



Evaluation of Linear Alkylbenzene Sulfonate (LAS) behaviour in agricultural soil through laboratory continuous studies



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HIGHLIGHTS

- Linear alkylbenzene sulfonate behaviour on soil is modeled through column studies.
- Retention, degradation and transport phenomena were simultaneously studied.
- The experimental set-up was preliminarily characterized with tracer experiments.
- A detailed modeling was conducted for each linear alkylbenzene sulfonate homologue.
- Prediction of surfactant environmental behaviour in a real scenario was performed.

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ABSTRACT

The behaviour of Linear Alkylbenzene Sulfonate (LAS) in agricultural soil is investigated in the laboratory using continuous-flow soil column studies in order to simultaneously analyze the three main underlying phenomena (adsorption/desorption, degradation and transport). The continuous-flow soil column experiments generated the breakthrough curves for each LAS homologue, C₁₀, C₁₁, C₁₂ and C₁₃, and by adding them up, for total LAS, from which the relevant retention, degradation and transport parameters could be estimated, after proposing adequate models. Several transport equations were considered, including the degradation of the sorbate in solution and its retention by soil, under equilibrium and non-equilibrium conditions between the sorbent and the sorbate. In general, the results obtained for the estimates of those parameters that were common to the various models studied (such as the isotherm slope, first order degradation rate coefficient and the hydrodynamic dispersion coefficient) were rather consistent, meaning that mass transfer limitations are not playing a major role in the experiments. These three parameters increase with the length of the LAS homologue chain. The study will provide the underlying conceptual framework and fundamental parameters to understand, simulate and predict the environmental behaviour of LAS compounds in agricultural soils.

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1. Introduction

The surfactants market is a complex industry that involves several producers and product lines as well as a broad spectrum of end applications, including household detergents, industrial washing products and conditioners, laundry additives, cosmetics, lubricants, coatings and paints (HERA, 2013). Surfactants can be classified into anionic and non-ionic according to the charge of the

hydrophilic moiety (Lara-Martín et al., 2006). Linear Alkylbenzene Sulfonate (LAS) is the main component of anionic surfactants. The most recent and realistic market survey was completed by the Ecosol companies, which estimated a total consumption tonnage of about 430 kt for the year 2005 in Europe (ECOSOL, 2005), with LAS being one of the most commonly used surfactants in the market. Its main use is in household detergents with a consumption of around 350 kt according to the HERA report (2013), which represents more than 80% of the total European consumption of LAS. Minor applications (<20%) include textiles and fibers, chemicals and agriculture, which are beyond the scope of the

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HERA report. Commercial LASs are composed of a mixture of 20 isomers and homologues, with a sulfonated aromatic ring at the para position and attached to a linear alkyl chain (10–13 carbon atoms) (Cavali et al., 1999).

With such an intensive and widespread use of LAS, it is not surprising its ubiquitous presence in urban wastewater. Despite the fact that most of urban wastewater is treated in wastewater treatment plants (WWTPs) and LAS removal is considered efficient in most of the situations (McAvoy et al., 1998; Matthijs et al., 1999), there is always a residual fraction that, given the high consumption and prevalent usage, gets to agricultural lands (Carlsen et al., 2002; Nimer et al., 2007). LAS enter agricultural soils through irrigation with WWTP effluents and untreated urban wastewater discharges or as a consequence of its presence in sludge used as fertilizer (Carlsen et al., 2002; Eichhorn et al., 2005; Schowanek et al., 2007). When released into the environment, LAS undergo a variety of physical and chemical changes, as described elsewhere (Holmstrup and Henning, 1996; Koefoed et al., 2003; Crovetto et al., 2009).

Several studies have been conducted in recent decades to better understand the distribution, environmental behaviour and fate of anionic surfactants in different environmental compartments, most of them included in the review by Ying (2006). Only a few studies have addressed the presence of LAS in soils, using batch (Ziqing et al., 1996; Fytianos et al., 1998; Broberg et al., 2003) or column (Branner et al., 1999; Boluda et al., 2010) experiments, obtaining however poor models, and therefore, deficient characterizations of its environmental behaviour (adsorption/desorption, degradation and transport) in soil. In general, there is a significant lack of fundamental information regarding the environmental behaviour of LAS in soil. The main purpose of this work is to gather high-quality fundamental data that will provide the basis to understand, simulate and predict the environmental behaviour of such an important type of surfactants in soil.

The environmental behaviour of any compound in soil is determined by the different phenomena that may take place. Adsorption/desorption, degradation and transport are the main phenomena for LAS, with adsorption/desorption being the most relevant due to its regulatory implications. The present work complements the findings from the batch study with continuous-flow soil column experiments (OECD, 2004). These type of experiments allow us to address these three phenomena simultaneously and consequently to obtain a better overall understanding of the environmental behaviour of LAS in agricultural soil. In this workflow, the batch and continuous-flow experiments are the necessary steps to yield fundamental information in order to design effective and conclusive experiments under realistic field conditions, which will be the object of further investigation.

In the present paper, the results of the continuous-flow soil column experiments are divided into two sets of laboratory studies with complementary goals. First, the experimental setup was defined in fundamental terms, using a potassium bromide solution as a tracer. KBr is neither degraded in nor adsorbed onto soil, and therefore works well as a tracer agent to better understand and test the soil column. Second, soil column displacement experiments with LAS solutions were performed in order to gather information regarding the dispersion, adsorption/desorption and degradation behaviour for each separate LAS homologue (C_{10} , C_{11} , C_{12} and C_{13}) and for total LAS. Breakthrough curves (BTC) were obtained for all soil column experiments under experimental conditions that better simulate field conditions, based on which it is possible to estimate the fundamental retention, degradation and transport parameters, and that will allow us to understand the environmental behaviour of LAS in soil, as well as to perform computational simulations for a variety of scenarios.

2. Experimental: materials and methods

2.1. Reagents

All reagents used in this study were of analytical grade unless otherwise specified. Commercial LAS mixture and LAS-2 ϕ C16 were kindly supplied by Cepsa Química S.A. (Madrid, Spain). LAS mixture consisted of an aqueous sodium salt solution with a LAS content of 53.79% (wt/wt) and the distribution of homologues was 13.98% C_{10} , 32.22% C_{11} , 30.80% C_{12} , and 23.00% C_{13} . Potassium bromide 98% was purchased from Panreac (Barcelona, Spain). N,N-dimethyltetradecylamine, LC-MS grade ethanol, acetic acid and triethylamine were purchased from Sigma-Aldrich (Madrid, Spain). Methanol was acquired from VWR BDH Prolabo (Barcelona, Spain). Stock solutions of LAS (500 mg L⁻¹), LAS 2- ϕ C16 (1000 mg L⁻¹) and N,N-dimethyltetradecylamine (1000 mg L⁻¹) were prepared in methanol and stored at 4 °C in the dark. Working standard solutions of LAS were prepared in Milli-Q water immediately before use. Water (18.2 M Ω cm) was purified using a Milli-Q system from Millipore (Bedford, MA, USA). The solutions were stable for at least six months. All glassware was washed with a chromic mixture to minimize contamination.

2.2. Instrumentation and software

The studies were performed on a peristaltic pump (ISM597A V2.10 Ismatec, Glattbrugg, Switzerland) and a fraction collector (Frac-200, Amersham Biosciences) with capacity for 95 tubes. A potentiometer (MicropH 2000, Crison Instrument, Barcelona, Spain) equipped with Ag/AgBr and reference electrodes were also employed in these experiments. Samples were analyzed with a high-performance liquid chromatography (HPLC) system, Agilent 1200 series (Agilent Technologies Inc., Palo Alto, CA, USA) coupled to an API 2000 (Applied Biosystems, Foster City, CA, USA) triple quadrupole mass spectrometer system. The electrospray ionization (ESI) interface was also employed in the analyses. Kinetex C₁₈ analytical column (100 Å pore size) of 100 mm $\times$ 2.10 mm and 2.6 μ m particle diameter (Phenomenex, Torrance, USA) was used for chromatographic separation. A Stuart Block Heater and a Stuart Sample Concentrator (Stone, Staffordshire, UK) were used for extract evaporation. An Ortoalresa Digicen 21 centrifuge (Madrid, Spain), an ultrasonic bath (P. Selecta, Barcelona, Spain) and a vortex-mixer (Yellow line, Wilmington, NC, USA) were also used during sample treatment.

The control of the LC-MS/MS instrumentation, data acquisition and analysis was performed with Analyst 1.4.2 software from Applied Biosystems. Statgraphics version 5.0 software Plus (Manugistics Inc., Rockville, Maryland, USA) was used for statistical and regression analysis of the calibration data. Matlab platform R2011a (MathWorks, Inc) and gProms software (Process Systems Enterprise Limited) were employed in the simulations and non-linear fitting of equilibrium and non-equilibrium transport models.

2.3. Soil

The studies were carried out using samples of agricultural soil from the Santa Maria farm located in the Vega de Granada, the fertile agricultural lands of Granada (37°11'11.87"N, 3°41'26.09"W) situated 5 km away from the city of Granada and one of the most important aquifers of Andalusia (Spain). Soil samples were collected from topsoil (A-horizon) to a maximum depth of 25 cm. Upon reaching the laboratory, samples were air-dried, ground, sieved through a 2 mm mesh and stored at room temperature. This soil was physically and chemically characterized (see [Supplementary Material, Table S1](#)).

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