to obtain environmental concentrations which can be used in risk assessments. The selected surfactants represent those which are most widely used in detergent formulations:

- Linear alkylbenzene sulfonates (LAS)
- Alcohol ethoxylates (AE)
- Alcohol ethoxy sulphates (AES)
- Alcohol sulphates (AS)
- Secondary alkane sulphonates (SAS)
- Soap

An adequate and validated analytical procedure is available for LAS [1], a tentative method for soap which is in the process of validation has also been published [2].

For the rest of the surfactants mentioned, there is good progress in methodology development although no validated method has yet been available for AE, AES, AS and SAS.

The first phase of the European study was designed as a pilot step to support the subsequent full scale study and comprises the monitoring of LAS as a reference surfactant.

A well operated sewage treatment plant as well as the receiving water system was chosen and monitored during several days to check the viability of the study.

The Spanish pilot study reported in this paper was carried out by Centro Superior de Investigaciones Científicas CSIC (Barcelona/Spain) with the assistance of Petresa.

2 Monitoring Site

The study was conducted at the sewage treatment plant of Manresa (Spain) operating with a conventional system of activated sludge and anaerobic digestion of sludges. The industrial contribution to this plant is around 30 % and the final effluent (treated water) is discharged into the Cardener river.

The plant is designed for a population of 80.000 inhabitants and during the sampling period (June/July 1993) the average daily influent flow rate was 30.500 m^3. The hydraulic retention time (HRT) of the plant is 4 hrs and the sludge (anaerobically digested) production is 6.35 tons/day.

Spanish per capita LAS consumption during the monitoring period was 5.5 g/inhabitant day which can be translated into an expected concentration of 14.7 mg/L in the raw sewage influent to the plant.

Cardener river flow at the sampling period was 388.000 m^3/day which provides a dilution factor of 12 for the effluent stream of the plant.

3 Materials and methods

Sampling

The sampling points used in our study are shown in Fig. 1. Water samples (raw, treated and river) were taken in two different campaigns:

- Daily composite flow proportional samples prepared during three consecutive days (June 1st. 2nd, 3rd, 1993) for LAS analysis and subsequent removal calculation.
- A study on water quality was conducted on July 17, 1993 taking samples in 2 hours intervals during 24 hours.

All samples were preserved on site adding 1 % formalin (40 % formaldehyde solution) and filtered through 1 µm discs to separate the corresponding suspended solids and to determine adsorbed and dissolved LAS separately.

Monitoring parameters

LAS determinations in water samples have been used to evaluate the following parameters:

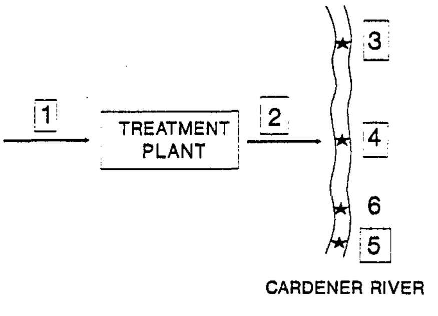

Fig. 1. Scheme of sampling points 1: raw sewage, 2: treated water, 3: up-stream river water, 4: sewage outfall, 5: 1 km down stream, 6: flow meter station

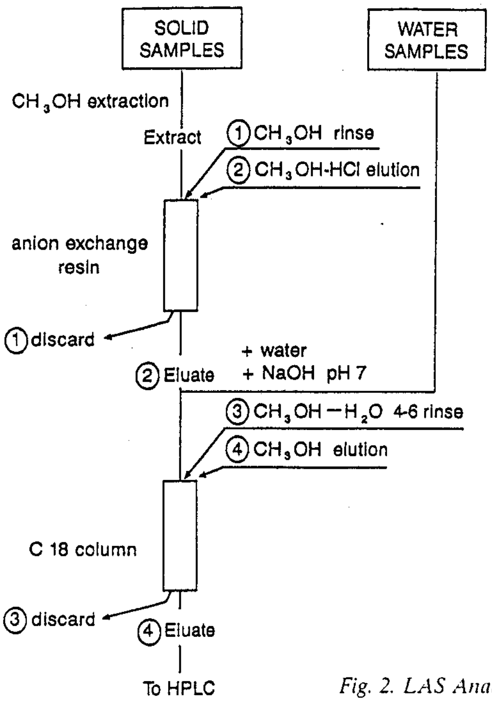

Fig. 2. LAS Analysis using HPLC

- Removal in the treatment plant
- Removal in river water
- Hourly fluctuation of LAS concentration during the treatment process in water samples (dissolved LAS)
- LAS concentration in suspended solids
- Daily fluctuation of LAS concentration

Analytical methods

The specific analytical determination of LAS in water samples was carried out by HPLC using the method developed by *Mathijs* and *De Henau* [1].

A summary of the different steps of this method is given in Fig. 2. The solid samples, i.e. suspended solids, were first extracted with methanol in a soxhlet reflux during 4 hours. The methanolic extract was then passed through an anion exchange column to concentrate the anionic material. LAS was eluted with acidified methanol and then concentrated on a C_{18} column following the procedure for water samples.

An additional final C_{18} column proved to be very effective in improving the resolution of the HPLC results.

4 Results

Sewage treatment plant

The average performance of the treatment plant during the three consecutive monitoring days is given in Table 1. The data represent normal operating conditions and no rainfall was recorded during such period. Average Biological Oxygen Demand (BOD) decrease was 93 %, and Chemical Oxygen Demand (COD) decrease averaged 80 %. The results of hourly LAS concentrations are summarized in Table 2 for dissolved LAS and in Table 3 for LAS determinations in suspended solids (SS) as well the SS concentrations in the raw sewage and treated water streams. Dissolved LAS was analyzed in 12 samples taken every two hours, while the adsorbed LAS was determined in two composite samples of influent SS and in one composite sample of effluent SS. These composite SS samples were prepared to avoid analytical errors of LAS determinations in small samples.

Table 1. Operating parameters of Manresa's treatment plant (June 1993)

Flow (m^3/D)	30.538
HRT (hrs.)	4
SRT (D)	4.95
MLSS (mg/L)	3.000
Dry Sludge (Tm/D)	6.35
Inhabitants covered	80.000
COD in (mg/L)	478
COD out (mg/L)	94
BOD_5 in (mg/L)	300
BOD_5 out (mg/L)	20
SS in (mg/L)	565
SS out (mg/L)	15
Water Hardness (ppm as $CaCO_3$)	300

Table 2. Hourly variation of raw sewage flow and dissolved LAS (July 17th, 1993)

Hour	Flow (m^3/h)	LAS (mg/L)	
		in	out
10	1600	2.61	0.81
12	1450	5.75	0.11
14	1450	5.62	0.10
16	1425	7.09	0.17
18	1440	9.09	0.13
20	1520	6.84	0.23
22	1450	5.00	0.14
24	1200	6.37	0.19
2	1040	5.71	0.15
4	960	3.02	0.19
6	900	1.61	0.36
8	1360	1.31	0.25
Average	1316	5.00	0.16

Table 3. Hourly variation of SS and adsorbed LAS conc. (July 17th, 1993)

Hour	in		out	
	SS (mg/L)	LAS (mg/g)	SS (mg/L)	LAS (mg/g)
10	216		25	
12	254		13	
14	259		19	
16	379	10.50	20	
18	251		13	
20	195		20	
22	182		22	1.59
24	177		17	
2	104		23	
4	46	10.92	18	
6	23		19	
	89		25	
8				
Average	181	10.71	20	1.59

Table 4. LAS concentrations in water (July 1st, 2nd, 3rd, 1993)

date	raw water (mg/L)	treated water (mg/L)
1/06/93	4.12	0.19
2/06/93	5.03	0.07
3/06/93	5.52	0.10
Average	4.89	0.12

Table 5. Average LAS concentrations in SS (July 1st, 2nd, 3rd, 1993)

	Suspended solids (mg/L)	LAS (mg/g)
Influent	565	8.30
Effluent	15	1.30

Table 6. LAS analysis in Cardener river water

Sampling point	Flow m^3/d	LAS (µg/L)
2	30.500	120
3	358.300	27
4	388.800	37
5	388.800	30

A peak in the LAS concentration in the raw sewage stream (influent to the plant) is observed around 16–18 hrs which can also be noticed a few hours later in the effluent stream (20 hrs). Another peak in the effluent is also observed around 6–8 hrs although it can not be correlated with a corresponding peak in the influent.

The observed average removal of SS was 85 %. During the three consecutive monitoring days the LAS concentrations found in both influent and effluent streams (Table 4) were also similar to the results obtained in the monitoring of July 17, 1993.

The results for the SS concentration and adsorbed LAS during the three consecutive days are shown in Table 5. The average SS concentration in the raw sewage was 565 mg/L, higher than the average hourly concentration observed during the monitoring conducted on July 17, 1993 (181 mg/L).

The LAS mass balance and its removal can therefore be calculated using the data shown in Tables 1, 4 and 5.

Influent: Dissolved LAS:
$30.538\ m^3/d \times 4.89\ mg/L =$ 149 kg/d
Adsorbed LAS:
$30.538\ m^3/d \times 5.65\ mg/L \times 8.3\ g/K =$ 143 kg/d
Total ..... 292 kg/d

Effluent: Dissolved LAS:
$30.538\ m^3/d \times 0.12\ mg/L =$ 3.7 kg/d
Adsorbed LAS:
$30.538\ m^3/d \times 15\ mg/L \times 1{,}3\ g/kg =$ 0.6 kg/d
Total ..... 4.3 kg/d

$$\boxed{\text{LAS Removal} = \frac{292 - 4.3}{292} \times 100 = 98.5\%}$$

In other similar sewage treatment plant monitorings [3] we observed higher LAS removals (99 % +) than in the present report. The difference can be explained by the relatively high percentage of industrial sewage treated in the Manresas' plant.

Approximately 50 % of LAS in the raw sewage is dissolved and 50 % adsorbed on the SS while in the treated water, most of the LAS is in the dissolved phase. Similar observations have been reported earlier [3]. Total LAS reaching the plants gives a concentration of 9.5 mg/L which is nearly 35 % lower than expected taking real LAS usage as a basis. This can be explained by a certain biodegradation degree in the sewers [4].

Cardener River

The Cardener river receives the treated water effluent from the plant. It was monitored above the discharge point (sampling point No. 3, Fig. 1), at the sewage outfall (point No. 4) and 1 km below this point. No other discharges are reported on this kilometer from the discharge of the treatment plant.

LAS concentrations were determined in water samples once a day during the three consecutive days of the monitoring. The average flow rate of the river up stream of the discharge point was at the time of the sampling 358,300 m^3/d, therefore the dilution factor for the treated water effluent is nearly 12.

The LAS concentrations found in river water samples are given in Table 6. The concentration in point No. 5 (1 km downstream) is nearly the same as in point 3 (upstream the sewage outfall) indicating a rapid disappearance of the LAS discharged with the treated water.

Conclusions

- The average LAS concentration (adsorbed + dissolved) reaching the treatment plant with the raw sewage is 9.5 mg/L. This value is substantially lower than the expected one based on normal Spanish percapita LAS consumption. The difference might be due to a biodegradation removal degree (35 % average) of LAS in the sewer system connecting the city and the treatment plant.
- Total LAS removal in the treatment plant (98.5 %) was higher than either BOD decrease (93 %) or COD decrease (80 %).
- Residual LAS reaching the associated receiving water system disappears very rapidly and average LAS concentrations found in river water are always below 0.05 mg/L.

References

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