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Sorption, degradation and transport phenomena of alcohol ethoxysulfates in agricultural soils. Laboratory studies

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HIGHLIGHTS

- The isotherms were obtained following the standard batch equilibration method.
- The isotherms were well fitted with both the linear and Freundlich models.
- Continuous-flow soil column experiments allow studying the breakthrough curves.
- Estimation of the fundamental parameters of the transport model was carried out.

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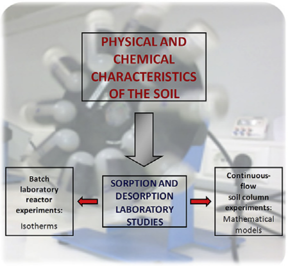
GRAPHICAL ABSTRACT



ABSTRACT

In the present work, laboratory studies were conducted in order to determine and model the sorption, degradation and transport processes of alcohol ethoxysulfates (AES), one of the most important groups of anionic surfactants. Adsorption/desorption isotherms were obtained for several structurally related AES ethoxymers (homologue AES-$C_{12}E_n$ with $n = 0–10$ ethoxymer units and homologue AES-$C_{14}E_n$ with $n = 0–7$ ethoxymer units) using a batch equilibrium method. Data were fitted to a linear and a Freundlich isotherm models. Additionally, experiments in continuous-flow soil columns were also carried out and the breakthrough curves observed for each compound were studied. Breakthrough curves were used to determine the fundamental parameters of the transport model (hydrodynamic dispersion coefficient, degradation rate constant and adsorption/desorption isotherm slope), that is the main phenomena that take place simultaneously when AES move through agricultural soil. When the results obtained for the AES ethoxymers are combined, they reveal a clear and consistent trend towards a sorption increase with the number of ethoxylated units and with the length of the alkyl chain that opens the possibility to estimate the values of the transport parameters for other structurally related ethoxymers.

1. Introduction

The term surfactant is a contraction of “surface active agent” and designates a substance capable of reducing the surface tension of a liquid, serving as a wetting agent or detergent (RAE, 2016).

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Surfactants are amphipathic molecules with a hydrophilic portion and a hydrophobic portion. Surfactants can be classified according to the nature of the hydrophilic group into four main classes: anionic, cationic, non-ionic and amphoteric (Wulf et al., 2010). Anionics are the most common type of surfactants worldwide and over 2.918 million tons of surfactants were produced in Western Europe alone in 2014 (CESIO, 2014). AES, one of the most used anionic surfactants, have an alkyl chain length of 12–16 and an ethylene oxide (EO) chain of 3–4 units (HERA, 2004).

The widespread use of surfactants in domestic and industrial applications has resulted in an increased number of possible contamination sources of wastewater that passes into wastewater treatment plants (WWTP) (Schröder, 2001; González et al., 2007, 2008; Gómez et al., 2011) prior to discharge into natural ecosystems such as seas, rivers, sediments, etc (Pojana et al., 2004; Lara-Martín et al., 2006a, b; Sibila et al., 2008; Gómez et al., 2011; Oliver-Rodríguez et al., 2013; Corada-Fernández et al., 2013). and used for irrigation (Wiel-Shafran et al., 2006; Müller and Deurer, 2011; Corada-Fernández et al., 2015). The sludge generated in these plants is rich in organic matter and adequately treated and dried can be used for sewage sludge composting. Direct application of sludge to soil can result in relatively high levels of surfactants in the environment (Matthijs et al., 1997; Petersen et al., 2003; Petrovic and Barceló, 2004). McDonough et al. (2016a, 2016b) found an AES concentration of 1.95 μg L^{-1} in effluent grab samples from several WWTPs and 4.1 mg kg^{-1} in aerobic sediment. Fernández-Ramos et al. (2014) studied AES levels in marine sediment and found concentrations ranging from 2.7 to 14.3 mg kg^{-1}. Sanderson et al. (2006) assessed the occurrence and hazard of alkyl ethoxysulfates in river sediments. The method used in this study showed broad applicability across various sediment types and the most common congeners of AS/AES and found AS/AES levels ranging from 0.025 to 0.117 μg g^{-1}. In this context, it is essential to monitor the presence of surfactants, their environmental fate and actual impact on natural ecosystems.

Although surfactants can be useful in the solubilization and removal of contaminants from soils and sediments (Di Cesare and Smith, 1994; Mulligan et al., 2001), data regarding the environmental behavior of AES in soil (Corada-Fernández et al., 2015), in particular regarding adsorption/desorption mechanisms, is still scarce. This is due in part to the complexity of the molecular structure of these type of surfactants and to the specific commercial formulations, which are generally complex mixtures of homologues and ethoxymers (Rodríguez-Cruz et al., 2005). Traverso-Soto et al. (2014) and Lara-Martín et al. (2014) studied degradation and sorption processes of alcohol ethoxylates (AE) and their polyethylene glycol (PEG) metabolites in seawater and found concentrations in the range of 1.4–4.5 μg L^{-1} in seawater and higher than 1 μg g^{-1} in suspended solids samples. The oxyethylene group promotes the solubility of AE and PEG and also enhances interaction with polar surfaces of clays, therefore increasing their sorption capacity.

Droge and Hermens (2010) investigated the competition for adsorption to mineral surfaces in marine sediment and kaolinite clay using simple mixtures of AE homologues and found that for both sorbents, adsorption sites on mineral surfaces can be blocked by an AE homologue with the strongest adsorption affinity. The strongly adsorbed AE forms a second sorption phase to which weakly adsorbing AE will sorb forming bilayers. In addition, they (Droge and Hermens, 2009) studied the nonlinear sorption of AE homologues as a function of their chemical structure and properties of marine sediments and clay minerals using a dual-mode model to describe the sorption process combining a Langmuir and linear sorption term and the results were successfully fitted. Sorption coefficients showed good correlation with the polar and nonpolar chain lengths of the AE. The enhanced nonlinearity of AE isotherms with longer ethoxylate chains is explained by the increased adsorption coefficient and decreased bilayer formation affinity with additional ethoxylate units. Taking into account the current relevance and widespread use of AES in household and industrial applications, and the lack of information regarding the fundamental parameters involved in their environmental fate, the main objective of the present study was to obtain rigorous data on the behavior of AE and to develop a mathematical model of the sorption, degradation and transport processes of AES in agricultural soil. In this context, a description of AES migration in soil systems was carried out and an analysis about the distribution of AES between the aqueous and solid phases and the main parameters for mathematical modeling were obtained. Two experimental settings using different features were evaluated: (i) *experiments in a laboratory batch reactor*, to obtain the adsorption-desorption equilibrium isotherms for AES ethoxymers; (ii) *experiments in continuous soil column*, to obtain the breakthrough curves (BTC) for each AES, which provide fundamental information about sorption, degradation and transport processes. Homologue AES-$C_{12}E_n$ with $n = 0–10$ ethoxymer units and homologue AES-$C_{14}E_n$ with $n = 0–7$ ethoxymer units were used for the tests. The mathematical models applied, were capable of describing the behavior of AES in agricultural soil with high accuracy.

2. Experimental: materials and methods

2.1. Chemicals and reagents

The commercial mixture of AES was supplied by Sasol, Italy (COSMACOL AES 70-2-24) as an aqueous solution of a sodium salt with an AES (AES-C_xE_n) content of 70.0% (w/w) with the following homologue distribution: AES-C_{12} (55.0%) and AES-C_{14} (45.0%) and an average number of EO units of 2.0. The sodium salt of 2-octylbenzenesulfonic acid (2ØC_8-LAS, 81% w/w) was used as internal standard and supplied by Cepsa Química S.A. (Madrid, Spain). Acetic acid, formaldehyde, water and triethylamine (LC-MS grade) were purchased from Sigma-Aldrich (Madrid, Spain); acetonitrile and methanol (both HPLC-grade) were supplied by Merck (Darmstadt, Germany). Finally, purified water (18.2 MΩ cm) was obtained using a Milli-Q system (Millipore, Bedford, MA, USA).

2.2. Soil

The studies were carried out using soil samples collected from the Vega de Granada region (37° 11.159′ N, 3° 41.391′ W). Soil samples were collected from the topsoil layer (25 cm) and placed in plastic containers and 3% (v/v) formaldehyde was immediately added for conservation and to prevent biological activity. Soil samples were dried at room temperature for 48 h and sieved through a 2 mm mesh. Finally, they were stored in the dark at 4 °C until analysis. Physical and chemical determinations indicated that the studied soil was calcareous fluvisol. (See Table S1, Supplementary Material).

2.3. Analysis of surfactants in solution

First, samples were centrifuged to remove particles and 2 mL of supernatant was transferred to an Eppendorf tube and centrifuged for 15 min at 13,000 rpm (10,530×g). An Agilent 1200 series (Agilent Technologies Inc., CA, USA) HPLC system with a binary pump, an automatic autosampler, an on-line vacuum membrane degasser and a thermostated column compartment was used for the analyses. An API 2000 (Applied Biosystems, CA, USA) triple quadrupole mass spectrometer system with atmospheric pressure