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Modelling the Fate of Linear Alkylbenzene Sulfonate in Agricultural Soil Columns during Inflow of Surfactant Pulses from Domestic Wastewaters

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Abstract: Linear alkylbenzene sulfonate (LAS), a widely used anionic surfactant, is present in wastewater and can be discharged, causing environmental damage. When biodegradation is negligible, adsorption and desorption reactions play an important role, depending on the media characteristics (organic matter and clays) and hydrodynamic parameters. Previously published laboratory column data are modelled with PHREEQC (version 2.18) in three scenarios of LAS input: spill (LAS pulse), continuous discharge (LAS adsorption step) and remediation (LAS desorption step). The distribution coefficients (0.1–4.9 × 10^{-3} L/g) in the sand columns are lower than those determined in this paper from batch tests and in columns of 25% and 50% agricultural soil mixtures (1–70 × 10^{-3} L/g). Considering the Freundlich constant parameters from the modelling, the results are similar to the distribution coefficients, but the linear isotherms are more consistent throughout. The mass transfer coefficient from the sand columns is lower than the agricultural soil columns (20–40 h^{-1}), indicating longer elution times for the heavier homologues and a higher percentage of agricultural soil. For lighter homologues, fast migration could cause contamination of aquifers. The great persistence of LAS in the environment necessitates the development of mitigation strategies using reactive transport models, which predict longer times for the remediation of LAS homologues.

Keywords: modelling; PHREEQC; reactive transport; LAS; column experiment; adsorption; desorption; sand; agriculture soil

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1. Introduction

At present, researchers are devoting much attention to the potential risks of emerging contaminants while placing less focus on historical pollutants such as the surfactant linear alkylbenzene sulfonate (LAS), which is a major anionic surfactant widely used in cleaners and detergents worldwide, for both domestic and industrial applications.

These anthropogenic compounds arrive at wastewater treatment plants or are discharged directly into bodies of water in concentrations ranging from 10 to 38,000 mg/L [1], either by accident or intentionally. They can generate environmental damage since they are toxic at certain concentrations in aquatic organisms and wildlife [2], causing serious alterations. In humans, they have been associated with colon cancer [3].

LAS has hydrophobic characteristics and persists in the topsoil layers for long periods of time. Although biodegradation is an important process in LAS elimination under aerobic conditions, it has been proven that in certain discharges where these compounds reach the saturated zone with a low oxygen content, biodegradation is very slow or even stops [4]. The fate of these compounds has recently been studied in lakes containing foam from undegraded domestic surfactants, of which LAS is the most dominant type. These surfactants do not degrade under the prevailing conditions and time frame, and their presence was also observed in the sediment of organic sludge [5], indicating that biodegradation does not exist or is negligible in several environmental cases, such as in freshwater sediments [6]. In these scenarios, the sorption process is predominant.

Moreover, in recent years, the growing demand for water, especially in arid regions, has necessitated the reuse of wastewater as a source of irrigation. Additionally, the use of wastewater sewage sludges for soil amendment has become a common practice to improve the physical properties of soil, to recover nutrients such as nitrogen and phosphorous [7], and to solve the disposal problem of the enormous amount of sewage sludge generated. However, sludge application in croplands may lead to the accumulation of harmful components in soil, such as heavy metals and organic compounds [8], causing these components to enter the food chain and producing reproductive and fetotoxic problems, as evidenced in some studies [9]. Other areas of growing interest are the application of surfactants in remediation technologies for treating soils or waters contaminated with organic compounds. Their use improves the remediation and requires less time than the use of water alone [10,11].

Once LAS enters the terrestrial environment, adsorption and desorption reactions play important roles in controlling its movement in soils and aquifers. However, these processes depend on the characteristics of the aquifer soil, such as the organic matter and clay content [12], as well as the determination of the sorption equilibrium, which is very important when modelling and predicting the transport and reaction of LAS in the saturated zone. Kinetic studies are also of interest since they allow for determining the rate of adsorption of the contaminant and predicting its concentration in the solution after a given contact time with the adsorbent [13]. For these reasons, it is very important to know the aspects that govern the behaviour of LAS, with models predicting the evolution of this pollutant in the natural environment, to apply corrective measures.

Currently, hydrogeochemical studies play a significant role in characterising natural systems, understanding the migration of contaminants [14–16], and carrying out remediation studies, among other tasks. The modelling of the transport and reaction processes (‘reactive transport’) of contaminants can be performed through the application of computer codes that enable hydrogeochemical modelling based on the principles of matter conservation equations and chemical balance.

Hydrogeochemical modelling must be supported by experimental data obtained either in the field or in the laboratory, where the influence of the variables involved can be carefully studied. Laboratory column tests for studying the reactive transport of contaminants like LAS are an essential tool for interpreting the processes that occur in the natural environment, as demonstrated in previous works [17–19]. Furthermore, obtaining data on the evolution of contaminant concentrations under certain conditions is essential to understanding the processes in which they are involved [20].

Codes such as PHREEQC [21] and ORCHESTRA [22] have been developed to combine geochemical processes (acid–base reactions, adsorption, dissolution–precipitation, etc.) with transport calculations. Additionally, there are specialised computational codes for three-dimensional transport modelling in saturated media coupled to geochemical codes, such as MODFLOW 6 [23]. PHREEQC has been used to simulate transport processes and a wide range of chemical reactions that occur in natural and contaminated waters. It includes the ability to model kinetic reactions with rate equations specified by the user using BASIC-type statements. However, examples of LAS-reactive transport governing by equilibrium and kinetics have not been found.

The objective of the present study was to model the physicochemical processes of transport and sorption of an organic pollutant (LAS) occurring in a saturated aquifer medium at a laboratory scale and with biodegradation eliminated. PHREEQC is an excellent tool to model this process, and in this work, it has been applied to experimental data collected through column tests, using previously published data [12], along with transport data obtained with a tracer.

The input parameters required by PHREEQC for modelling were obtained from a test tracer for the transport and the distribution coefficients for adsorption/desorption. These last were obtained in experimental batch tests carried out in this work, and these distribution coefficients establish the initial and maximum values for modelling. These parameters can be used in environmental models to predict the effects that may occur during continuous or accidental LAS discharges, or in the remediation of contaminated soils.

The interpretation of the physicochemical processes occurring in the environment is difficult due to the multiple variables involved. The use of LAS is very common and the factors that can influence in the interaction between LAS homologues and the natural environment are very important. PHREEQC is a tool that allows interpretation of the effects observed in the environment and prediction of variations for new strategies applicable in control methods.

2. Materials and Methods

This work used experimental results from tests carried out in laboratory columns. The characteristics and methodology of these tests are described in previous studies [12]. This section includes important details describing the selected tests and the fundamental parameters necessary for modelling reactive transport using the PHREEQC (version 2.18.3-5570) software.

2.1. Description of the Experimental Column Tests Used in the Modelling with PHREEQC

A previously reported reactive transport study [12], involving a spill of LAS into a laboratory column (one-dimensional study) filled with different types of porous media (sand and agricultural soil), examined the sorption of different LAS components. Table 1 presents the main characteristics of the selected tests with different porous media saturated with irrigation water. The results were obtained in a column taken as a blank T0, which was filled with sea sand, and two additional columns filled with a mixture of the aforementioned sand with different proportions of agricultural soil (sand (23.6%), silt (38.0%) and clay (38.4%)) in tests T25 and T50.

Table 1. Main characteristics of the modelled pulse experiments [12].

Test	Porous Medium	Sediment (g)	LAS (mg/L)
T0	100% sea sand	163.3	91
T25	75% sea sand + 25% soil	152.0	98
T50	50% sea sand + 50% soil	129.6	110

The LAS spill, or pulse, was carried out by introducing irrigation water, previously prepared with a high LAS concentration (around 100 mg/L), for 5 h to simulate wastewater. Subsequently, irrigation water was continuously introduced until the LAS components were eluted, and the concentration variation as a function of the time was observed under specific conditions.

In other previous experimental research [24], continuous discharge (LAS adsorption step) and remediation (LAS desorption step) were performed. In the adsorption step, the constant input concentrations of the total LAS (4 mg L^{-1}) with the different homologues were introduced until the maximum concentration was obtained. In remediation (LAS desorption step), the same columns were submitted to a constant input of irrigation water free of LAS until the concentration of each homologues dropped to zero.

Modelling with PHREEQC requires that the user defines the composition of the LAS homologues used, as well as the composition of the irrigation water, which is shown in Table 2. The LAS used in the previous experimental study came from Petroquimica Española S.A. (PETRESA), with the composition of the homologues studied being as follows: 12.1% C_{10}LAS, 34.1% C_{11}LAS, 30.6% C_{12}LAS and 23.2% C_{13}LAS. The data for the modelling were taken from the results, where the adsorption of LAS in the porous medium was the predominant reactive process, as biodegradation was inhibited [12].

Table 2. Irrigation water [12] used in different modelled column experiments.

	Ion Concentration (mg/L)						
Test	**Ca^{2+}**	**Na^{+}**	**K^{+}**	**Mg^{2+}**	**Cl^{-}**	**$SO_4{}^{2-}$**	**$HCO_3{}^{-}$**
T0	35	70	2.0	35	115	55	180
T25	138	116	2.9	45	240	100	320
T50	70	70	2.8	38	150	80	220

The hydrodynamic parameters are important for characterising transport in the column [24]. Prior to the LAS pulse, an input with a tracer ($CaCl_2$) provided the breakthrough curve (concentration versus time). These data allow for the calculation of the hydrodynamic parameters (Table 3), including the exact flow and column length, by means of the AcuaIntrusion Transport (version 1.00) code [25], which provides the best fit for the breakthrough curves. The parameters include the mean residence time (t_m (L/ν)), Péclet number (Pe), effective porosity (ε), interstitial velocity (ν(u/ε)), longitudinal dispersion coefficient D_L and dispersivity (α(L/Pe)). These were transformed into PHREEQC language and used in the LAS transport model.

Table 3. Hydrodynamic parameters of the experiments carried out in columns obtained with AcuaIntrusion Transport [12].

Test	Flow (mL/min)	Length (cm)	t_m (h)	Pe ($\nu L/D_L$)	Effective ε	ν (cm/h)	D_L (cm^2/h)	α (cm)
T0	0.479	22.4	1.77	315	0.46	12.66	0.90	0.071
T25	0.458	22.4	1.89	67	0.47	11.86	3.94	0.332
T50	0.473	20.2	1.79	103	0.51	11.26	2.20	0.196

2.2. Description of the Experimental Batch Tests

It is important to know the values of the distribution coefficients obtained in batch adsorption studies in order to model the contaminant transport in columns with an adsorption process by using experimental data. The dynamic column experiments have distribution coefficients with values lower than those obtained in a batch, where the adsorbent is more accessible as it remains in suspension. These maximum values serve as a guide to starting the modelling process.

In batch tests, the adsorbent material (Table 1) comes into contact with a solution containing a known concentration of the species susceptible to adsorption. After sufficient time, equilibrium is reached between the dissolved and adsorbed concentration of the species, providing the adsorption isotherm. The numerical value of the distribution coefficient is a function of the properties of the solid substrate and the composition of the solution and must be calculated experimentally for each system of interest, as it cannot be easily transferred from one system to another [26].

The concentration used in the batch experiments has been selected based on values found in different effluents with LAS. In untreated domestic wastewater, concentrations ranging from 1 to 10 mg/L have been observed, while in the case of industrial wastewater, concentrations can reach 38,000 mg/L [1]. In the inlet waters of the treatment plants in Spain, concentrations are typically around 4 mg/L [27]. Other batch studies have used concentrations between 0 and 300 mg/L to investigate remediation treatments using LAS in a natural environment [28].

In this study, batch tests of the sorption equilibrium, with different proportions of sand/soil, were performed by adding 50 mL of LAS (20 mg/L) to 5 g of sorbent (sand or a mixture of sand–soil). This concentration corresponds to 0.2 mg/g of adsorbent, within the range used in the remediation studies mentioned above [28]. A mechanical rotatory shaker was used to agitate the samples at 15 rpm for 24 h. Once equilibrium was reached, the flask was centrifuged at 9000 rpm for 10 min, after which the supernatant was filtered through a 0.45 µm nylon syringe filter unit. LAS determination followed the same procedure mentioned above. From these results, the distribution coefficient between the adsorbed and dissolved concentration was obtained for each of the homologues studied.

The relationship established in the linear adsorption equilibrium between the dissolved and adsorbed concentrations of the contaminant species is expressed through the distribution coefficient, k_d:

$$C_{ads} = k_d\, C_{dis}, \tag{1}$$

where C_{ads} is the adsorbed concentration of the solute in the solid phase (mg/kg adsorbent) and C_{dis} is the concentration of the solute in the solution (mg/L solution). The numerical value of the distribution coefficient, k_d, is a function of the properties of the solid substrate and the composition of the solution.

The Freundlich model is an empirical equation that does not assume homogeneity in the energy of the sites on the surface, imposes no limit on the maximum adsorption load, and exhibits an exponential distribution of active centres characteristic of a heterogeneous surface, as represented by Equation (2):

$$C_{ads} = k_F\, (C_{dis})^{1/n}, \tag{2}$$

where k_F is the Freundlich constant parameter characterising the capacity, and n is the adsorption intensity.

2.3. Modelling with PHREEQC

2.3.1. Tracer and LAS Transport

Using the PHREEQC program, it was possible to model one-dimensional advective–dispersive transport in column tests. To simulate the tests, the program has a data input module called TRANSPORT, where the initial solution in the column and the introduced solution were previously defined. Data output was carried out using the SELECT OUTPUT module, where the output file was specified with the data of interest and processed using spreadsheet software.

For the tracer test, the data obtained with AcuaIntrusion Transport were used (Table 3), and the specific transport parameters were introduced into PHREEQC to achieve the best settings for the tracer breakthrough curves. Additionally, the initial concentration of the solution and the tracer input solution were introduced.

Regarding LAS transport, the species not found in the PHREEQC database, such as LAS homologues (C_{10}LAS, C_{11}LAS, C_{12}LAS, C_{13}LAS), were included in the data entry by indicating the molecular weights so that they appear as species. Also, the irrigation water initially in the column and the water with LAS were included. To model the transport of the LAS pulse, it was necessary to introduce two transport modules, one that refers to the LAS adsorption process and another to model the desorption process, to finally obtain a column free of LAS.

2.3.2. LAS Reactive Transport

To model the chemical processes related to kinetically controlled reactions, it is necessary to incorporate data blocks such as RATES or KINETICS, which allow code in BASIC language [21] to be incorporated into the program to introduce variables and user-defined reaction rate equations.

PHREEQC includes a module where an equation can be introduced to characterise the rate of the adsorption reaction (RATES module). This module includes the expressions of this rate for each of the LAS homologues, first defining all the parameters that appear in it, so that the program can interpret this subroutine and incorporate it into the global calculations. A statement has also been introduced as a limiting factor to indicate that the moles of reactant adsorbed are, at most, those established for equilibrium.

Next, another KINETICS module must be entered into the template with the current and initial reactant moles and reaction parameters, along with those used in the Runge–

Kutta method. This method of solving differential velocity equations, which are integrated over a time step, uses time subintervals to maintain specified errors within tolerances.

The kinetic study of adsorption allows us to determine the rate at which the contaminant is adsorbed and to predict its concentration in solution after a certain contact time with the adsorbent has elapsed. In dynamic column tests, the retardation of contaminants due to the process of adsorption can be modelled with a linear reversible sorption expression [29]. The rate expression for kinetic sorption involving species i is given by Equation (3):

$$r_i = -k_m \left(C_{dis} - \frac{C_{ads}}{k_d} \right), \tag{3}$$

where r_i is the rate of species i in liquid phase (mol/L/h), k_m is the mass transfer coefficient (h^{-1}), C_{dis} is the aqueous concentration of species i (mol/L), C_{ads} is the adsorbed concentration of species i (mol/g sediment) and k_d is the distribution coefficient for linear equilibrium adsorption (L/g). The expression within the parentheses is the thermodynamic distance from equilibrium. The mass transfer coefficient represents the rate limitations due to the transport of the adsorbing species between the bulk solution and the mineral surface.

If the Freundlich isotherm is used, the equation is modified to include the n and k_F ((mg/g) $(\mathrm{mg/L})^{-1/n}$), as shown in Equation (4):

$$r_i = -k_m \left(C_{dis} - \left(\frac{C_{ads}}{k_F} \right)^n \right) \tag{4}$$

where k_m is the mass transfer coefficient, k_d or k_F is the distribution coefficient and n is the adsorption intensity with solids. Here, it is necessary to convert adsorbed moles/gram of sediment to adsorbed moles/L.

3. Results and Discussion

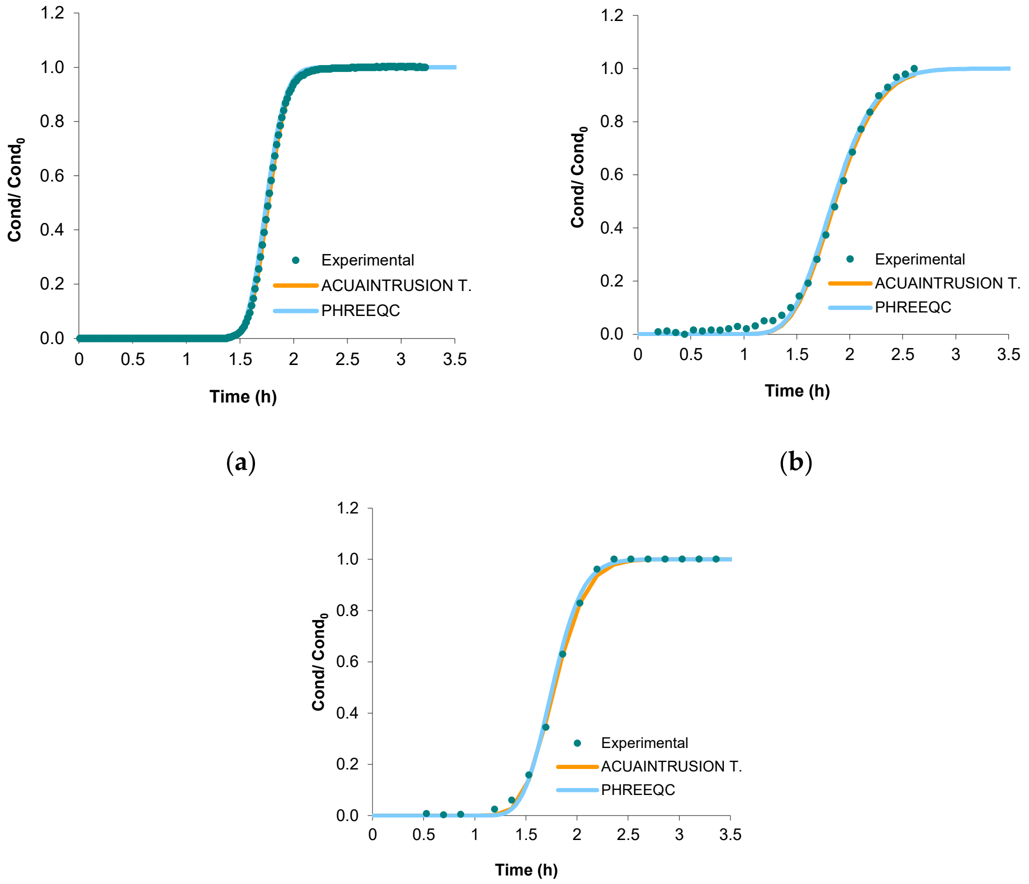
3.1. Transport Modelling in PHREEQC

3.1.1. Tracer Transport

To model the transport of LAS, the TRANSPORT data block of PHREEQC required the input of the parameters that were previously obtained from the experimental breakthrough curve of the tracer ($CaCl_2$). This adjustment required numerous trial and error tests, so the AcuaIntrusion Transport (version 1.00) software was chosen because it provides the best fit to the breakthrough curve. It also uses the column length and diameter with flow rate to provide the hydrodynamic parameters.

Figure 1 shows the fit of the experimental tracer breakthrough curves with those modelled using AcuaIntrusion Transportand PHREEQC. These results indicate that the transport parameters obtained with the AcuaIntrusion Transport software (Table 3) were transformed and used in PHREEQC. As can be seen, PHREEQC shows a good fit, confirming that AcuaIntrusion Transport software facilitates the task of fitting the experimental tracer breakthrough curves.

The simulations carried out in PHREEQC use the block TRANSPORT with the following parameters: cells (the number of cells into which the total length of the column is divided (50)); shifts (the number of steps in which the simulation will be carried out, calculated by dividing the total test time by the time the solution needs to pass through each cell); time step (the result of dividing the length of a cell by the interstitial velocity of the fluid); and the length and dispersivity of each cell. The program also requires the diffusion coefficient, which has been considered to be zero, and it must indicate that the results should be printed.



(**a**) (**b**)

(**c**)

Figure 1. Comparison of the breakthrough curves obtained through experimental tests and modelled with AcuaIntrusion Transport and PHREEQC: (**a**) T0; (**b**) T25; and (**c**) T50.

3.1.2. LAS Transport

Once the suitability of applying PHREEQC has been demonstrated for tracer transport, these parameters were used to model the transport of LAS homologues. As mentioned in Section 2.1, a total pulse of LAS (100 mg/L) was maintained for 5 h, followed by the entry of irrigation water free of this family of compounds, until they were removed in the outlet water. The simulation with PHREEQC requires two TRANSPORT blocks, with the parameters used for the column filled with sand appearing in Table 4.

Table 4. Input parameters of PHREEQC used to model the transport of pulse tests with LAS injection in the sand-filled column.

PHREEQC Parameters	T0
Time step (s)	124
Cell length (m)	4.48×10^{-3}
Shifts (input LAS)	145
Shifts (input-free LAS)	3036
Cell dispersivity (m) (input LAS)	0.71×10^{-3}
Cell dispersivity (m) (input-free LAS)	0.71×10^{-3}

3.2. Reactive Transport of LAS Modelled in PHREEQC

3.2.1. Sand Column Tests Modelled

First, the pulse test was studied in a column filled with sand and compared with previous studies carried out, both in batch and in column, with step adsorption and step desorption.

As mentioned, it is important to know the batch values used as a reference, as they will be the maximum compared to those obtained in the column simulations. The column step simulations for both the adsorption and desorption of LAS provide parameters that can be used as a starting point for the pulse simulation.

PHREEQC modelled the pulse input for a total LAS concentration of around 100 mg/L (100 ppm) with homologue proportions of C_{10}LAS (12.1%), C_{11}LAS (34.1%), C_{12}LAS (30.6%) and C_{13}LAS (23.2%) for 5 h. This modelling accurately predicts the variations observed in the experimental data for all the compounds, whose complete elution takes 60 h. The proportions of the homologs at the input are not maintained at the output (Figure 2). C_{11} shows a value three times higher than C_{12}, even though the input the proportions were similar. For the two lighter homologues (C_{10} and C_{11}), the response is closer to the proportions of the input concentrations and their elution is very rapid, with an initial abrupt increase for both, while for the two heavier homologues (C_{12} and C_{13}), elution was slower over time, appearing much later. The signal obtained for C_{13} presents much lower values than C_{10}, even though its proportion at the input is double and shows a much more delayed elution compared to C_{12}. The modelling presents a good fit with the experimental data using linear adsorption. The values of the parameters k_d and k_m were calculated by trial and error after several simulations (Table 5).

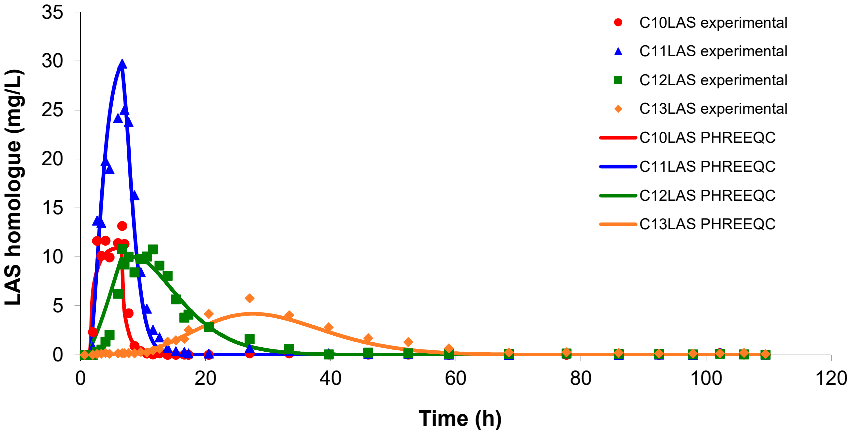
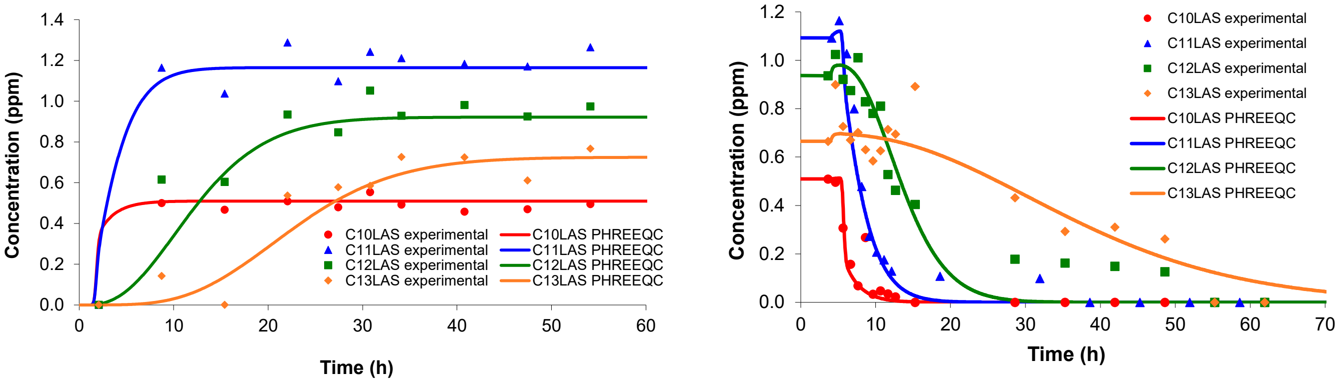


Figure 2. Variation of the LAS homologue concentrations obtained in a column test pulse. The lines showing the fits were obtained with PHREEQC (version 2.18) software in each case.

Table 5. Distribution coefficient, k_d, for batch (Ads. batch) and column test (pulse, adsorption (Ads. step) and desorption (Des. step)) and the mass transfer coefficient, k_m, for the sand column tests introduced in the PHREEQC model.

	k_d 10^3 (L/g)				k_m (h^{-1})		
Homologues	**Ads. Batch**	**Pulse**	**Ads. Step**	**Des. Step**	**Pulse**	**Ads. Step**	**Des. Step**
C_{10}LAS	1.00	0.10	0.10	0.10	0.40	0.25	0.25
C_{11}LAS	1.93	0.35	0.36	0.36	2	1	1
C_{12}LAS	3.76	1.50	1.80	1.30	2	4	4
C_{13}LAS	9.80	4.90	3.50	4.90	8	8	4

In previous studies (Figure 3), experimental step adsorption and desorption tests were carried out [24], in which the constant input concentration of the different LAS homologues occurred in the proportions indicated above, until saturation was achieved. For desorption, the same columns were subjected to a constant input of irrigation water free of LAS until the concentration of each homologue dropped to zero. In this work, the simulation of these step tests has been carried out, and the parameters are very similar to those obtained for the LAS pulse tests (Table 5). Furthermore, Table 5 shows the distribution constants for the linear adsorption obtained in batch (k_d), which are higher in all cases. These constants have been obtained from the experimental isotherms, as discussed in Section 3.2.3.



(**a**) (**b**)

Figure 3. Modelling of sand-filled column tests: (**a**) adsorption; and (**b**) desorption of LAS with input step of 4 mg/L of total LAS.

Comparing Figures 2 and 3, the pulse adsorption and desorption phenomena have very similar shapes to those obtained in the step tests, which is reflected in the similarity to the parameters (Table 5). The longer chain homologues are retained to a greater extent by the porous medium, presenting a higher value of the distribution coefficient k_d. The mass transfer coefficient k_m shows the same trend, with the larger homologues showing greater delay.

In conclusion, the simulations carried out in pulse and step for adsorption and desorption in columns filled with sand show similar values of distribution constants for these two stages, corresponding to the symmetric profiles of the experimental results, with sharp rises and falls. This behaviour agrees with the experimental results obtained in previous works carried out in sand columns for other polluting substances.

3.2.2. Agricultural Soil Column Test Modelling

When replacing part of the sand with agricultural soil, the published pulse tests [8] show very significant variations, making it interesting to model the LAS in solution and obtain the adsorbed concentrations. This approach allows for the evaluation of the surfactant concentrations that would be adsorbed after a wastewater spill in a specific location, which is crucial for studying the environmental impact. Surfactants that are not retained can migrate to deeper areas and contaminate aquifers [30].

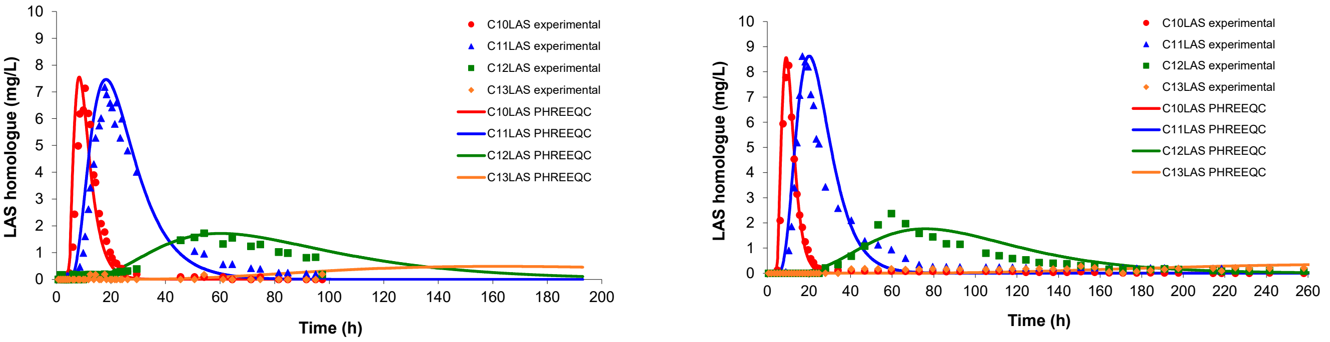
The simulation process with PHREEQC is identical to that discussed in the previous sections for the case of sand, but now the processes are more complex due to the interactions with agricultural soil, which has a varied composition and includes different adsorbent substances that interact with LAS homologues.

New simulations were carried out for columns with a mixture of soil and sand for the pulse tests, considering the transport parameters of the previous tests obtained with the tracer (Figure 1b,c) and applying a linear adsorption and desorption model. To simulate the desorption of LAS, irrigation water was introduced. However, it was necessary to modify the dispersivity in these columns to obtain simulation data closer to the experimental data, which showed slow elution of the homologues. The dispersivity was increased tenfold to achieve a better fit, and the calculation time was also increased (shifts (input-free LAS)). The parameters used in the TRANSPORT module are shown in Table 6.

Table 6. Input parameters used in PHREEQC to model the transport of pulse tests with LAS injection in the tests in agricultural soil columns.

PHREEQC Parameters	T25	T50
Time step (s)	135	130
Cell length (m)	4.48×10^{-3}	4.04×10^{-3}
Shifts (input LAS)	133	138
Shifts (input-free LAS)	5000	8000
Cell dispersivity (m) (input LAS)	3.32×10^{-3}	1.96×10^{-3}
Cell dispersivity (m) (input-free LAS)	33.2×10^{-3}	19.6×10^{-3}

The experimental and modelled LAS homologue concentrations show a good fit (Figure 4). The input homologue proportions remained constant, as in the sand test (C_{10}LAS (12.1%), C_{11}LAS (34.1%), C_{12}LAS (30.6%) and C_{13}LAS (23.2%)). However, the results show that C_{10} and C_{11}, with similar maximum concentrations for both T25 and T50, had a small difference in the elution times, in contrast with T0, where both homologues increased their concentrations simultaneously and maintained the inlet proportions. Although C_{11} and C_{12} have the same proportion in the input LAS, the responses obtained are very different, with a C_{12} concentration that is four times lower and a substantial delay in the elution time. In the case of C_{13}, although its concentration was double that of C_{10}, the elution occurred with a much greater delay over a long time and at very low concentrations near to the analysis detection limit.



(**a**) (**b**)

Figure 4. Concentration of LAS homologues during the assay, as obtained experimentally and with PHREEQC: (**a**) T25; and (**b**) T50.

The simulation carried out with PHREEQC for a LAS pulse of 5 h matched the variations observed in the experimental data. After 60 h, there was complete elution for C_{10} and C_{11}, while for C_{12}, complete elution was reached at 200 h. However, complete elution for C_{13} could not be determined due to the long elution time. The modelled result presents a good fit with the experimental data for C_{10}. In the case of C_{11}, the desorption part presents slight differences, which are also observed for C_{12}. The values of the parameters k_d and k_m for this pulse simulation are shown in Table 7.

The behaviour of the adsorption parameters follows the same trends observed in the sand column results, showing longer elution times for the heavier homologues and higher values in the columns with increasing amounts of agricultural soil present. The batch adsorption values showed higher k_d values in all cases, as expected.

Table 7. Mass transfer coefficient k_m, distribution coefficient k_d, and k_d ads. batch (batch values) obtained for the tests in sand column (T0) and columns with agricultural soil mixtures (T25 and T50), introduced in the PHREEQC model.

	T0			T25			T50		
Homologues	k_m (h^{-1})	k_d 10^3 (L/g)	k_d **Ads. Batch** 10^3 **(L/g)**	k_m (h^{-1})	k_d 10^3 (L/g)	k_d **Ads. Batch** 10^3 **(L/g)**	k_m (h^{-1})	k_d 10^3 (L/g)	k_d **Ads. Batch** 10^3 **(L/g)**
C_{10}LAS	0.4	0.10	0.995	20	1.00	1.86	20	1.12	4.27
C_{11}LAS	2	0.35	1.93	20	3.4	5.64	20	3.70	10.9
C_{12}LAS	2	1.50	3.76	20	14	16.1	20	17.0	29.2
C_{13}LAS	8	4.90	9.80	40	40	47.4	40	70.0	81.8

The modelled results obtained for the experimental data of the homologues in solution also allows PHREEQC to obtain the values of the adsorbed concentrations of these homologues, as calculated at the end point of the column (Figure 5). In this figure, the normalised concentrations have been calculated, considering the maximum value obtained from the sum of the concentrations of the different homologues, for both the dissolved and adsorbed species. At this point in the column, there is a perfect fit between the normalised maximum concentrations of each homologue in solution and the adsorbed ones, and these maintain their proportions according to the LAS entry (C_{10}LAS (12.1%), C_{11}LAS (34.1%), C_{12}LAS (30.6%) and C_{13}LAS (23.2%)). C_{10} presents a higher proportion in solution than on the adsorbed material. Two homologues with a longer linear chain present the inverse behaviour, highlighting the high adsorbed concentrations of these homologues. In the case of C_{11}, high normalised concentrations are obtained for both the dissolved and adsorbed species, with a much faster elution than those with a longer chain.

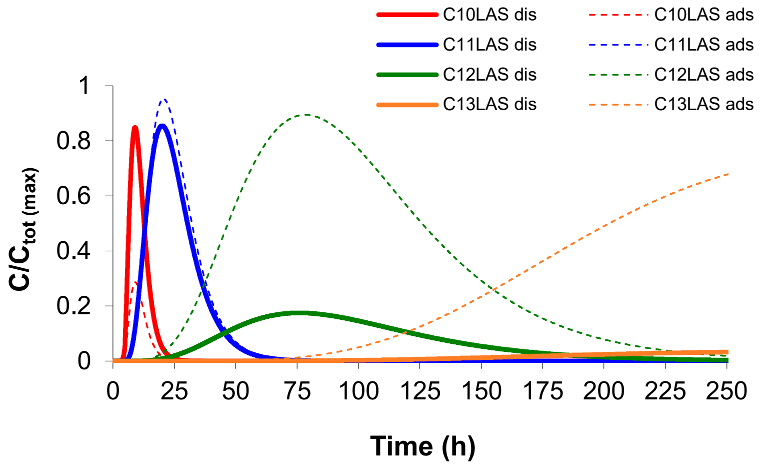


Figure 5. Normalised concentration with respect to the time at the end of the column for both dissolved (dis) and adsorbed (ads) species.

3.2.3. Experimental Batch Isotherms and Proof to Confirm the Use of Linear Adsorption Model in PHREEQC

This section includes the data obtained experimentally for batch isotherms and shows the values of the parameters obtained for linear and Freundlich adsorption, with the latter being preferentially used in LAS adsorption. As explained previously, the batch tests provide data to calculate the adsorption isotherms with different models, providing the maximum values of these coefficients that could be obtained in a dynamic column test. These values can serve as initial guidelines in the PHREEQC model, where the expressions for linear and Freundlich adsorption have been included. The corresponding parameters with the best fit to the experimental curves have been obtained by trial and error with both models. Linear adsorption shows the most consistent results, as will be justified in this section.

Table 8 shows the batch test values of k_d and k_F for the linear and Freundlich adsorption isotherms. These tests were repeated three times and present a relative standard uncertainty, calculated as $u_r(x) = u(x)/x = 2\%$. The results show a very similar increase for both models when the alkyl chain is longer and when different proportions of agricultural soil increase in the sorption medium. This is because the agricultural soil contains organic matter and clays that have great adsorption capacity, consistent with previous work [6]. For linear fits, n is 1, and for Freundlich fits, n decreases as the length of the surfactant chain increases, but no clear trend is observed with an increasing soil percentage. The fits obtained for each isotherm present a coefficient of determination (r^2) ≥ 0.97. The mean absolute percentage error (MAPE) between the experimental and calculated compositions for all the components is also presented in Table 8, with values less than 0.19. As both settings are very similar, both models were tested with PHREEQC for modelling the column pulses.

Table 8. Parameters determined from the adsorption in batch experiments for the linear and Freundlich isotherms.

		C_{10}LAS			C_{11}LAS			C_{12}LAS			C_{13}LAS			
	10^3		r^2	n		r^2	n		r^2	n		r^2	n	MAPE
T0	k_d	0.995	0.982	1.0	1.93	0.989	1.0	3.76	0.994	1.0	9.80	0.996	1.0	0.190
	k_F	1.23	0.999	1.4	2.91	0.999	1.3	4.75	0.982	1.2	9.90	0.980	1.1	0.161
T25	k_d	1.86	0.982	1.0	5.64	0.993	1.0	16.1	0.997	1.0	47.4	0.991	1.0	0.032
	k_F	1.74	0.996	1.5	6.41	0.996	1.2	15.4	0.989	1.2	66.5	0.979	0.7	0.012
T50	k_d	4.27	0.970	1.0	12.7	0.970	1.0	29.2	0.986	1.0	81.8	0.990	1.0	0.094
	k_F	3.95	0.981	1.3	12.7	0.993	1.3	30.4	0.996	1.2	140	0.993	0.6	0.063

The modelling of column tests requires introducing the adsorption parameters. The values of the distribution constants in Table 8 have been taken as the initial values; however, it has been necessary to modify these values until good agreement was obtained between the experimental data and the predictions with PHREEQC. Table 9 includes the results of the mass transfer coefficient (k_m), the distribution coefficient (k_F) and the adsorption intensity (n) for the Freundlich model, which were used with PHREEQC for all the tests carried out. As previously mentioned, Freundlich isotherms are preferentially used in LAS adsorption. Initially, this model was used in PHREEQC, providing a good fit to the experimental data, as can be seen in Figure 6, for the T50 test. Note that for each column, n increases with the percentage of soil, showing a greater intensity of adsorption in this medium. Additionally, k_F increases with the length of the alkyl chain.

Table 9. Mass transfer coefficient k_m, distribution coefficient k_F and the adsorption intensity n for the Freundlich model that have been used in PHREEQC for all the tests.

Homologues	**T0**			**T25**			**T50**		
	k_m (h^{-1})	k_F 10^3	n	k_m (h^{-1})	k_F 10^3	n	k_m (h^{-1})	k_F 10^3	n
C_{10}LAS	0.4	0.10	1.0	8.0	0.043	1.5	6.2	0.019	1.7
C_{11}LAS	2.0	0.35	1.0	6.0	0.12	1.5	7.0	0.059	1.7
C_{12}LAS	2.0	1.50	1.0	6.0	0.28	1.5	10.5	0.13	1.7
C_{13}LAS	8.0	4.90	1.0	8.0	31.3	1.5	8.0	31.3	1.7

Note: k_F (mg g^{-1} (mg $L^{-1})^{-1/n}$).

However, k_F decreases when the proportion of agricultural soil increases in the sorption medium. This does not agree with the batch results and suggests that adsorption decreases as the proportion of agricultural soil increases. For this reason, these fits have been discarded, and the linear model has been considered instead. It should be noted that the Freundlich model has an additional parameter (n), which improves the simulation (mean deviation 0.097, lower than 0.168 from the linear model), but the mass transfer and distribution coefficients lose their physical meaning. In simulations carried out in previous works, simpler models with fewer parameters were preferred, even if the fit was not ideal.

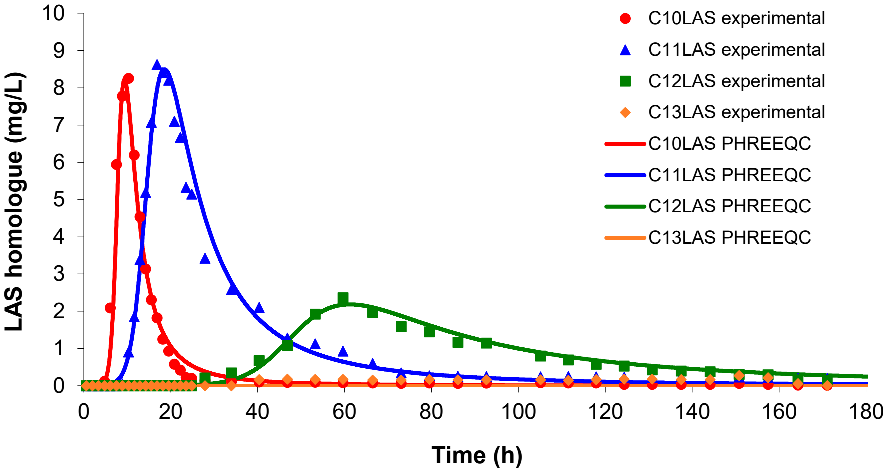


Figure 6. Concentration of LAS homologues during the assay, as obtained experimentally and with PHREEQC at T50, with the Freundlich isotherms.

4. Conclusions

Modelling column experiments allows us to interpret the observed effects at the environmental level and to predict changes when an LAS spill occurs under different conditions. In a sandy soil, the continuous discharge of LAS and the inverse remediation process present similar values of adsorption and desorption constants, which also coincide with those obtained for a point discharge of higher concentration.

In agricultural soil, the additional content of organic matter and clays influences the adsorption capacity. The modelling of these variations demonstrates the increase in adsorption with the length of the alkyl chain and the increasing proportions of agricultural soil, which has been quantified using PHREEQC. The elution times for the heavier homologues and in the columns with a higher percentage of soil are very long, leading to great persistence in the environment due to their adsorption. In the case of contamination of the soil with wastewater, with surfactants, the heavier homologues remain adsorbed for longer periods. Conversely, the lighter homologues, due to their rapid elution and lower adsorption, could be transferred to aquifer formations with a higher proportion of sand, thus contaminating the groundwater and contributing to environmental pollution.

To model the specific discharges of LAS in agricultural soils (25 and 50%), experimental batch tests were carried out in this work to obtain the range of adsorption constants that were used in PHREEQC. These batch isotherms were fitted using linear and Freundlich adsorption models, both of which showed good regression coefficients.

PHREEQC modelled the point discharges with a good fit with the Freundlich model. However, lower values of k_F were observed when increasing the soil–sand proportion, which was not reasonable. For this reason, these fits were discarded, and only the linear model was considered.

The interpretation of environmental data is very challenging, and it is necessary to have models that can predict the effects that may occur during continuous or accidental discharges of surfactants or when they are used in the remediation of contaminated soils.

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