Reactivity and fate of synthetic surfactants in aquatic environments

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Synthetic surfactants are among the chemicals that are produced and consumed in the largest volumes in the world, due to the variety of their applications, mainly as key ingredients in detergents and cleaners. Particular attention has been given to anionic and non-ionic surfactants, which account for up to 90% of overall production of these chemicals, so understanding their distribution, behavior and final fate once they reach aquatic environments is very important.

It is first necessary to develop reliable analytical methodologies for field sampling and laboratory assays, but also to identify the presence and the distribution of possible degradation intermediates. We provide an overview of techniques and protocols currently used – from extraction and purification techniques (e.g., pressurized fluid extraction or solid-phase extraction) – to separation and determination via gas or liquid chromatography coupled to mass spectrometry.

Laboratory tests carried out under controlled environmental conditions are also required for complete characterization of the reactivity of these compounds in both water and sediment columns, mainly by monitoring the influence of the processes of sorption and degradation. We also discuss this topic, taking into account the results from previous laboratory experiments.
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1. Introduction

Since the second half of the twentieth century, there has been exponential growth in production and consumption of organic compounds world-wide. About 1500 new compounds are introduced to the market every year, according to the European Environment Agency (EEA). For most of these substances, most aspects of their environmental behavior are completely unknown, as is their possible impact on ecosystems once they are discharged after use.

Among these compounds, synthetic surfactants are some of the most significant. Demand for these chemicals in 2003 was estimated at more than 9 million tons [1], so they are of special interest. Considerable efforts have been devoted to determining and monitoring them, both through laboratory assays and in the environment, especially in aquatic systems, where they are introduced after their discharge from wastewater treatment plants (WWTPs) and the agricultural use of sludges originating from WWTPs.

Surfactants are employed in a wide variety of applications, mainly in formulation of detergents, but also as ingredients in personal-care products, paints, pesticides, and many other products. As a consequence, many different types of surfactant have been synthesized, although they can be classified in four different groups according to their charge. Most of them belong to the two main groups, anionics and non-ionics, which account for more than 90% of the European output. With respect to anionics, linear alkylbenzene sulfonates (LASs) are the most widely-used surfactants, with total annual production of 434,000 tons in Europe alone, according to data from CESIO (Comité Européen des Agents de Surface et de leurs Intermediaries Organiques). They are commonly employed in household detergents and all-purpose cleaners.

Alkyl ethoxysulfates (AESs) and alkyl sulfates (ASs), which are mostly used as ingredients in shampoos and other personal-care products due to their excellent foaming properties, are second in output, with a combined production of 404,000 tons.

Of the non-ionic surfactants, alcohol polyethoxylates (AEOs) are currently produced in the greatest volume, 747,000 tons in Europe in 2000, and are employed in both domestic and industrial cleaners. In second place by volume are alkylphenol ethoxylates (APEOs), although these compounds have experienced a significant decrease in production volume in recent

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years as a consequence of restrictive environmental policies, aimed at preventing the negative effects, such as estrogenicity, shown by their degradation intermediates.

For several reasons, it is complicated and tedious to identify and to monitor the levels of surfactants once they reach aquatic environments, and to study their behavior and fate in these systems. First, surfactants are often sold as commercial mixtures, which can comprise hundreds of different homologues, isomers and/or ethoxymers, each showing physico-chemical properties that can differ significantly from one to another (e.g., the calculated log K_{ow} for AEOs is 2.67–6.69, depending on the homologue or ethoxymer). Hence, separation and quantification of the components of these mixtures are necessary for better understanding of the environmental behavior of surfactants. This requires the development of powerful analytical methodologies, most of them based on using gas chromatography (GC) or liquid chromatography (LC) and mass spectrometry (MS), as we discuss below. Moreover, analysis of surfactants in environmental matrices presents an additional challenge, especially when dealing with solid samples (e.g., sediment and suspended solids) but also aqueous samples because target compounds tend to be present below the ppb level. Thus, reliable extraction, purification and preconcentration protocols have to be developed for solid and aqueous samples in order to remove as many interferences as possible without sacrificing high recovery values for surfactants and their metabolites.

Knowledge of the reactivity of these compounds in aquatic systems can be partially inferred from available field-sampling data. Degradation and sorption have in this way been identified as the two main processes responsible for removal of surfactants not only after, but also before, they reach aquatic environments [2]. Once used, these chemicals are disposed down the drain to sewers, where it is estimated that 50% by volume is degraded, with 25% sorpted to suspended solids and 25% dissolved [3]. Later, surfactants reach WWTPs, where 95–99% is commonly removed during WWT [4].

Most surfactants used are aerobically biodegraded during secondary treatment, but a considerable fraction is also eliminated in the form of sludges (15–37% in the case of LASs [3] to more than 90% for the most hydrophobic, nonylphenols (NPs) [5]). These sludges, often used in agriculture after previous anaerobic digestion, are also a potential source of contamination for soils, groundwater and adjacent rivers, because they tend to contain relatively large concentrations of surfactants (several g/kg), among other contaminants.

Finally, once surfactants reach the water column, they degrade relatively fast; estimated half-lives are several hours to a few days, depending on the surfactant and environmental factors (e.g., temperature and salinity). However, significant proportions (from about 10% for LASs and AESs to more than 50% for APEOs and AEOs [6]) are attached to suspended solids and end up in sediments, where, below a depth of a few cm, anoxic conditions prevail, so surfactants can be degraded only by slow anaerobic pathways, and they tend to be preserved along the sedimentary column.

Taking all this into account, the behavior of surfactants can be fully understood only after proper characterization of sorption and degradation processes in the laboratory under controlled conditions. In this way, the influence of these processes can be adequately examined and several parameters (e.g., sorption coefficients, half-lives or bioconcentration factors) can be calculated to improve risk assessment of these compounds.

We review procedures for extracting the main synthetic surfactants (i.e. LASs, AESs, APEOs and AEOs) and their metabolites from environmental samples, and for their subsequent identification and quantification, which, in most cases, are performed after purification and preconcentration of extracts. In addition, we also offer an overview of the main findings obtained from previous laboratory tests on degradation and sorption with respect to the study of the environmental behavior of these compounds.

2. Analysis of surfactants and their metabolites in environmental samples

2.1. Extraction

For several decades now, sonication, Soxhlet extraction and liquid-liquid extraction (LLE) have been the techniques most commonly used. Table 1 shows methodologies previously developed using these traditional extraction techniques. Anionic surfactants (e.g., LASs and their degradation intermediates, sulfophenyl carboxylic acids (SPCs)), have been extracted from sediments and suspended solids using Soxhlet extraction and LLE [7–12], which can take 4–14 hours per sample, using methanol as solvent. Sonication, followed by centrifugation, is another option [13], although recoveries tend to be 10–20% less, using the same solvents.

For APEOs and their metabolites, methodologies have been similar to those used for LASs [7,14,15], although methanol tends to be substituted by other more non-polar solvents (e.g., hexane [16,17] or dichloromethane [18]), in order to enhance the extractability of hydrophobic compounds (e.g., NPs). With respect to the extraction of AESs and AEOs from solid matrices, there are fewer papers available, but the use of methanol during Soxhlet extraction [19–21] and of dichloromethane for LLE [22] and sonication [23] has been described.

However, more recently, new extraction techniques have been developed not only to save time, but also to reduce solvent consumption without losing efficiency. Automation is also possible in some cases, such as

Table 1. Overview of extraction protocols applied to major surfactants and their metabolites in environmental samples (sorted by technique)

Compound	Matrix	Technique	Solvent	Time	Clean-up	Recovery	Detection	Ref.
LAS	Soil, sludge	Reflux	Methanol	4 h	C_{18}	>84%	HPLC-FL	[12]
LAS	Sediment, sludge, soil	Reflux	Methanol	2 h	SAX + C_8	>84–87%	HPLC-UV	[11]
NPs, $NPE_{1-2}Os$	Sediment	Reflux	Cyclohexane	3 h	Alumina	82–105%	HPLC-UV	[16]
LAS	Soil, sludge	Soxhlet	Methanol	4 h	SAX	>99%	GC-MS	[8]
LAS, SPC	Sediment	Soxhlet	Methanol	12 h	C_{18} + SAX	75–105%	HPLC-FL	[10]
APs, AEOs, APEOs	Sludge	Soxhlet	Methanol	4 h	C_{18}	69–92%	GC-MS, LC-MS	[20]
LAS, APEOs, APs	Sediment, soil, sludge	Soxhlet	Methanol	4–12h	Not required	85–100%	HPLC-UV	[7]
NPEOs	Sediment	Soxhlet, sonication	Hexane, isopropanol, acetone	18 h	Cyanopropyl	45–103%	HPLC-UV-FL, LC-MS	[17]
NPEOs, NPs	Sediment	Sonication	Methanol	10 min	C_{18}	64–127%	LC-MS	[15]
LAS, DATS	Sediment	Sonication	Methanol	10 min	C_8	65–103%	GC-MS	[13]
LAS, NPEOs, APs, NPECs, PEGs	Sludge	Sonication	Methanol, dichloromethane	20 min	C_{18}	>84%	LC-MS	[23]
LAS, SPCs	Soil	PFE	Methanol, water	15 min	C_{18}	52–85%	LC-MS	[24]
LAS, AES	Sediment	PFE	Methanol	20 min	C_{18}	55–125%	LC-MS	[19]
APs, APECs, APEOs	Sediment	PFE	Methanol, acetone	15 min	C_{18}	73–97%	LC-MS	[26]
LAS, AS, AES, NPEOs, AEOs, SPCs, APECs	Sediment	PFE	Methanol	20 min	C_{18}	70–107%	LC-MS	[27]
NPs, NPEOs	Sediment	Soxhlet, PFE, MAE	Methanol	10 h, 15–20 min	Alumina, Florisil	Not spec.	HPLC-FL	[25]
LAS, SAS	Sludge	SFE	CO_2	15 min	Not required	>90%	GC-MS	[28]
NPECs	Sludge	SFE	Water, ethanol	20 min	SAX	>98%	GC-MS	[30]
LAS, DATS, SAS, AS, AES, NPEOs, APs, NPECs	Sludge	SFE	Water	27 min	GBC	>87%	LC-MS	[29]
LAS	Sediment	MAE	Water	90 min	C_{18}	>90%	HPLC-FL	[31]
LAS, SPCs	Fish	MSPD	Hexane, ethyl acetate, methanol, water	Not specified	GBC	>65%	HPLC-FL	[40]

pressurized fluid extraction (PFE). Table 1 also shows an overview of different protocols recently developed using these more modern techniques. Regarding PFE, also known as accelerated solvent extraction (ASE) or pressurized liquid extraction (PLE), high temperatures (100–200°C) and pressures (about 150 atm) are used to allow solvents to remain in their liquid state and to increase the efficiency of the extraction process. Previously tested on persistent organic pollutants (e.g., polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs)) PFE can obtain an extract in less than 20 min with a low solvent consumption (<50 mL) and without sacrificing high recovery values.

For surfactants, there are still relatively few studies dealing with this approach: most of them refer to their extraction from WWTP sludges and, less frequently, from sediments. Methanol is commonly used as solvent to perform the extraction of LASs [24], NPEOs [25] and metabolites, although solvent mixtures using acetone or hexane can be also employed for NPs and other more hydrophobic compounds [26]. Temperatures of 100–120°C are often employed, and a standard pressure of 150 atm, although Petrovic et al. [26] observed volatilization of NPs under these conditions, so they suggested a lower extraction temperature (50°C). With respect to AESs and AEOs, there are only a few recent protocols for performing their extraction from marine sediments [19,27] using PFE and methanol as solvent.

Supercritical fluid extraction (SFE) is another recent extraction technique that has been applied sometimes for extracting surfactants from environmental samples. It uses CO_2 or water instead of organic solvents to carry out the extraction within 15 min and, in most cases, no further clean up is required. SFE has been successfully applied to the extraction of LASs from sludges [28], as well as for the extraction of anionic and non-ionic surfactants [29] and polar metabolites such as nonylphenol ethoxycarboxylates (NPECs) [30].

Microwave-assisted extraction (MAE) also functions well for extracting LASs, NPEOs and their degradation

intermediates from river sediments and sludges [25]. Extractions are achieved in less than 20 min at 120°C, using methanol as solvent in most cases. Apart from its rapidity, another advantage of MAE is that it can also be combined with Soxhlet extraction [31] in order to increase its efficiency, and even water can be used instead of organic solvents for extracting LASs.

2.2. Preconcentration and purification

Both sediment extracts and aqueous matrices commonly contain organic and inorganic compounds that can cause interference when trying to identify and to quantify the concentration of surfactants and their metabolites in samples. In addition, the presence of these target compounds in river and marine waters tends to be at the ppb level or below. These are two of the main reasons why it is necessary, in most cases, to perform purification and preconcentration before proceeding with analysis.

There are several techniques to accomplish this step, although SPE has become the most widely used. Several specific materials (e.g., some silica compounds) can retain surfactants and their metabolites within the solid phase while the rest of the liquid sample passes through them, removing water, salts and other contaminants from the sample in the process. Later, target compounds can be eluted from the material using an organic solvent, so that a clean extract is obtained.

SPE has been widely used for isolating LASs from water samples, using octadecyl silica (C_{18}) or octasilica (C_8) as the solid phase [12,13,24], while methanol (the same solvent as was used for extraction) is commonly used as elution solvent.

Better purification is obtained if strong anionic-exchange (SAX) SPE cartridges are also used [10,11] due to the negative charge of these surfactants and their metabolites (SPCs). It is advisable to lower the pH of the sample and/or add significant amounts of sodium chloride [10] (salting-out effect) to improve the retention of these degradation intermediates due to their high polarity, especially in the case of short-chain homologues, where low recoveries are often obtained. In some cases, SAX has been used alone [8,9], with methanol mixed with hydrochloric acid being selected as elution solvent, whereas other authors [32] have preferred to use graphitized black carbon (GBC). All these materials – silica, SAX and GBC – have also been successfully employed to isolate AESs from river [33] and marine waters [19].

In recent decades, a wide variety of different protocols has also been developed for extracting non-ionic surfactants from water samples (e.g., NPEOs and their more polar metabolites (NPECs) can be isolated by means of GBC cartridges [34]), which are eluted using dichloromethane or methylene chloride as solvents. Octadecyl silica has also been employed by many authors to carry out the extraction of NPs and short-chain NPEOs ($NPE_{1-3}Os$) [26].

Other options include the use of alumina [18,25], SAX [30] or various polymers [17]. With respect to AEOs, most authors have opted for a silica cartridges, of the various types available (from C_2 to C_{18}), to deal with water samples. Elution is performed with solvent mixtures containing methanol, dichloromethane and/or acetonitrile [35]. Other materials recommended for this use include alumina [21], SAX [36] and GBC [37]; GBC can also retain polyethylene glycols (PEGs), which are polar degradation intermediates of AEOs.

However, for application of SPE to simultaneous purification of several types of surfactants, the variety of validated protocols is severely limited. Most authors employ C_{18} cartridges because they are suitable for a wide range of organic pollutants. In this context, Marcomini et al. [38] used C_{18} for simultaneous extraction of LASs, NPEOs and NPs from marine waters and wastewaters, using acetone as elution solvent, although methanol is also effective. In addition, AEOs can also be isolated using mixtures of hexane, dichloromethane and methanol [23]. These solvents have been employed in recent protocols [20,39] for isolating both non-ionic surfactants (NPEOs and AEOs) and their metabolites (from NPs to NPECs and PEGs), in a single stage, by fractional elution. The simultaneous extraction of anionics and non-ionics, as well as their carboxylated metabolites (SPCs and NPECs), from river and marine waters has been reported [27]. GBC cartridges are useful for extracting NPEOs and their degradation intermediates as well as several anionics (e.g., LASs and AESs) at the same time [29,33].

In the past few years, advances in SPE have resulted in the development of new related techniques (e.g., matrix solid-phase dispersion (MSPD), which allow target compounds to be extracted and purified simultaneously from solid matrices). In the case of surfactants, this has been applied mainly to fish samples [40], where aliquots are taken and mixed with octadecyl silica in a column, in order to isolate LAS and SPCs, as well as non-ionics. First, the column is eluted using strong non-polar solvents (e.g., hexane) to remove fats. A clear extract containing surfactants is then obtained after another elution with methanol or a similar solvent.

Solid-phase microextraction (SPME) and stir-bar sorptive extraction (SBSE) are two of the latest options for significantly reducing the time needed for sample preparation. Most protocols described were developed for analysis of regulated compounds (e.g., pesticides, hydrocarbons and other volatile organic compounds), although some authors have attempted to use them for the extraction of AEOs [41] and alkylphenols (APs) [42] from aqueous samples.

In analysis of regulated compounds, SPME polyacrylate fibers were used as passive samplers in marine water, so freely-dissolved AEOs diffused from the aqueous phase onto the polymer coating of the fiber. AEOs were

then extracted from the fibers using methanol. Concentrations in water samples could therefore be calculated after correct characterization of the polymer-water partitioning coefficient of AEOs.

SBSE is a similar technique, but the amount of polymer is increased from 0.5 μL in SPME fibers up to 300 μL in SBSE bars, thus boosting sensitivity. In addition, and due to the volatility of APs, these compounds can be thermally desorpted from the bars for direct analysis by GC.

2.3. Separation, identification and quantification

Over the years, analysis of surfactants in environmental samples has been carried out using several methodologies. Spectrophotometric methods using methylene blue, capillary electrophoresis or potentiometric detection have been tested, although their sensitivity and/or specificity tend to be low. Chromatographic techniques, both GC and high-performance LC (HPLC), coupled to various types of detector are preferred in most cases due to their ability to separate and to identify each component in a surfactant mixture. In this respect, although GC is more suitable for volatile compounds, it has been successfully applied to analysis of anionics in water samples using flame-ionization detectors (FIDs) [43]. Moreover, GC columns have proved to be very effective for identifying each isomer present in LASs due to their good capability for separation. The main drawback of GC is that anionic surfactants and their metabolites need to be derivatized before injecting them into the GC system because they are not volatile. Several reactants (e.g., trifluoroethanol [9,32,43]) have been tested to make this possible.

With respect to non-ionics, some metabolites (NPs and short-chain NPEOs) are volatile enough to be analyzed directly by GC, but most NPEOs and AEOs needs to be derivatized first, using methylene iodure [30], n-propanol/acetylene chloride, pentafluorobenzyl bromide [18] or hydrogen bromide [37]. After separation, MS is commonly used to detect target compounds. MS is preferred over other detectors because it allows analytes to be identified unequivocally by measuring their parent masses and displaying specific fragmentation patterns after their ionization and rupture, respectively (e.g., there are several papers dealing with simultaneous GC-MS analysis of LASs and SPCs [32], as well as other anionics (e.g., dialkyl tetralin sulfonates (DATSs) [13], secondary alkane sulfonates (SASs) [28] or tetrapropylenebenzene sulfonates (TPSs) [9]).

Both electron impact (EI) and chemical ionization (CI) modes are used, although CI is recommended for anionics due to its higher sensitivity.

LC is currently one of the most commonly used techniques for analyzing surfactants in the environment, partly due to its advantages over GC because prior derivatization is unnecessary in most cases. In addition, the presence of a benzene group facilitates the use of ultraviolet (UV) and fluorescence (FL) detectors coupled to HPLC, for identifying aromatic surfactants (e.g., LASs and APEOs) and their degradation intermediates.

Reverse-phase HPLC columns are often employed for LASs and SPCs, mainly RP-18 [11,12] and RP-8 [7,10], with solvent mixtures containing water, acetonitrile and/or methanol as the mobile phase. Better separation of different homologues and isomers is achieved when salts (e.g., $NaClO_4$ and tetraethyl ammonium hydrogen sulfate) are used as modifiers. Simultaneous analysis of LASs and NPEOs in water samples is also possible with RP-18 and RP-8 columns and UV-FL detectors [7,14,38].

Apart from reverse-phase HPLC columns [25], normal-phase HPLC columns made of amino-silica can also perform efficient separation of each NPEO ethoxymer and some of their metabolites [7,16], although the elution order is reversed (i.e. more hydrophobic compounds, such as NPs, elute first and NPECs last) and stronger non-polar solvents (e.g., hexane, iso-octane, and methylene chloride) are preferred.

However, determination of aliphatic surfactants (e.g., AEOs and AESs) has not been studied so much because they lack FL, so prior derivatization is required (e.g., HPLC-UV-FL was employed for the analysis of AEOs, previously derivatized using phenyl-isocyanate [44]). There are also a few studies [33,36] on AESs and PEGs, which were previously derivatized using naphthyl isocyanate and naphthyl chloride. RP-18 columns and methanol/water or acetonitrile/water mixtures were used as mobile phases.

Development of new interfaces (e.g., electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI)) has represented a huge advance in analysis of all kind of polar organic pollutants, including surfactants, because they allow HPLC-MS to be used. Before this, several authors had been able to identify a wide range of surfactants from their mass spectra, using flow-injection analysis (FIA) [39].

Nowadays, HPLC-MS has replaced HPLC-UV-FL in most studies because HPLC-MS provides unequivocal identification of surfactants by means of their molecular weight, retention time and mass spectra. Moreover, detection limits can be lowered to the ppt level if MS^n is employed, as reported in the recent review by González et al. [45], who discussed in detail the utilization of different MS detectors for analysis of surfactants in wastewater.

LASs and SPCs were determined in both freshwater [24] and marine environments [46], preferably by means of HPLC-MS under negative ion (NI) mode, due to the presence of a sulfonate group. The quasi-molecular ions $[M-H]^-$ and their characteristic fragment $m/z = 183$ were used for identification and quantification.

AESs have also been monitored in aquatic systems [19] in a similar way, but $m/z = 97$, corresponding to $HO - SO_3^-$, was selected as the characteristic fragment.

Non-ionic surfactants are analyzed by positive ion (PI) mode, scanning their molecular ions $[M + H]^+$ and, in most cases, adducts created when these compounds are associated with water $[M + H_3O]^+$, sodium $[M + Na]^+$ or other salts. Thus, sodium acetate [15,17,26] or ammonium acetate [34] are commonly added to the samples or mobile phase in order to increase the MS response of NPEOs and AEOs and to stabilize the generation of $[M + Na]^+$ or $[M + NH_4]^+$ ions. In this way, each ethoxymer can be quantified, although those containing few ethylene groups (typically 0–4) show low signal intensities. Some authors have avoided this issue by using derivatizing agents [35].

Another advantage of MS compared to other detectors is that several types of surfactant can be analyzed in a single run (e.g., NPEOs and AEOs, and even PEGs, can be separated using an adequate gradient and later analyzed under PI [20,22]).

However, determination of metabolites (e.g., NPs and NPECs) is often carried out in another run [20,26,29] under NI, and occasionally at the same time as anionics [23].

But, recent methodologies [15,17,34] allow simultaneous determination of NPEOs, NPs and NPECs, switching the polarity from NI to PI (or vice versa). This has been also applied for the analysis of anionic and non-ionic surfactants and their carboxylated metabolites (SPCs and NPECs) in marine and freshwater samples [27] (Fig. 1).

3. Laboratory tests for studying the reactivity of surfactants

3.1. Sorption assays

Sorption processes are responsible for removing surfactants from the water column and facilitating their transport to the riverbed or seabed. They also inhibit degradation because the bioavailability of these compounds can be severely reduced by sorption processes. Field sampling has shown that sorption percentages for LASs onto suspended solids were <3% in rivers, 11–59% in estuaries and 30–59% in the sea, so there is a clear relationship between salinity and sorption for LASs, which can also precipitate in the form of calcium and magnesium salts [47]. However, more polar LAS metabolites (SPCs) have shown sorption percentages below 1% [48]. But, NPEO sorption can reach 25–75% [49]. More detailed information is obtained when particular homologues and/or ethoxymers are considered [50]: the more hydrophobic compounds (e.g., NPs, $NPE_{1-2}Os$ and $C_{13}LAS$) show higher concentrations in sediment and suspended solids, whereas those having a higher solubility (e.g., NPECs, short-chain SPCs and $C_{10}LAS$) are predominant in the dissolved form. A similar tendency can be inferred for AESs and AEOs from the few studies of their occurrence in the field [6,50].

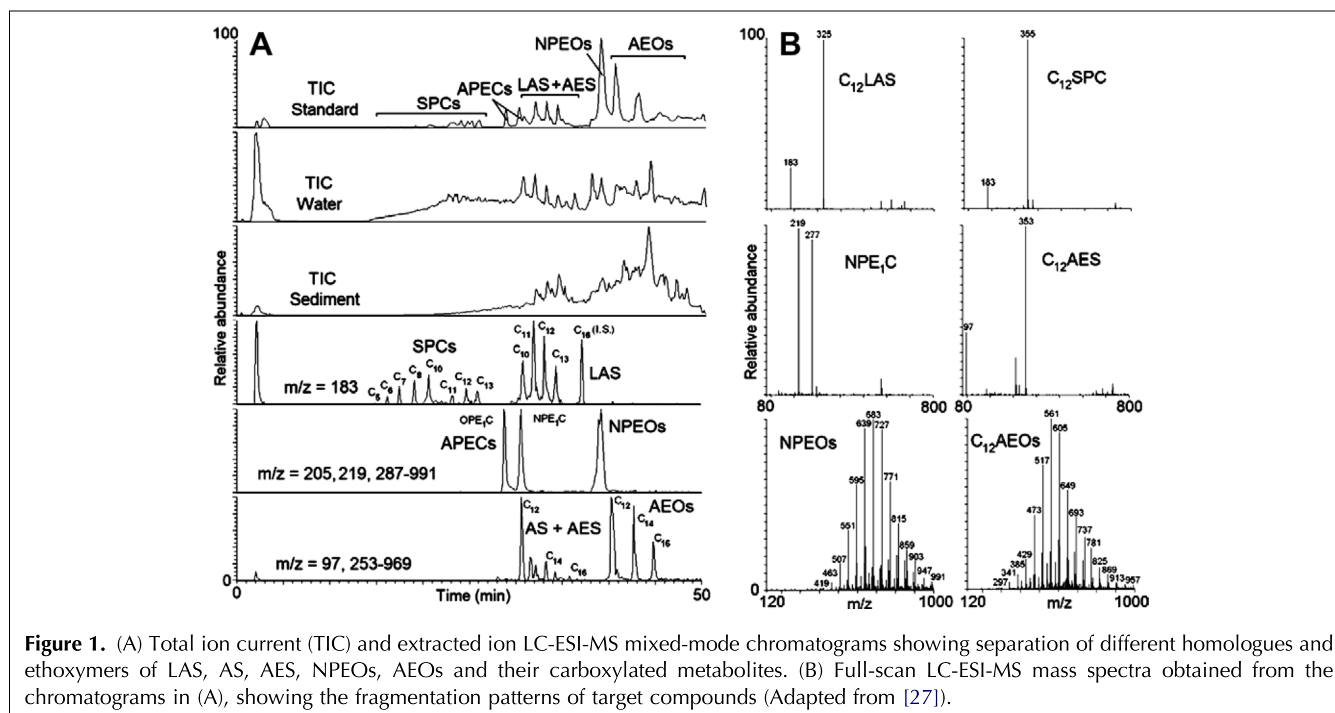

Figure 1. (A) Total ion current (TIC) and extracted ion LC-ESI-MS mixed-mode chromatograms showing separation of different homologues and ethoxymers of LAS, AS, AES, NPEOs, AEOs and their carboxylated metabolites. (B) Full-scan LC-ESI-MS mass spectra obtained from the chromatograms in (A), showing the fragmentation patterns of target compounds (Adapted from [27]).

Table 2. Overview of sorption experiments carried out with major surfactants (sorted by target compound)

Compound	Matrix	Parameters	Value	Detection	Ref.
LAS	Marine sediment	K, n	78–1145, 0.74–1.38	HPLC-FL	[51]
LAS	Sediment	log K, n	0.58–2.27, 0.86–0.93	Radiolabeled LAS	[53]
LAS	Marine sediment	K, 1/n	22.3–208, 0.63–1.17	Methylene blue	[52]
LAS, SPC	Marine sediment	K	40–459, 1–7	HPLC-FL	[55]
LAS	River sediment	log K	1.65–3.48	Radiolabeled LAS	[54]
AS	Estuarine sediment	K, n	2440–2700, 1.09	Radiolabeled AS	[56]
NPEOs	River sediment	K	230–1460	HPLC-UV	[58]
AEOs	River sediment	K, n	110–590, 0.45–0.97	Radiolabeled AEOs	[61]
AEOs	Sludge, river suspended solids	K	1740–19400, 770–8970	Radiolabeled AEOs	[62]
AEOs	Sediment	log K, n	1.60–1.79, 0.74–0.88	Radiolabeled AEOs	[60]
AEOs	Lake sediment	log K	1.61–3.79	HPLC-UV	[57]

Laboratory studies carried out with surfactants have enabled field observations to be confirmed and the sorption process to be understood in detail. Table 2 gives an overview of the main results. However, as also found with field data, most laboratory assays have been conducted only on LASs, which are sorpted relatively rapidly onto suspended solids (often only 4 h or less are needed to reach equilibrium [51]). This sorption takes place by a hydrophobic mechanism in which Van der Waals interactions are predominant. The sorption process can be fitted to a Freundlich isotherm in most cases [51–53] and it is strongly influenced by environmental factors (e.g., pH, salinity and the carbon and clay content of the particulate phase). LAS-sorption capacity therefore increases when the values of any of these factors increases [53]. LAS-sorption capacity also increases as the length of the alkyl chain increases, as well as for most external isomers. On this point, the sorption coefficient (K_d) for LAS homologues was calculated in marine sediments to be in the ranges 78–96 L/kg for C_{10}LAS, and 1112–1145 L/kg for C_{13}LAS [51].

Hand and Williams [54] estimated that K_d values increased by 2.8 for every carbon unit that was added to the alkyl chain and by 2 from internal to external isomers. However, LAS metabolites have very low K_d values – about 1 L/kg for C_{11}SPC according to Léon et al. [55] – due to the introduction of a carboxylic group. The behavior of other anionic surfactants (e.g., ASs and AESs) is not so well characterized, although they seem to have a sorption capacity similar to LASs, since K_d values for sodium dodecyl sulfate in estuarine sediments have been found to be 2440–2700 L/kg [56].

With respect to non-ionics, two different sorption mechanisms have been considered to explain the results obtained from laboratory tests. As in the case of LASs, the first mechanism is accounted for by hydrophobic interactions between the alkyl chain of NPEOs and AEOs and the particulate phase; hence, the sorption capacity of homologues is directly proportional to the length of this hydrocarbon chain [57]. Hydrophilic interactions between ethylene groups of these surfactants and sediments, via hydrogen bonds, have been also characterized [58], so, although those ethoxymers containing a reduced number of these groups tend to be firmly attached to particulate matter (e.g., $NPE_{1-2}Os$), it has been observed that sorption capacity increases in line with the length of the ethoxylated chain.

Droge and Hermens [59] have recently described the sorption of AEOs onto marine sediments using a model that combines Langmuir and linear sorption. This model considers that, at low aqueous concentrations, as found in the field, adsorption is predominant over absorption, so K_d values for these compounds are higher than when high aqueous concentrations are employed during laboratory tests. In addition, and in contrast to anionic surfactants, changes in environmental conditions regarding pH, salinity and carbon content have shown little, if any, effect on the sorption of AEOs, according to Brownawell et al. [60]. Sorption-coefficient values have been calculated in river sediments [57,61,62] for this surfactant (40–7000 L/kg) and for NPEOs [58] (230–1460 L/kg).

3.2. Aerobic degradation assays

Aerobic degradation tests are carried out in the laboratory to characterize the process whereby surfactants are removed from the water column, enabling description of:

- mineralization rates and half-lives to be calculated;
- the influence of environmental factors (e.g., temperature, salinity, pH, and microbial populations) to be determined;
- degradation products to be identified; and,
- even the metabolic pathways involved in this process.

Table 3 gives an overview of the main results from previous aerobic degradation tests carried out on target compounds. In general terms, both anionic and non-ionic surfactants undergo rapid degradation in the presence of oxygen, which is in accordance with the current environmental legislation. For example, it can observed that LAS primary degradation is complete in 4–5 days in fresh waters [63,64], LASs showing an average half-life of some 10–15 h.

Table 3. Overview of aerobic degradation experiments carried out with major surfactants (sorted by matrix)

Compound	Matrix	Parameters	Values	Time	Detection	Ref.
LAS, iso-LAS, DATS	Fresh water	Degradation %, mineralization %	100% in 5, 10 & 17 d, 100%, 60% & 65% after 5 months	>5 months	LC-MS	[63]
AEOs	Fresh water	Degradation %	100%	2 weeks	LC-MS	[77]
AS, NPEOs, AEOs	Fresh water	Degradation %	41–98%, 31%, 44–88%	30 d	Radiolabeled NPEOs & AEOs	[75]
AEOs	Fresh water	Half-life, degradation %	10–58h, 4–10 d	16 d	HPLC-FL	[74]
Iso-LAS, DATS	Fresh water, soil, sediment	Half-life, mineralization %	2–20 d, 3–50%	40 d	Radiolabeled LAS & DATS	[66]
NPEOs	River water	Degradation %	99% after 4 d	31 d	LC-MS	[71]
LAS	River water, sediment	Half-life	15–33 h	21 d	Radiolabeled LAS	[65]
AES, AEOs	Estuarine water	Half-life, mineralization %	2.3 d, 75–97%	30 d	Radiolabeled AES & AEOs	[76]
NPEOs	Estuarine water	Degradation %	100% after 4–14 d	90 d	GC-MS	[69]
LAS, SPC	Seawater	Degradation %,	>99%	400 h	HPLC-FL	[67]
LAS, SPC	Seawater	Half-life, degradation %	6.2 d, 9.6 d, 100%	42 d	HPLC-FL	[64]
APEOs, $APE_{1-2}Os$, APs	Sludge	Half-life, mineralization %,	8.2–13.6 d, >90% after 35 d	35 d	GC-MS, HPLC-FL	[70]

Larson et al. [65] reported that mineralization of LASs reached 70–90% in less than 1 week (an average half-life of about 24 hours), whereas these values were lower (56–76% in 30 days) in other tests conducted by Nielsen et al. [66]. The speed of this process is significantly affected by the temperature [64] (from 7 days at 25°C to 25 days at 13°C), as well as by the acclimatization period needed for the microbial populations before starting the test. The microbial populations found in seawater differ in nature, so degradation can be slower [67]. With respect to the different LAS homologues and isomers, it has been found that those with longer alkyl chains and with the benzene group in an external position are more susceptible to biodegradation. LAS co-products (e.g., iso-LAS and DATS) are also more persistent than LASs, due to the presence of branches and cycles in the alkyl chain, respectively. Although their primary biodegradation is complete [66], LAS co-products have longer half-lives (up to 20 days) and they were still not fully mineralized after one month. With respect to the LAS-degradation pathway, this starts with an initial ω-oxidation in the alkyl chain, so an SPC of the same length as the parent compound is generated. Successive β-oxidations and α-oxidations then take place until the compound is fully mineralized. Complete degradation of these intermediates is slower than for LASs, taking 12.5 days compared with 6 days in seawater [67], with those with alkyl-chain lengths of 6–9 predominant. This aerobic degradation pathway has been confirmed in many papers describing the presence and the distribution of SPCs and the disappearance of parent compounds in aquatic systems, especially in surface waters. SPC acids have been identified in rivers in several parts of the world [5,48], where they generally have concentrations under 50 μg/L, or even lower in coastal zones [50]. However, there are exceptions (e.g., where circulation is restricted and/or wastewater discharges are untreated) where concentrations of more than 100 μg/L have been detected [48]. Although disulfophenyl carboxylic acids (SPDCs) account for a much lower proportion, Di Corcia et al. [63] have observed these intermediates being generated when two ω-oxidations occur. In addition, the presence of α,β-unsaturated SPCs, also known as SPC-2H, has been confirmed in laboratory assays [68].

For non-ionic surfactants, most laboratory tests have been carried out with NPEOs. Their primary biodegradation is relatively fast, taking 4–24 days, depending on the conditions, and their mineralization is typically 50–80% [69–71]. Those NPEO ethoxymers with higher molecular weight appear to be more recalcitrant [72].

Most previous studies have confirmed that degradation takes place by progressive shortening of the ethoxylated chain in successive hydrolysis reactions and, finally, oxidations [69,73]. There is therefore an accumulation of $NPE_{1-2}Os$ and $NPE_{1-2}Cs$. Most recent studies [70–72] have shown that oxidation of the ethoxylated chain can prevail over hydrolysis because NPECs are the most abundant metabolites, accounting for 69–98%. From analysis by LC-MS, long-chain NPECs that were degraded to NPE_2C have been identified [71]. CAPECs (alkylphenol diethoxycarboxylates) have also been identified recently, appearing as a consequence of ω-oxidation and later α,β-oxidation of the alkyl chain [71]. Field sampling has confirmed the occurrence of these metabolites in the environment. Levels of NPs, $NPE_{1-2}Os$ and NPECs have therefore been monitored along several rivers and coastal areas, where concentrations of a few ppb are often found [2,15,17].

Finally, although AESs and AEOs have received less attention from the scientific community, especially in

Table 4. Overview of anaerobic degradation experiments carried out with major surfactants (sorted by matrix)

Compound	Matrix	Parameters	Values	Time	Detection	Ref.
LAS	Sludge	Half-life	2.1–2.6 d	21 d	Radiolabeled LAS	[65]
LAS	Sludge	Removal %	64–85%	3–4 months	HPLC-FL	[87]
LAS	Sludge	Removal %	0–12%	42 d	LC-MS	[89]
LAS	Sludge	Removal %	20–37%	130 d	GC-MS	[86]
$NPE_{1-2}Os$	Sludge	Degradation %	>80%	150 d	Radiolabeled NPEOs, GC-MS	[82]
LAS, DATS, AS, AES, NPEOs, NPECs, NPs, AEOs	Sludge	Removal %	5–7%, 6–11%, 6–30%, 3–21%, 40–60%, 74–97%, 0%, 33–86%	14 d	LC-MS	[29]
AS, AEOs, NPEOs	Sludge	Removal %	60–85%, 30–40%	50 d	Pressure transducer	[78]
AEOs	Sludge	Mineralization %	85–99% after 22–25 d	40 d	HPLC-FL	[80]
AES, AS	Sludge	Mineralization %	88% after 17 d, 80 after 15 d	28 d	Radiolabeled AES and AS	[79]
AEOs	Sludge	Mineralization %	16–93%	40–109 d	LC-MS	[81]
LAS	Sediment	Half-life, degradation %	90 d, 13–79%	165 d	LC-MS	[88]
LAS, AEOs	Sediment	Mineralization %	0%, 3–40%	87 d	Radiolabeled LAS and AEOs	[84]
NPEOs	Sediment	Half-life	289 d	120 d	Radiolabeled NPEOs, LC-MS	[72]

studying occurrence and distribution in aquatic systems, their aerobic degradation has been investigated by several authors. Primary degradation of ASs or AESs and linear AEOs is fast, as they are reported to disappear completely from fresh waters after 2.5–6 days and 3–4 days, respectively [33,74]. They are also mineralized [75,76] (64–almost 100% in 30 days, and with an estimated half-life of 3–4 hours and 2.3 days). Degradation seems to be more efficient for those linear AEOs with shorter alkyl and/or ethoxylated chains [74], and their degradation pathway involves the central cleavage of the ether bond between the two chains, so fatty acids and polyethylene glycols (PEGs) appear. These PEGs are biodegraded via generation of carboxylic acids, although this process is slower. However, branched AEOs are less susceptible to degradation, showing lower percentages of primary degradation and mineralization (44% after 30 days) [77]. Their degradation pathway differs from that of the linear AEOs, and it starts with the ω-oxidation of the alkyl chain, followed by successive α,β-oxidations, so alkylcarboxylated metabolites (named CAEOs) are generated. Identification of ethoxycarboxylates (named AEOCs) proves that a progressive shortening and oxidation of the ethoxylated chain also occurs. Generation of dicarboxylic acids (named CAEOCs) is also described in laboratory tests during the final stages of degradation. These products are more persistent than the metabolites described above. Identification of all these metabolites in field samples from aquatic environments is still pending.

3.3. Anaerobic degradation assays

Unlike aerobic degradation, the removal of surfactants in the absence of oxygen has not been studied very much, in part due to the difficulty of conducting anaerobic degradation tests, as anaerobic conditions must be strictly maintained during the entire duration of the experiment, which takes considerably more time than aerobic assays. Another reason is that the anaerobic degradability of a compound is not required under the current environmental legislation. However, relatively high concentrations of surfactants are commonly found in river and coastal sediments [6,47,50], which not only act as sinks for these and other relatively hydrophobic organic compounds but also present anaerobic conditions below a depth of few mm. Hence anaerobic degradation is very relevant for understanding fully the final fate of these chemicals.

If oxygen is present, the processes of biodegradation in surface sediments do not differ too much from the processes that have been described in the water column. Thus, Larson [65] and Nielsen et al. [66] did not find any significant differences in LAS half-lives between these two environmental compartments.

Complete removal of NPEOs in less than 100 days from oxic river sediments has been also monitored in the laboratory [72]. However, once oxygen is no longer present in the column of sediment, the degradation of surfactants – if they do degrade – must take place by anaerobic pathways that involve different microbial populations as well as different mechanisms.

Laboratory assays have confirmed that anaerobic degradation of most surfactants does take place, although obviously this process is slower than in the aerobic case. Also, most tests have been performed using only WWTP sludges, in which the concentration of these compounds is extremely high (of the order of several g/kg) compared to values in sediments and suspended solids.

Table 4 gives an overview of the main results from previous anaerobic degradation tests carried out on target compounds (e.g., mineralization rates have been measured for ASs, AESs, NPEOs and AEOs in anoxic sludges and sediments).

According to Salanitro and Díaz [78], they were 60–85% after 15–30 days for ASs and linear AEOs, whereas these values are lower for NPEOs (30–40%). Nuck and Federle [79] reported higher mineralization percentages (about 80%) for ASs and AESs during the same period of time.

Other authors [29] confirmed that primary degradation of NPEOs and AEOs also occurs in anaerobic sludge digesters (about 40–70% of the original compound disappears). Degradation pathways for these ethoxylated surfactants [72,80] involve progressive reduction in the number of EO units, and this process has been observed to be more intense for short-chain, linear AEOs, although it appears to be inhibited for branched ethoxymers [81].

Regarding NPEOs, their degradation finishes with the generation of NPs [82], metabolites considered to be very recalcitrant and whose presence has been widely reported in sediments [15,17,49,50,83]. However, more work is necessary to determine the final fate of AESs and AEOs in the environment, as there is virtually no information available on this subject.

The topic of the anaerobic degradation of LASs as well as other related compounds such as SASs (secondary alkane sulfonates) has aroused significant controversy. Initial experiments conducted on river sediments and sludges showed negative results [84,85], so LASs were considered to be persistent in the absence of oxygen, which was in agreement with the higher concentration detected in WWTP sludges (5–15 g/kg) after anaerobic digestion. Inhibition of microbial activity due to the higher concentrations commonly employed during these tests can partly explain these early results. However, LAS removal was observed during more recent experiments at lower concentrations (5–100 ppm) performed using upflow anaerobic sludge blanket (UASB) reactors [86,87]. Moreover, anaerobic degradation of LASs can reach up to 70% in 165 days in marine sediments [88] via the generation of SPCs. This process takes place preferentially on the short-chain LAS homologues, due to their higher bioavailability as a consequence of their lower sorption capacity. However, when the concentration of LASs exceeds 50 ppm, these intermediates are no longer detected, because degradation is inhibited [89]. It has been proposed that *Sedimentibacter* bacteria take part in this process, although other species have also been described as being capable of accounting for the degradation of LASs through desulfonation mechanisms [90]. The anaerobic transformation of LASs into SPCs was also observed during previous field samplings [83] where marine sediment cores were taken.

4. Conclusions

Sorption and degradation are among the main processes controlling reactivity, behavior and final fate of synthetic surfactants in aquatic environments, and it is very important to develop reliable analytical protocols to study these processes.

In the past decade, advances in MS have enabled considerable steps to be taken in this direction, not only because they have facilitated quantification of every single homologue, ethoxymer and/or isomer in surfactant mixtures, but also due to the capacity of MS to identify both known and unknown degradation intermediates occurring in aqueous and solid matrices.

New extraction techniques (e.g., PFE or SPME) have also been introduced, giving many advantages including reproducibility, speed, automation, and low solvent consumption.

Finally, in addition to conducting field sampling to obtain data, from which occurrence and distribution of surfactants and their metabolites in aquatic systems can be established, laboratory experiments (e.g., sorption and degradation tests) are necessary for more accurate, complete characterization of the processes involved in reactivity and fate of these compounds. The existing literature is very biased towards LASs and NPEOs, which are by far the most frequently studied surfactants, whose sorption and aerobic degradation processes are now known in detail. By contrast, the behavior of other major surfactants, especially those non-aromatics (e.g., AESs, ASs or AEOs) is still relatively unknown. Only a few laboratory experiments have been carried out on the processes affecting their reactivity and there are practically no studies on their occurrence and fate in aquatic systems.

Another key point is the anaerobic degradation of surfactants, which is still an open field with many questions to be answered regarding degradation mechanisms, identification of new metabolites and species of bacteria, and the influence of environmental factors.

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