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Development of an analytical procedure to study linear alkylbenzenesulphonate (LAS) degradation in sewage sludge-amended soils☆

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ABSTRACT

A procedure for determining linear alkylbenzenesulphonates (LASs) in sewage sludge and amended soils has been developed. Extraction by sample treatment with 0.5 *M* potassium hydroxide in methanol and reflux was compared with a previously described extraction procedure in Soxhlet with methanol and solid sodium hydroxide in the sample. Repeatability results were similar with savings in extraction time, solvents and evaporation time. A clean-up method involving a C_{18} cartridge has been developed. Analytes were quantified by a reversed-phase HPLC method with UV and fluorescence detectors. Recoveries obtained were higher than 84%. The standing procedure was applied to high doses of sewage sludge-amended soils (15%) with increasing quantities of added LASs. Degradation data for a 116-day period are presented.

INTRODUCTION

Linear alkylbenzenesulphonates (LASs) are the major surfactants currently used. Commercial LASs are complex mixtures of homologues of C_{10}–C_{13} chain-lengths compounds and phenyl positional isomers, except those isomers with the aromatic ring bonded to the two terminal methyl groups. Their formula is presented in Fig. 1.

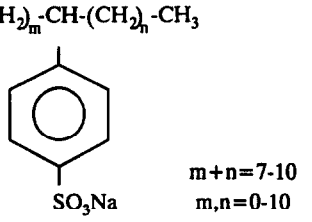

Fig. 1. Structural formula of LASs.

As LASs are extensively used as household laundry detergents, their direct disposal results in high concentrations in waste water, about 5–20 mg/l [1,2]. Sewage treatment plants break down LASs only partly; some of them remain in effluent and other fraction is adsorbed in sewage solids, in which LASs are major synthetic compounds in quantities between 2 and 5 g/kg [3–5]. Through waterways and sewage sludge disposal LASs are discharged into the environment.

The potential fertility of sewage sludge is well known, and in order to avoid health and environmental hazards guidelines [6] have been developed regarding its heavy metal content for agricultural land utilization. Our research team has been studying the possibility of exploiting greater sludge quantities in limy soil [7–9], including a laboratory study that takes into account degradation or accumulation of sewage sludge organic pollutants in soils, including LASs.

An experiment involving limy soils amended

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with high doses of sewage sludge (15%) and increasing quantities of added LASs has been designed. The aim was to evaluate the effects of high surfactant concentrations on the degradation of LASs. This required an analytical procedure to analyse LASs in sewage sludge and amended soils.

Although there is a well-established analytical method to determine LASs in water samples [1,2], a variety of procedures have been used to analyse them in solid samples: methanol reflux and anionic exchange and C_{18} cartridge clean-up [2]; methanol Soxhlet extraction and anionic exchange and C_{18} cartridge clean-up [5]; and methanol in Soxhlet with solid sodium hydroxide in the sample (20%, w/w) [10]. Each procedure uses an HPLC separation for the final analysis.

We have previously tested the existing methods of analysing LASs in sewage sludge and amended soils. Soxhlet extraction with methanol and sodium hydroxide gave the best results. We attribute this to the ability of basic medium to prevent LAS sorption on sewage sludge lipid organic matter. Based on our previous experience in lipid analysis of sewage sludge, we tested a direct basic treatment with potassium hydroxide in methanol under reflux.

This report compares both methods, extraction through sample treatment with methanolic 0.5 *M* potassium hydroxide under reflux and methanol Soxhlet extraction with sodium hydroxide in the sample, with a C_{18} cartridge clean-up in both cases. Analyses were completed with a reversed-phase HPLC method with UV and fluorescence detection.

EXPERIMENTAL

Reagents and materials

Acetonitrile and methanol were of HPLC grade and were supplied by Merck (Darmstadt, Germany). Milli-Q water was obtained with a Millipore system from Waters (Milford, MA, USA). HCl (0.1 *M*) was prepared from concentrated hydrochloric acid from Panreac (Barcelona, Spain). Potassium hydroxide and sodium perchlorate analytical grade were obtained from Merck. Sep-Pak C_{18} cartridges were supplied by Waters. A commercial mixture of linear alkylbenzenesulphonic acids with C_{10}–C_{13} chain lengths was used as received from K.A.O. (Barcelona, Spain): 50, 100, 500 and 1000 μg/ml standard solutions were made in methanol.

Instruments

An analytical LiChrospher 100 RP-18, 125 × 4 mm, 5-μm column and a LiChroCART 4-4, 100 RP-18, 5-μm precolumn, both from Merck, were used. The chromatography system consisted of a Waters 600E pump with a Rheodyne (Cotati, CA, USA) sample 20-μl loop injector. A Model 991 photodiode-array detector ($\lambda = 225$ nm) with integration software from Waters, a Model 470 fluorescence detector ($\lambda_{ex}/\lambda_{em} = 225/295$ nm) from Waters and a Model D-2000 integrator from Hitachi (Tokyo, Japan) were also used.

Chromatography conditions

Acetonitrile and acetonitrile–water (25:75) containing 0.1 *M* $NaClO_4$ were used as gradient eluents with a 1 ml/min flow-rate. After 1 min of 15% acetonitrile, a linear gradient elution was applied for 19 min leading to 40% acetonitrile, followed by a 2-min isocratic elution and a 3-min linear gradient elution to 70% acetonitrile, which was maintained for 10 min.

Procedure

About 0.5 g of sewage sludge or 2 g of amended soil were treated with 50 ml of 0.5 *M* potassium hydroxide in methanol under reflux for 4 h. The extract was vacuum evaporated to 1 ml on a 35°C bath and dried under a gentle stream of nitrogen on a 70°C bath. About 10 ml of methanol–water (30:70) were added and the pH adjusted to 1.0 with concentrated hydrocloric acid. The sample was sonicated for at least 1 min, to dissolve potassium chloride. A C_{18} cartridge was rinsed with 2 ml of methanol and 3 ml of 0.1 *M* HCl before use. The entire sonicated solution was percolated through the octadecylsilica cartridge. The column was washed with 2 ml of 0.1 *M* HCl. LASs were eluted with exactly 10 ml of methanol. The methanol eluate could be injected directly into the HPLC system. LAS concentration could be quantified by measuring peak heights and comparing them with external standards.

TABLE I

SPIKED AND TOTAL AMOUNT OF LASs IN SEWAGE SLUDGE (15%)-AMENDED SOIL EXPERIMENTS

Experiment	LAS spiked amount (g/kg)	LAS total amount (g/kg)
COA	0.00	1.87
COB	0.00	1.87
LAS 1A	3.59	5.46
LAS 1B	3.59	5.46
LAS 10A	18.00	19.87
LAS 10B	18.00	19.87

Experiment design to assess LAS degradation in sewage sludge-amended soils

Anaerobically digested sewage sludge came from Dargisa, a sewage aerobic treatment plant in Girona (Spain). Sludge was air-dried and ground to less than 0.4 mm before analysis or soil addition. Limy soil from Bellaterra (Vallés Occidental, Spain) was ground and sieved to less than 2 mm.

High doses of sewage sludge (15%)-amended soil were prepared in 6-kg polyethylene containers. LASs were added to sludge in the form of sodium linear alkylbenzenesulphonate and homogenized by grinding. Three experiments were performed in duplicate: the first used sewage sludge-amended soil with no added LASs (COA, COB), the second amended soil to which LASs were added to three times the normal concentration (LAS 1A, LAS 1B) and the third used amended soil to which LASs were added to ten times the normal concentration (LAS 10A, LAS 10B). The added and total amounts of LASs used in the experiments are reported in Table I.

Experimental soils were watered to maintain 20% humidity. Homogeneous samples were guaranteed by sampling and mixing throughout the container depth. The samples were preserved by the addition of 1% (w/w) formaldehyde and stored in the dark at +4°C. They were also dried at 70°C for 12 h before analysis.

RESULTS AND DISCUSSION

High-performance chromatography

An eluent gradient was developed to separate LAS homologues and the greater part of their isomers. Individual LASs were quantified by comparing their peak heights with those of an external standard injected daily. UV detection ($\lambda = 225$ nm) provides a linear response between 20 and 2000 μg/ml and a detection limit of 20 μg/ml. Fluorescence detection (225/295 nm) reduces the detection limit to 16 ng/ml.

Procedure

Basic methanol treatment of samples improves LAS extraction because LAS sorption on lipid organic matter decreases. Soxhlet extraction with solid sodium hydroxide provides these conditions only in first cycles. When the sample is submitted to a continuous basic methanolic treatment, lipids are saponified, scission of the lipid organic fraction of sewage sludge occurs and interactions between organic matter and mineral matrix are abolished. Therefore, associations between surfactants and lipid and mineral sludge fractions are reduced and extraction is made easier.

The strong basic medium after saponification or the subsequent increase in salt content that a neutralization would represent makes direct injection of the extract on HPLC impossible. Therefore, it is advisable to perform a C_{18} microcolumn cleaning to obtain LAS elution in a clear methanol solution. This purification allows the elimination of polar compounds and inorganic salts simultaneously.

Direct methanolic extract clean-up is not possible, because LASs are too soluble in methanol and would not interact with the C_{18} phase in the microcolumn. However, addition of water to the methanolic solution to be cleaned improves the affinity of LASs for the stationary phase. Cartridge behaviour has been studied as a function of methanol–water proportion in the solution to be cleaned. LAS standards (100 μg/ml) were prepared with methanol contents between 0 and 70% (v/v). The pH of standards was adjusted to 1.0 in order to protonate surfactant sulphonic group, to increase the affinity for the stationary reversed phase.

Results are reported in Fig. 2. Quantitative LAS recoveries were obtained with methanol contents of 0–30%. However, 30% methanol in water must be used when applying purification to sewage sludge extract, as only 30% methanol

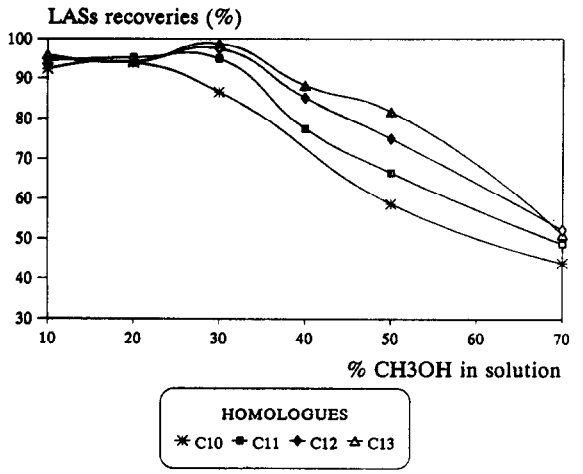

Fig. 2. LAS recoveries in C_{18} cartridge clean-up according to the methanol–water proportion in the solution before cleaning.

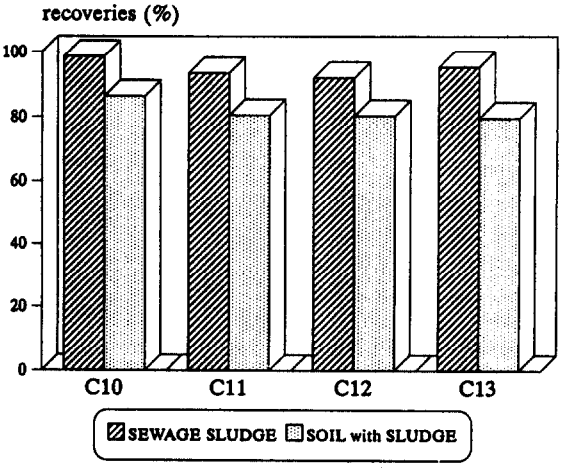

Fig. 3. Recoveries of various homologues in sewage sludge and amended soils.

completely dissolves the sludge-extracted fraction. In lower proportions methanol would form emulsions that would envelop LASs and prevent their interaction with the stationary phase.

A sample basic treatment for 4 h is enough to extract all LASs in sewage sludge: 14.8 g of LAS per kg in four replicates [$s_{n-1} = 0.8$, relative standard deviation (R.S.D.) = 6%]. A second extraction of the same samples recovers only 0.6% of total LASs.

Table II compares the proposed procedure with the one described in literature [10] using Soxhlet extraction and solid sodium hydroxide within the sample. Each procedure with C_{18} clean-up was applied in triplicate to 2 g of sewage sludge-amended soil. The repeatability obtained is similar in both methods.

The accuracy of the procedure was measured by a standard additions analysis. Sewage sludge and sludge-amended soils (15%) were spiked with increasing quantities of LASs (0, 15, 30 and 45 g of LAS per kg of sewage sludge) in order to ensure medium recoveries in samples with different LAS concentrations. The recoveries obtained were 94% and 81% for sewage sludge and for amended soils, respectively. There is no difference between LAS homologues in extraction as similar recoveries were obtained for them all (Fig. 3).

Finally, the results of the proposed method are consistent with those obtained by a previous method [10]. This new procedure reduces solvent use and analysis time. Only 4 h are needed in comparison with the 7 h required for the procedure described in literature.

LAS degradation results

LAS degradation in sewage sludge-amended soils over a 116-day period was studied. The degradation of LASs varied depending on the

TABLE II

REPEATABILITY[a] OF THE PROCEDURES APPLIED TO SEWAGE SLUDGE-AMENDED SOIL

Procedure	Mean (g of LAS per kg)	n^b	$s_{n-1}{}^b$	R.S.D.[b]
Reflux/KOH 0.5 M/C_{18} clean-up	2.2	3	0.32	14.5
Soxhlet/solid NaOH/C_{18} clean-up	2.7	3	0.30	10.9

[a] Repeatability, in 1 day.
[b] n = Repetitions; $s_{n-1} = n - 1$ standard deviation; R.S.D. = relative standard deviation (%).

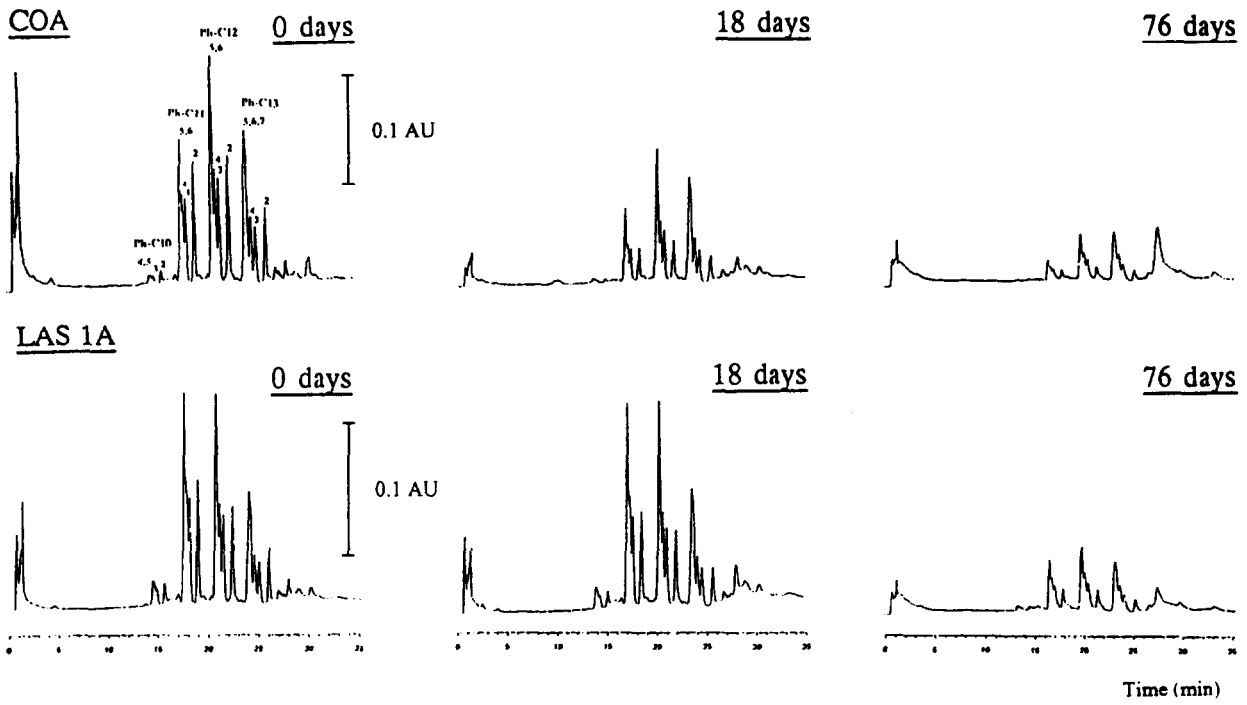

Fig. 4. Chromatograms of LASs in COA and LAS 1A samples after 0, 8 and 16 days of degradation. Peaks: Ph-C_{10}, Ph-C_{11}, Ph-C_{12} and Ph-C_{13} are groups of LAS homologues; the numbers above each peak show the phenyl position on the alkyl chain for every isomer.

amount added, as shown in the chromatograms in Fig. 4. In soils with no added LASs (COA) degradation was 50% in 18 days, whereas no degradation occurred in soils spiked with three times the normal concentration of LASs (LAS 1A). However, after 76 days both soil types exhibited low surfactant levels, only about 15% of the initial concentration. Quantitative results were subjected to statistical treatment to produce an evolution curve. Moreover, there was a variation in homologue and isomer distribution during degradation. Homologues with small number of carbon atoms and external phenyl positional isomers appeared to be more degraded. These results will be reported in the near future.

Results treatment

A period of time with no LAS variation was observed in every experiment when mathematically evaluated. It was named accommodation time (t_0). There is no statistical difference between the initial points as they do not fit any curve. They only reflect method deviation. This means that there is no immediate degradation of LASs. An initial period of time without LAS degradation is reported to be usual when organic compounds are submitted to microbial breakdown [11].

In order to study LAS degradation times, the curve that provides the minor error was adjusted to experimental points with degradation. Every experiment seemed to follow:

$$C_t = e^a \cdot t^{-b}$$

for $t > t_0$

where C_t is the concentration of LAS (g of LAS per kg of sewage sludge-amended soil) and t the time (days) elapsed from the beginning of the experiment as the only parameter. Fig. 5 presents adjusted curves and experimental data. Relative errors were generally less than 11% (Table III).

Table IV reports degradation parameters of spiked experiments: accommodation time (t_0), half-life time to 50% degradation ($t_{1/2}$) and apparent time to 95% degradation ($t_{0.05}$).

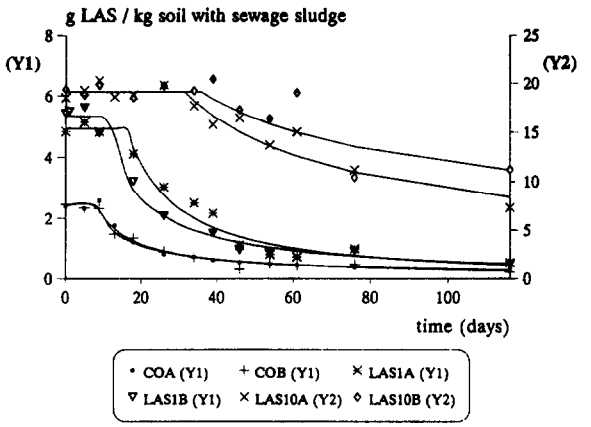

Fig. 5. Variation in LAS concentration in sewage sludge amended soil for every experiment (COA, COB, LAS 1A and LAS 1B on axis Y1, LAS 10A and LAS 10B on axis Y2) versus the time elapsed from the start of the experiment. Points correspond to experimental values and curves have been mathematically adjusted.

In degradation:

(1) Accommodation time until surfactant degradation begins (t_0) increases with initial LAS concentration in sewage sludge.

(2) Half-life time to 50% degradation of surfactants ($t_{1/2}$), increases with LAS quantities in sludge.

(3) Apparent degradation time until 5% LAS remains ($t_{0.05}$) is greater for experiments with higher surfactant concentrations.

TABLE IV

EVOLUTION PARAMETERS IN LASs EVOLUTION EXPERIMENTS

Experiment	t_0 (days)[a]	$t_{1/2}$ (days)[b]	$t_{0.05}$ (days)[c]
COA	7	18	335
COB	8	19	292
LAS 1A	16	29	196
LAS 1B	10	20	225
LAS 10A	31	94	3665
LAS 10B	35	162	24 698

[a] t_0 = Accommodation time.
[b] $t_{1/2}$ = Half-life time.
[c] $t_{0.05}$ = Apparent degradation time.

CONCLUSIONS

The procedure described appears to be suitable for the study of LAS degradation in sewage sludge-amended soils. LAS degradation can be predicted when amending soil. The higher the LAS concentration in sewage sludge, the lower the LAS biodegradation rate in amended soil.

TABLE III

CURVES ADJUSTED TO LAS DEGRADATION EXPERIMENTS

Experiment	$C_t = e^a \cdot t^{-b}$ ☆		Average error	
	a	b	ϵ_A [a] (g of LAS per kg)	e_r (%)[b]
COA	2.4388	0.781538	0.049	6.9
COB	2.66719	0.842782	0.059	8.0
LAS 1A	4.92125	1.197900	0.290	21.0
LAS 1B	3.82776	0.950372	0.137	10.9
LAS 10A	5.12006	0.629331	1.047	7.6
LAS 10B	4.59151	0.458242	1.602	9.9

☆ C_t = LAS concentration (g of LASs per kg of sewage sludge-amended soil); t = time from experiment start (days).
[a] ϵ_A = Absolute error.
[b] e_r = Relative error.

However, complete LAS elimination is always predictable.

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