Environ Sci Pollut Res (2016) 23:3195–3216
DOI 10.1007/s11356-015-5803-x

REVIEW ARTICLE

Surfactants in aquatic and terrestrial environment: occurrence, behavior, and treatment processes

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Received: 23 July 2015 / Accepted: 11 November 2015 / Published online: 21 November 2015

Abstract Surfactants belong to a group of chemicals that are well known for their cleaning properties. Their excessive use as ingredients in care products (e.g., shampoos, body wash) and in household cleaning products (e.g., dishwashing detergents, laundry detergents, hard-surface cleaners) has led to the discharge of highly contaminated wastewaters in aquatic and terrestrial environment. Once reached in the different environmental compartments (rivers, lakes, soils, and sediments), surfactants can undergo aerobic or anaerobic degradation. The most studied surfactants so far are linear alkylbenzene sulfonate (LAS), quaternary ammonium compounds (QACs), alkylphenol ethoxylate (APEOs), and alcohol ethoxylate (AEOs). Concentrations of surfactants in wastewaters can range between few micrograms to hundreds of milligrams in some cases, while it reaches several grams in sludge used for soil amendments in agricultural areas. Above the legislation standards, surfactants can be toxic to aquatic and terrestrial organisms which make treatment processes necessary before their discharge into the environment. Given this fact, biological and chemical processes should be considered for better surfactants removal. In this review, we investigate several issues with regard to: (1) the toxicity of surfactants in the environment, (2) their behavior in different ecological systems, (3) and the different treatment processes used in wastewater treatment plants in order to reduce the effects of surfactants on living organisms.

Keywords Contamination · Surfactants · Toxicity · Treatments · Future trends

Abbreviations

LAS	Linear alkylbenzene sulfonate
PFOA	Perfluorooctanoate
PFOS	Perfluorooctane sulfonate
QAC	Quaternary ammonium compound
APEO	Alkylphenol ethoxylate
AEOs	Alcohol ethoxylate
NP	Nonylphenol
OP	Octylphenol
EPA	Environmental protection agency
NPEOs	Nonylphenol ethoxylate
APEOs	Alkylphenol ethoxylate
PS	Perfluorinated surfactants
CS	Cationic surfactants
EDCs	Endocrine-disrupting compounds
DTDMAC	Dimethyl ammonium chloride
TMAC	Trimethyl ammonium chloride
BDMAC	Alkyl benzyl dimethyl ammonium chloride
EC10	Concentration that induces 10 % of the substance maximum effect
EC50	Concentration that induces 50 % of the substance maximum effect

Responsible editor: Hongwen Sun

Paper submitted to be published in Environmental Science and Pollution Research

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LC50	Concentration required to kill half the members of a tested population
AOPs	Advanced oxidation processes
COD	Chemical oxygen demand
TOC	Total organic compounds
EQSD	European Union Environmental Quality Standards Directive
BDD	Boron-doped diamond
K_{ow}	Partition coefficient
OPEOs	Octylphenol ethoxylates
NPEOs	Nonylphenol ethoxylates
NPECs	Nonylphenol carboxylic acids
BACs	Benzylalkyldimethylammonium compounds
ATMACs	Alkyltrimethylammonium compounds
DTDMAC	Ditallow dimethyl ammonium chloride
DWTP	Drinking water treatment plants
OECD	Organization for economic co-operation and development
EU	European Union
EC20	Concentration that induces 20 % of the substance maximum effect

Introduction

Over the past few years, environmental problems associated with hazardous and toxic pollutants present in water have attracted much attention. Municipal and industrial wastewaters are one of the most important pollution sources affecting the quality of surface and ground water adversely in many developed countries (Koparal et al. 2006).

Surfactants are regarded as one of the major and most undesirable pollutants detected in the aquatic and terrestrial environment (Arslan-Alaton and Erdinc 2006, Gomez et al. 2011, Huang et al. 2012, Olmez-Hanci et al. 2011). Some of the surfactants like quaternary ammonium compounds (QACs) are organic micropollutants that are included in the category of emerging contaminants (Clarke and Smith 2011, Díaz-Cruz et al. 2009). Due to the excessive occurrence of surfactants and their continuous presence in the environment, there is a considerable interest in surfactant residues. Surfactants are considered as amphipathic molecules consisting of a hydrophilic polar head group and a hydrophobic hydrocarbon tail (Damrongsiri et al. 2013, Fatma et al. 2013, Rosen and Kunjappu 2012). The hydrophobic part may consist of a single chain or it may have up to four, whereas the hydrophilic head can be a charged or uncharged polar group. According to the nature of the head group, surfactants are classified into anionic, cationic, non-ionic, and zwitterion (Gül and Dönmez 2012). The most common classes of surfactants used around the world are shown in Fig. 1. Owing to their favorable physicochemical properties, surfactants are in widespread use throughout the world in many sectors such as pharmaceuticals, textiles, tanneries, cosmetics, detergents, agriculture, biotechnology, food, paints, microelectronic, mining, oil recovery, pulp and paper among others (Aboulhassan et al. 2006, Arslan-Alaton and Erdinc 2006, Cserháti et al. 2002, Olmez-Hanci et al. 2011, Rivera-Utrilla et al. 2012). The annual worldwide consumption of surfactants has been steadily increasing day by day.

For example, the annual consumption of surfactants recorded in 2008 in Western Europe was 2.98 Mt and 1.413 Mt for the non-ionic forms, while the consumption of anionic, cationic and amphoteric forms reached 1.22, 0.25, and 0.093 Mt, respectively (CESIO 2008). As reported by previous research works (Aboulhassan et al. 2006, Knepper and Berna 2003), the anionic surfactants have a wide applications owing to their excellent detergency properties and their higher performance. After use, residual amounts of surfactants and their degradation products are discharged into wastewater treatment plants (WWTPs) or directly to surface waters and ground waters, and then dispersed into different environmental compartments (Arslan-Alaton and Erdinc 2006). Today, a considerable number of commercial surfactants used by different industries are biodegradable (Koparal et al. 2006, Petrović and Barceló 2004, Ying 2006). However, due to their higher consumption, surfactants have been found at relatively high concentrations in surface waters, sediments, sludge, and soils (Gomez et al. 2011, Lara-Martín et al. 2012, McAvoy et al. 1993, Olmez-Hanci et al. 2011, Ying 2006). The introduction of these residual compounds into the environment through different sources will lead to serious environmental problems including ecological risk and human health damage (Arslan-Alaton and Erdinc 2006, Huang et al. 2012). As reported by Arslan-Alaton and Erdinc (2006), different classes of surfactants show different degradation behavior and toxicity in the environment. In aquatic environment, surfactants can foam and reduce the re-oxygenation rate and oxygen levels, resulting in deterioration of water quality and toxic effects to organisms living there (Huang et al. 2012, Koparal et al. 2006). They cause pathological, physiological, biochemical, and other effects on aquatic animals (Koparal et al. 2006). Surfactants are also able to cause a toxic effect on aquatic plants species. For example, surfactants are able to break-up the chlorophyll-protein complex, to damage the membrane's cell which delays the metabolism and the growth (Larson et al. 1993).

Likewise, the surfactants metabolites (such as octylphenol and nonylphenol) in wastewaters can be sufficient to disrupt endocrine function in human bodies (Ying et al. 2002). Usually, there are three methods used for the treatment of wastewaters contaminated by surfactants including, (1) physical methods employing precipitation, adsorption, flocculation, electro-flocculation etc., (2) chemical methods including oxidation (using oxygen, ozone, NaOCl or H_2O_2, as oxidant), and (3) biological methods including aerobic and anaerobic

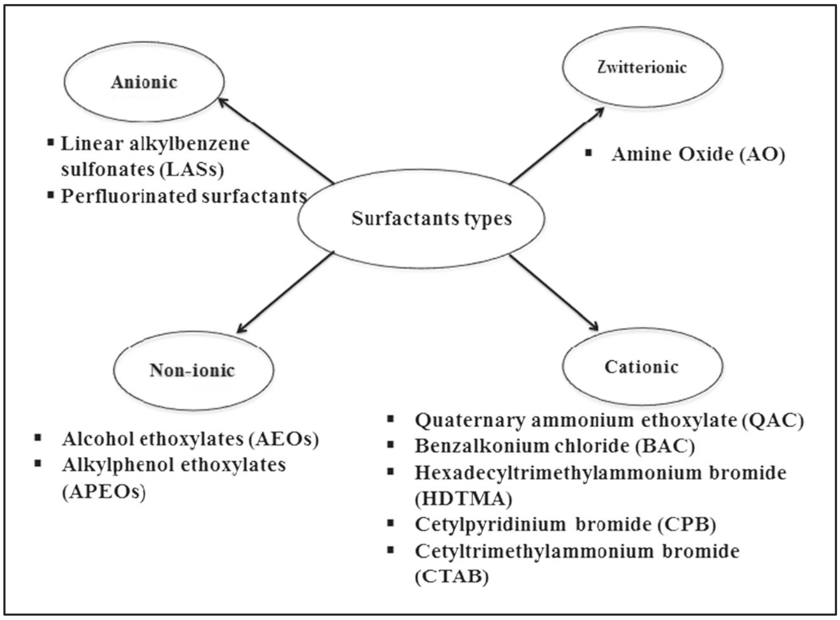


Fig. 1 The most common classes of surfactants

degradation. According to Zangeneh et al. (2014), these methods have high operational costs, need long reaction time and contain the secondary pollution, since solid wastes would be produced in these biological processes, which can bring another environmental problem of sludge treatment and disposal. Therefore, an affordable and easy-operated control technology without the formation of sludge is needed. This review highlights various issues concerning the occurrence of surfactants, their toxicity, their distribution, fate and the different technologies applied for their removal.

Guideline aspect

Surfactants are harmful to human beings, fishes, and vegetation; and are responsible for causing foams in rivers and effluent treatment plants and for reducing the quality of water. In order to protect human exposure from surfactants, different environmental agencies have the authority to regulate the concentrations of surfactants in water. Many environmental and public health regulatory authorities have fixed stringent limits for anionic detergent as standard 0.5 mg L^{-1} for drinking water and up to 1.0 mg L^{-1} for other purposes (Rao et al. 1995). Concentrations of 0.2, 2.0, 4.0, and 0.5 mg L^{-1} are allowed by Italian legislation for discharge into drinking water, surface water, sewage and for reuse in agriculture, respectively (Borghi et al. 2011, Ferella et al. 2013). Some other countries such as France have recommended the same maximum value of surfactants in drinking water (0.2 mg L^{-1}).

In Japan, the ministry of Health, Labor, and Welfare has set permissible concentrations of 0.2 mg L^{-1} and 0.02 mg L^{-1} in drinking water for anionic and non-ionic surfactants, respectively (Borghi et al. 2011). Although the toxicity of some surfactants is relatively low, concerns over the toxicity of metabolites have received a great of attention. Given this fact, it is not surprising to find many critical studies trying to determine its toxicity levels and to set a limit for the tolerable concentration in water. For instance, some nonylphenolic compounds such as 4-nonylphenol (NP) and 4-*tert*-octylphenol (OP) have been included in the list of hazardous substances in water and listed as a top-priority environmental pollutant according to EQSD (2008). Currently, the EPA has accepted the risks of nonylphenol and has prepared at the same time a guideline for ambient water quality that recommends nonylphenol concentrations in freshwater below 6.6 μg L^{-1} and in salt water below 1.7 μg L^{-1} (Soares et al. 2008). Besides, the predominant toxic effects of NP toward environment and human health have resulted in calls from various organization and countries to replace NP with other surfactants that do not show such properties. In most European countries, in Canada and Japan, nonylphenol ethoxylates are being replaced by other surfactants as alcohol ethoxylates (AEO) which are considered to be environmental friendly (Campbell 2002). Nevertheless, no action has been taken by many others countries such as India, China, and South American countries among others to reduce or eliminate their usage (Soares et al. 2008). According to Environnement Canada (1999), the concentration of AEO in waters should not exceed certain values recommended by the Canadian legislation. Table 1 summarizes these values for three fish species, four invertebrate species, and three plant species.

Table 1 Toxicity data used for developing the Federal Water Quality Guideline for alcohol ethoxylates (Environnement Canada 1999)

Species type	Organisms	End point	Concentration μg L $^{-1}$
Fishes			
	Rainbow trout (*Oncorhynchus mykiss*)	56d EC_{20} (dry weight)	135
	Fathead minnow (*Pimpehales promelas*)	35d EC_{20} (percent hatch)	181
	Bluegill (*Lepomis macrochirus*)	35d EC_{20} (percent hatch)	233
Invertebrates			
	Midge (*Chironomus tentans*)	10d LC_{20} (survival)	346
	Water flea (*Daphnia magna*)	21d EC_{20} (reproduction)	124
	Bivalve (*Corbicula fluminea*)	56d EC_{20} (length gain)	50
	Amphipod (*Hyalella azteca*)	10d LC_{20} (survival)	370
Plants			
	Green algae (*Scenedesmus subspicatus*)	72 h EC_{20} (growth rate)	646
	Duckweed (*Lemna minor*)	7d EC_{20} (frond count)	741
	Green algae (*Chlorella vulgaris*)	72 h EC_{20} (growth rate)	5281

Type of Surfactants

Anionic surfactants

Anionic surfactants are the most abundant class of surfactants, which widely applied in high volume in the formulation of household detergent and industrial cleaning products (Aboulhassan et al. 2006, Mousavi et al. 2011) As reported by Jangkorn et al. (2011), more than 90 % of surfactants produced are anionic. In anionic surfactants, the hydrophilic head group interacts strongly with water molecules while the hydrophobic tail group interacts preferentially with non-aqueous phase liquid molecules (Damrongsiri et al. 2013). The most abundant anionic surfactants especially used as detergents in household and in surface cleaners are linear alkylbenzene sulfonates (LAS) because of its great cleaning properties and relatively low cost (Krogh et al. 2007, Mungray and Kumar 2009). In 2003, the global consumption of LAS was estimated to 18.2 million tons compared to 9, 4.5, 1.7, 0.5, 0.1 and 2.4 million tons of soap, anionic, non-ionic, cationic, amphoteric, and other surfactants, respectively (Mungray and Kumar 2009). According to Khleifat (2006), LAS is the primary cleaning agent used in many laundry detergents and cleaners at concentrations up to 25 % in consumer products and up to 30 % in commercial products. These compounds have alkyl chains varying from C10 to C14, where a sulfonated benzene ring can be attached at various isomer positions (usually between 2 and 7) (Fountoulakis et al. 2009, Gomez et al. 2011). As reported by García et al. (2005), commercial LAS is a mixture consisting of approximately 20 different compounds of closely related homologues and isomers, each containing an aromatic ring, sulfonated at the para-position, attached to a linear alkyl chain. According to Lara-Martín et al. (2008), LAS is mostly used in household detergents and as a component of shampoos and other personal care products. Owing to their amphophilic nature, LAS tends to be sorbed onto suspended particles once discharged into waters (González-Mazo et al. 1998, Hampel et al. 2012, Jangkorn et al. 2011). The sulfonate group gives LASs its water solubility, while the linear hydrocarbon chain makes the molecule more compatible with oil and grease. Thus, LAS are very soluble in water but at the same time its octanol-water coefficient log K_{ow} that ranges between 2.5 and 4.5 defines its hydrophobic character and its adsorption capacities onto suspended compounds such as sludge (García et al. 2005).

Perfluorinated surfactants (PS) are another group of anionic surfactants that should be mentioned. PS surfactants (PS) represent special chemicals with specific technological properties. They are used for coatings of textiles, papers, and carpets to achieve oil, stain, and water repelling properties. Furthermore, they are employed as performance chemicals in fire-fighting foams and ingredients in consumer products such as floor polishes and shampoos (Skutlarek et al. 2006). Recently, more attention has been given to two types of PS, perfluorooctane sulfonate (PFOS), and perfluorooctanoate (PFOA) (Xiao et al. 2015). According to Xiao et al. (2013b), PFOS and PFOA are included in the category of persistent organic pollutants that have been found to be ubiquitous in the environment. Due to their extensive production, PFOS and PFOA can be detected in numerous water and groundwater sites around the world. With the electronegativity of fluorine replacing some hydrogen atoms, the polarity of the C–F bond is reversed and the binding stronger compared to C–H bond. So, chemical and thermal resistances of fluorinated compounds are highly increased compared to hydrocarbon ones (Baudequin et al. 2011).

Thus, the removal of these pollutants from wastewater before being released into the environment has become necessary due to their high toxicity.

Non-ionic surfactants

Nonionic surfactants are considered to be amphiphilic compounds (ElSayed et al. 2013). They do not ionize in aqueous solution because they have a non-dissociable hydrophilic group (e.g., alcohol, phenol, ester, ether, or amide) and they are less sensitive to electrolytes than are ionic surfactants (ElSayed et al. 2013, Singla et al. 2009). Therefore, non-ionic surfactants are compatible with other types of surfactants and are excellent components for use in complex mixture. They are commonly found in a large number of domestic and industrial applications. These surfactants are also good detergents, wetting agents, and emulsifiers and some have good foaming properties (Singla et al. 2009). The most abundant non-ionic surfactants in use are alcohol ethoxylates (AEOs) and alkylphenol ethoxylates (APEOs) (Gomez et al. 2011). Usually, the alkyl chain of AEOs has between 12 and 16 carbon units and between 1 and 23 ethoxylate (EO) units. In APEOs, the number of EO units is the same, whereas the alkyl chain can be either 8 or 9 units in length and are known as octylphenol ethoxylates (OPEOs) or nonylphenol ethoxylates (NPEOs) (Gomez et al. 2011). The chemical structure of different non-ionic surfactants is presented in Fig. 2.

Since 1984, the use of APEOs has been restricted because they are partially degraded and their breakdown products (nonylphenol (NP) and octylphenol (OP)) are more toxic and more persistent in the environment than APEOs themselves (Scott and Jones 2000). The metabolites of APEOs usually formed during the degradation show the highest concentrations in the aquatic environments, where they may persist for decades because of their low biodegradability in sediments (Lara-Martín et al. 2012). To this end, some major detergent suppliers to the consumer sector have agreed to not use NPEOs in their product formulations allowing other kinds of surfactants to float in the market. One of the most used surfactants since the restriction of NPEOs is AEOs that shows a better biodegradability (Lara-Martín et al. 2012).

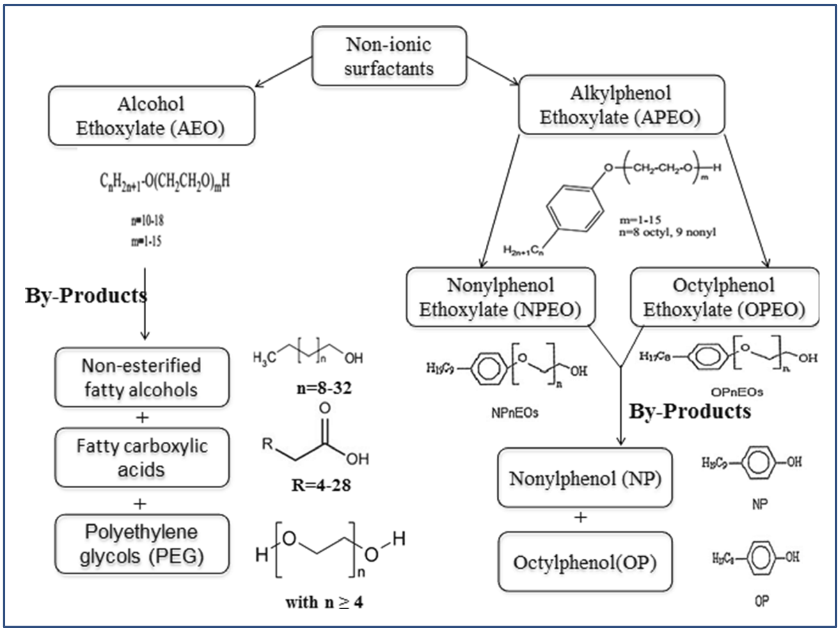
Currently, alcohol ethoxylates (AEOs) are the most non-ionic surfactant produced in worldwide, especially in Canada (Campbell 2002). In 1996, the worldwide production of AEOs has been estimated to 7×105 tons, whereas in Canada the production of AEOs reached 72,000 tons (Tolls et al. 2000). The AEOs are principally used in industrial purposes as well as domestic detergents such as cleaning products and wash detergents. They are also used in the agricultural sector, cosmetics, textiles, papers, and petroleum products (Madsen et al. 2001, Talmage 1994). In 2000, the consumption of AEOs in Canada and USA was estimated to be 216,800 tons (Modler et al. 2002). Unfortunately, the widespread use of AEOs increases their importance as environmental pollutant. The question of their biodegradability and ultimately their environmental fate constitutes the decisive criterion in their environmental compatibility assessment (Singla et al. 2009). The growing production and the extensive use of AEOs lead to their accumulation in the aquatic environment (Tolls et al. 2000). Due to their hydrophobic character, AEOs can be adsorbed on solid particles and accumulated in sediments (McAvoy and Kerr 2001) and soil (Marks et al. 2002). As a consequence, aquatic and terrestrial organisms are continuously exposed to AEOs.

Cationic surfactants

Cationic surfactants (CS) including quaternary ammonium ethoxylate and cetrimonium chloride are molecules with at least one hydrophobic long alkyl chain attached to a positively charged nitrogen atom (Nałęcz-Jawecki et al. 2003, Olmez-Hanci et al. 2011). Usually, most of the cationic surfactants have straight alkyl chain(s) with lengths between 8 and 24 carbon atoms. The annual global production of cationic surfactants is around 350,000 tons (Vanginkel et al. 1995). This amount accounts only for about 4–5 % of total surfactant production (Merino et al. 2003). By comparison to the anionic and non-ionic surfactants, cationic surfactants are more toxic and essentially non-replaceable for some specific industrial applications. This group of surfactants is widely used in various fields such as fabric softening, textile industry, biocides, road construction, disinfectants, biocides, emulsifiers, hair conditioning, cosmetics industry, and wetting agent among others (Koner et al. 2011, Puchta 1984). According to previous research studies (Giolando et al. 1995, Nałęcz-Jawecki et al. 2003), quaternary ammonium compounds (QACs) are the most abundant cationic surfactants. In Europe and the USA, their annual industrial consumption exceeds 32,000 tons each. These compounds are commonly used in industrial sanitizer formulations in order to keep food contact surfaces clean and pathogen-free (Hajaya and Pavlostathis 2013, Kümmerer et al. 2002).

In fact, QACs compounds can be found in the environment in the form of three different structures: (i) DADMACs, with

Fig. 2 Chemical structure of non-ionic surfactants



double *n*-alkyl chains of even carbon alkyl lengths varying between C8 and C18; (ii) alkyltrimethylammonium compounds (ATMACs), with a single *n*-alkyl chain between C12 and C22; and (iii) benzylalkyldimethylammonium compounds (BACs), with alkyl chain lengths between C12 and C18 (Li et al. 2014). According to Scott and Jones (2000), cationic surfactants such as QACs are positively charged. As a consequence, 20 to 40 % of these compounds can be adsorbed onto suspended solids which are negatively charged. The anaerobic degradation in that case should occur in order to remove cationic surfactants during the treatment. However, available data on their anaerobic degradation is scarce. Therefore, it can be assumed that cationic surfactants are not anaerobically biodegradable. Consequently, serious environmental problems occur, causing toxic effects on aquatic and terrestrial species.

Surfactants toxicity

Up to now, more attention has been paid to ecological risk and potential toxic effect of surfactants residues in the environment (Ivanković and Hrenović 2010, Ying 2006). Due to their antimicrobial effects, these surfactants residues promote the evolution and the development of resistant bacteria, which can induce adverse effect to human health when present in drinking water or irrigation water used for fruit and vegetable (Shao et al. 2005).

Given this fact, it is not surprising to find many researches trying to determine and estimate the toxicity of surfactant on aquatic and terrestrial species, and even their estrogenic effects (Ivanković and Hrenović 2010, Jensen 1999, Mungray and Kumar 2009, Nałęcz-Jawecki et al. 2003).

Estrogenic effect of surfactants

Although the toxicity of alkylphenol ethoxylates (APEOs) is relatively low, concern over their metabolites has received a great attention, especially those with one or two ethoxylate groups or those with none (alkylphenols) (Chen et al. 2007, de la Fuente et al. 2010, Horikoshi et al. 2002). Borghi et al. (2011) have indicated that nonylphenol ethoxylates and octylphenol ethoxylates are much less toxic to aquatic organisms than their degradation products (nonylphenol and octylphenol) which are classified as endocrine-disrupting chemicals. These substances are considered endocrine-disrupting chemicals if they alter the normal functioning of the hormonal system of mammalians, fishes and amphibians (de la Fuente et al. 2010, Horikoshi et al. 2002, Neamțu and Frimmel 2006). Among the various non-ionic surfactants, some nonylphenolic compounds such as 4-nonylphenol (NP) and 4-*tert*-octylphenol (OP) are classified as endocrine-disrupting compounds (EDCs) (Chen et al. 2013, ElSayed et al. 2013, Ferguson et al. 2001). Based on the previous results of numerous studies concerning their wide spread, both nonylphenol and octylphenol have been included in the priority list of Hazardous substance in water by the European Union (EQSD 2008). Besides, the Taiwan Environmental Protection Administration has included both nonylphenol and octylphenol in the Drinking Water Contaminant Candidate list due to their wide spread and potential threat of these chemicals to human health. The first evidence that nonylphenol could be estrogenic was published in 1983 by

Dodds and Lawson (Soares et al. 2008). However, the harmful effects of nonylphenol on estrogenic characteristics were accidentally discovered by Soto et al. (1991) during laboratory experiments on natural estrogen in animals (Chen et al. 2013, Soares et al. 2008). According to Jobling et al. (1996), 4-nonylphenol (NP) and 4-tert-octylphenol (OP) exhibits about 10^{-5} and 3 10^{-5} the estrogenic activity of 17β-estradiol. In fact, NP and OP are able to induce the production of vitellogenin in male fish, a protein usually only found in sexually mature female under the influence of estrogens (Pedersen et al. 1999, Ying 2006).

Based on the literature, vitellogenin is a precursor of major egg yolk protein involved in energy reserves for embryonic development and is synthesized in the liver of vertebrate or in the fat body, the equivalent organ in insects. The vitellogenin gene is usually silent in males but it could be expressed under the exposure of NP. In the case of *Bombyx mori*, an ideal lepidopteran model insect, the exposure of females to 0.05 and 0.2 g kg^{-1} of NP decreased the vitellogenin gene expression. Under the same NP concentrations, vitellogenin gene was expressed in *Bombyx mori* males (Yuan et al. 2013). According to Flouriot et al. (1996), the vitellogenin gene expression is believed to be under the control of estrogen receptor pathway in invertebrates. However, it remains unclear if all the effects of nonylphenol in organisms are due solely to its estrogen receptor-binding activity. As reported by Watanabe et al. (2004), the tissue-specific effects should also be considered in order to elucidate the distinct effects of nonylphenolic compounds. For instance, when nonylphenol was placed in direct contact with the liver, another set of genes that were distinct from estrogen-responsive genes was activated. Another group of researchers studied the effects of 19 μg L^{-1} of NP on the adrenal gland of *Triturus carnifex*. The results showed that NP was able to decrease the synthesis and the release of corticosteroids hormones. The same effects were also reported for the secretion of norepinephrine (Capaldo et al. 2012) suggesting that NP effects are not limited to their capacity to mimic estrogen action.

By comparison to nonylphenolic compounds, AEOs which are another group of non-ionic surfactants are less toxic, less persistent and having less estrogenic metabolites (ElSayed et al. 2013). Nevertheless, AEOs could cause a non-specific narcosis that depends on the ethoxylates unit numbers (Müller et al. 1999, Roberts 1991). The narcosis is a reversible and non-specific phenomena caused by the presence of hydrophobic organic chemical products that develop a perturbation in the cell's activities. AEOs can disrupt the function of the bronchial apparatus membrane of fish, invertebrates, and amphibians which induces an inflation and huge secretion of the epithelial cell's mucous (Cardellini and Ometto 2001, Moore et al. 1987). Therefore, the cell's membrane will be disrupted and the oxygen distribution will change which will induce a suffocation (Cardellini and Ometto 2001, Moore et al. 1987). The capacity of non-ionic surfactants to disrupt the endocrine system is frequently found to be far higher than their concentrations found in the environment. In addition to the non-ionic surfactants effect, there exists more than one stress factor or contaminants in the environment that might adversely affect the organisms. Usually, even at low concentrations, the effect of two or more compounds with endocrine disruption capacity could be additive or synergistic (Kwak et al. 2001, Silva and Volpato 2002).

Aquatic toxicity

According to Ying (2006), different types of surfactants have been detected in sewage effluents with concentrations up to 1090 μg L^{-1} for anionic surfactants (e.g., LAS), up to 332 μg L^{-1} for non-ionic surfactants (e.g., AFEOs), and up to 62 μg L^{-1} for cationic surfactants (e.g., DTDMAC). Although efficient treatment in wastewater plants will result in discharge of very low levels of surfactants in the environment, the massive release of these compounds exposes a wide variety of aquatic ecosystems to potential risks. Some recently published toxicity data for the three classes of surfactants on several aquatic species have been presented in Table 2. Most of the research is devoted to cationic group as it exhibited the most toxic effect (Ivanković and Hrenović 2010). The toxicity of seven surfactants (immobility EC50-48 h) on six freshwater microbes has been tested by Singh et al. (2002). They found that cationic surfactants were more toxic than anionic and non-ionic surfactants. Due to their antimicrobial properties, several researches are conducted on the toxicity of cationic QACs. Utsunomiya et al. (1997) studied the toxic effects of LAS and three QACs (alkyl trimethyl ammonium chloride (TMAC), dialkyl dimethyl ammonium chloride (DADMAC) and alkyl benzyl dimethyl ammonium chloride (BDMAC)) on unicellular green algae *Dunaliella* sp. The 24-h median effective concentrations were 3.5 mg L^{-1} for LAS and 0.79, 1.3, and 18 mg L^{-1} for the three QACs. The toxic potencies were in the order of TMAC>BDMAC>LAC>DADMAC. According to Nałęcz-Jawecki et al. (2003), the biological activity of QACs is very high. This class of cationic surfactants has been widely studied for activity against various aquatic bacteria (Nałęcz-Jawecki et al. 2003, Pernak et al. 2001, Skrzypczak et al. 1997). For instance, the toxicity of cetyltrimethylammonium bromide to the freshwater amphipod *Echinogammarus tibaldii* was 7.7 mg L^{-1}, whereas the toxicity of benzalkonium chloride to daphinids is even higher with an LC50 from 0.1 to 1.0 mg L^{-1} (Kümmerer et al. 2002, Nałęcz-Jawecki et al. 2003). Garcia et al. (2001) carried out acute toxicity tests on *Daphnia magna* and *Photobacterium phosphoreum* for two families of monoalkyl quaternary ammonium surfactants. For the six cationic surfactants, the 24-h immobilization EC50 on *D. magna* ranged from 0.13 to

Table 2 Chronic toxicity of surfactant to aquatic species

Organisms	Species	Surfactants	End point	Conc.mg L^{-1}	References
Bacteria	*Vibrio fischeri*	LAS	EC_{50}-Luminescence 30 min	109.7	(Ivanković and Hrenović 2010, Sütterlin et al. 2008)
	Vibrio fischeri	QAC	EC_{50}-Luminescence 30 min	0.5	(Ivanković and Hrenović 2010, Sütterlin et al. 2008)
	Photobacterium phosphoreum	QAC	EC50-immobilization 24 h	0.15–0.63	(Garcia et al. 2001)
	Dunaliella sp.	LAS	EC_{50}-24 h	3.5	(Ivanković and Hrenović 2010, Sütterlin et al. 2008)
	Dunaliella sp.	QAC	EC_{50}-24 h	0.79	(Ivanković and Hrenović 2010, Sütterlin et al. 2008)
Algae	*Scenedesmus subspicatus*	AEO	EC_{10}	0.03	(Belanger et al. 2006)
	Selenastrum	AEO	EC_{10}	9.791	(Belanger et al. 2006)
	Pseudokirchneriella subcapitata	PFOS	EC_{50}	146 μM	(Latała et al. 2009)
	C.vulgaris	PFOS	EC_{50}	96 μM	(Adam Latała and Stepnowskib 2009)
Crustaceans	*Daphnids*	QAC (benzalkonium chloride)	LC_{50}	0.1–1.0	(Kümmerer et al. 2002, Nałęcz-Jawecki et al. 2003)
	Daphnia magna	QAC	EC_{50}-immobilization 24 h	0.13–0.38	(Garcia et al. 2001)
Amphipod	*Echinogammarus tibaldii*	QAC (cetyltrimethylammonium bromide)	LC_{50}	7.7	(Boeije et al. 2005, Nałęcz-Jawecki et al. 2003)
Invertebrate	*Daphnia magna*	AEO	EC_{50}	0.36 -50.5	(Boeije et al. 2005)

0.38 mg L^{-1}, whereas the EC50 on *P. phosphorem* was ranged from 0.15 to 0.63 mg L^{-1}. Besides, QAC can have a detrimental effect on biological activity in wastewater treatment plants (Sütterlin et al. 2008). As reported by Boethling (1984), the nitrification in wastewater treatment plants is particularly sensitive to QACs because the specific uptake mechanism for ammonium in nitrifying bacteria may be affected. It has been proved by Tubbing and Admiraal (1991) that the response of the microbial population was significantly affected even at low nominal concentration of QACs, which ranged from 0.01 to 1.0 mg L^{-1}.

Furthermore, the toxic effect of anionic surfactants on aquatic species has received increasing attention due to their high consumption and the absence of adequate treatment process. The exposure of LAS concentrations may not be lethal for the affected species, but may have effects on internal functions and structures and may reduce the effectiveness of vital functions, such as resistance to environmental and competitive stress, reproduction, and growth (Hampel et al. 2012).

Venhuis and Mehrvar (2004) have reported that the presence of 0.02–1.0 mg L^{-1} of LAS in aquatic environment can damage fish gills, cause excess mucus secretion, decrease respiration in the common goby, and damage swimming patterns in blue mussel larva. Some of the previous research studies have found that LAS concentrations of 0.36 and 0.25 mg L^{-1} had no effect on biological population and aquatic organism, respectively (Fairchild et al. 1993, van de Plassche et al. 1999). It has been reported also that LAS at a 0.2 mg L^{-1} do not affect the rainbow trout (*Oncorhynchus mykiss*). However, the exposure of 0.2 mg L^{-1} of LAS in aquatic environment during 54 days reduces the swimming capacity of rainbow trout.

Another anionic surfactant, PFOS showed toxic effects on fish muscles with concentrations around 3.21 ng g^{-1} in *silver carp* and 11–90 ng g^{-1} in *common carp fillets* (Yuanyuan Pan et al. 2011). The toxic effects of the same compound on green alga *Chlorella vulgaris*, the diatom *Skeletonema marinoi* and the blue-green alga *Geitlerinema amphibium*, which are species representative of the alga flora of the Baltic Sea, showed that EC50 values range from 0.28 to 12.84 mM. For the same compound PFOS, EC_{50} around 146 and 96 μM were also reported for green algae *Pseudokirchneriella* subcapitata and *C. vulgaris* respectively (Latała et al. 2009). Unfortunately, data about the acute toxicity of PFCAs toward ecotoxicological markers such as aquatic plants are still very scarce.

Overall, most pronounced toxic effect on aquatic species was well documented for anionic and cationic surfactants. Nevertheless, the toxic effects of non-ionic surfactants to aquatic species such as algae, vertebrates and invertebrates have been widely studied. Belanger et al. (2006) conducted the risk assessment of AEOs to organisms ranging from algae to fathead minnow. The effective concentrations at 10 % inhibition (EC10) for AEOs toxicity to multiple algae species varied from 0.030 to 9.791 mg L^{-1} (Belanger et al. 2006). Previous studies have demonstrated that fishes and invertebrates were the most responsive to the effects of AEOs. Nonionic AEOs and nonylphenol ethoxylate exhibited acute toxic effects in tadpoles of four Australian and two exotic frogs (Mann and Bidwell 2001).

The effective concentrations at 50 % inhibition (EC_{50}) for nonylphenol ethoxylates toxicity ranged between 1.1 and 12.1 mg L^{-1}, whereas for the AEOs toxicity the effective concentrations EC_{50} varied between 5.3 and 25.4 mg L^{-1} (Mann and Bidwell 2001). Moreover, the toxic effect of non-ionic surfactants on invertebrates such as *D. magna* has been also conducted. Boeije et al. (2005) found that the effective concentration at 50 % inhibition (EC50) for *D. magna* was ranged between 0.36 and 50.5 mg L^{-1}. Although the toxicity of non-ionic surfactants on aquatic ecosystem has been widely studied, special concern over the toxic effect of their metabolites, such as nonylphenol on algae, invertebrates and fishes has received a great attention. In a study performed on two generations of the fish *O. latipes*, it was noted that nonylphenol affected the first generation by reducing the embryo survival and development of sex characteristics (Soares et al. 2008). Another study of *D. magna* established that the embryo-toxicity resulted from the exposure of gravid females to nonylphenol and not through direct exposure of the embryo. This result shows that nonylphenol interferes with the maternal provision of some maternal constituents critical to the normal development of the embryo (LeBlanc et al. 2000).

Terrestrial toxicity

Significant amounts of surfactants can enter into the soils through sewage sludge increasingly applied on agricultural lands as fertilizers for plants. Surfactants are also present in agrochemicals because they ensure high stability to agrochemicals formulations, bind granules, and disperse, solubilize and wet or emulsify active ingredients (Asok and Jisha 2012, Ivanković and Hrenović 2010). Thus, the terrestrial environment has become a significant sink of surfactants. Although most surfactants used are aerobically biodegraded during secondary treatment, a considerable fraction could be eliminated in the form of sludge (15–37 % in the case of LAS to more than 90 % for the most hydrophobic, nonylphenols).

This sludge, 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 (Lara-Martín et al. 2008). The occurrence and the distribution of these surfactants in soil by the application of sewage sludge present a potential ecotoxicological risk. Exposure of soil to surfactants makes it hostile for microorganisms. The effects of surfactant on microorganisms were mainly due to the reactions at the cell surface. According to Jensen (1999), a depolarization of the cell membrane by the absorption of surfactant may result in a decreased absorption of essential nutrients and oxygen consumption or a decreased release of toxic metabolic products from the cell leading to a build-up (Domene et al. 2009). The toxicological effect of surfactants on terrestrial environment is found in Table 3.

Recent study of Asok and Jisha (2012) shows high sensitivity of bacteria to LAS exposure concentrations (from 0 to 16 mg kg^{-1}) compared to fungi and actinomycetes. The same research group shows that the LAS treatment reduced significantly the dehydrogenase activity while adding between 10 and 50 mg of LAS kg^{-1}. Moreover, the direct exposure of LAS to the plants destroyed the root cell membrane, and changes the fine structure and the permeability when applying 1 to 1000 mg kg^{-1} of LAS (Jensen 1999). Regarding PFOS and PFOA, the latter was detected at elevated levels in surface soils (median, 12.2 ng PFOS/g dw and 8.0 ng PFOA/g dw). Due to their migrant capacities, their concentrations increase with the depth of the soil which may present a potential risk of aquifer contamination (Xiao et al. 2015). Humans can be exposed to PS through fish or drinking water consumption (Xiao et al. 2013a). According to Skutlarek et al. (2006), PFOS and PFOA concentrations were below 100 ng L^{-1} in the Rhine river which may not be acutely toxic. However, their bioaccumulation in human liver and human serum by bonding to existing proteins may raise long-term concerns about their metabolic effects. In fact, these two chemicals have been detected in more than 95 % of the blood samples collected during US national surveys at elevated concentrations of several to tens of milligrams per liter (Xiao et al. 2015). They also present significant effects, including mortality, in cynomolgus monkeys (oral doses of 0.75 mg kg^{-1} day^{-1}), 12 rabbits (oral doses of 3.75 mg kg^{-1} day^{-1}), and 13 rats (oral doses of 1.6 mg kg^{-1} day^{-1}).

Non-ionic surfactants like NPEOs could also be found in soils destined for agriculture purposes. The main sources of NPEOs are sewage sludge applications, landfilling, and accidental spillage. Although almost 59 % of NPEOs are removed using wastewater treatment plants, their concentrations are considered to be high in effluents and sewage sludge treatments. Once they are found in soils, these surfactants are easily biodegradable leading to the accumulation of the simplest chemical forms of nonylphenol ethoxylates (NP, NP1EO, and NP2EO) and nonylphenol carboxylic acids (NP2EC or NP1EC) (Domene et al. 2009). Usually, the toxicity of NPEOs increases as the length of the hydrophobic chain increases. Besides, toxicity may occur by partition into lipid membranes in the organism, for example the mitochondrial membrane, leading to the uncoupling of energy production (Argese et al. 1994). According to Staples et al. (2001), the degradation products of NPEOs (NP1EO, NP2EO, and especially NP) are more toxic than the parent compound itself. In fact, nonylphenol was shown to affect the growth and nitrification capacity of soil microorganisms such as *Azobacter* sp. at concentrations between 18.8 and 37.6 mg kg^{-1} (Mårtensson and Torstensson 1996). By comparison, it has been reported by Gejlsbjerg et al. (2001) that the nitrification capacity of

Table 3 Toxicity of different type of surfactants against various terrestrial organisms

Organisms	Species	Surfactants	End point	Conc. mgL^{-1}	References
Soil fauna	*Eisenia foetida*	LAS	Mortality (14 days)	1000 mg kg^{-1} in OECD soil	(Jensen 1999)
	Lumbricus terrestris	LAS	Mortality (14 days)	1000 mg kg^{-1} in OECD soil	(Jensen 1999)
	Platynothrus peltifer	LAS	Mortality (LC$_{50}$)	319 mg kg^{-1} in LUFA soil	(Jensen 1999)
	Isotoma viridis	LAS	Mortality (LC$_{50}$)	661 mg kg^{-1} in OECD soil	(Jensen 1999)
Bacteria	Azobacter sp.	NP	-	18.8–37.6 mg kg^{-1}	(Mårtensson and Torstensson 1996)
Algea	*Navicula peliculosa*	LAS	EC$_{50}$, 96 h	1.4	(González et al. 2012)
Crustaceans	*Arcatia tonsa*	LAS	EC$_{50}$, 48 h	1.11	(Garrido-Perez et al. 2008, González et al. 2012)
	Arcatia tonsa	NPEs	LC$_{50}$, 48 h	359	(González et al. 2012, TenEyck and Markee 2007)
Fish	*Pleuronectes plateas*	LAS	EC$_{50}$, 96 h	1.0	(Garrido-Perez et al. 2008)
	Promelas Pimephales	NPEs	LC$_{50}$, 96 h	190	(TenEyck and Markee 2007)
Invertebrate	*Folsomia fimetaria*	NP	EC$_{50}$ (21 days)	5–133 mg kg^{-1}	(Scott-Fordsmand and Krogh 2004, Sørensen and Holmstrup 2005)
	Folsomia candid	NP	EC$_{50}$ (21 days)	5–133 mg kg^{-1}	(Scott-Fordsmand and Krogh 2004, Sørensen and Holmstrup 2005)
Terrestrial Plants	*Brassica rapa*	LAS	EC$_{50}$ (14 days) (Growth)	137.7 mg kg^{-1}	(Jensen 1999)
	Malvia pusilla	LAS		204.2 mg kg^{-1}	(Jensen 1999)
	Solanum nigrum	LAS		169.2 mg kg^{-1}	(Jensen 1999)
	Chenopodium album	LAS		164.3 mg kg^{-1}	(Jensen 1999)
	Ryegrass Lolium	LAS		500 kg ha^{-1}, strong effects	(Jensen 1999)

others types of microorganisms was affected at high exposition of nonylphenol concentrations (343 mg kg^{-1}). According to Soares et al. (2008), this difference is mainly attributed to the experimental design and the type of soil and other stress conditions imposed during toxicity tests. Given the harmful toxicity of surfactants on living organisms, recent research emphasizes the need to develop efficient processes able to remove surfactants and its metabolites from the different environmental compartments.

Treatment of surfactant

Surfactant in water and wastewater

Surfactants can reach the aquatic environment as a result of discharge from wastewater treatment plants (WWTPs) into rivers, ocean, lakes, and estuaries or by direct discharge of raw sewage (Olmez-Hanci et al. 2011). Its occurrence in surface waters is mainly correlated with anthropogenic activities such as storm water discharges and run-off and the direct discharge of effluents from industrial and urban area.

In domestic wastewater, the average concentration of surfactants is ranging between 1 and 10 mg L^{-1}, whereas their concentration from the surfactants-manufacturing industry exceeds 300 mg L^{-1} (Rivera-Utrilla et al. 2012). LAS which is the most popular anionic surfactant, has been detected at concentrations ranging from 2 to 21 mg L^{-1} (Fountoulakis et al. 2009) and from 400 to 14,000 mg L^{-1} (de Wolf and Feijtel 1998) in raw wastewater and untreated sludge, respectively. LAS concentrations of 1090 to 1100 μg L^{-1} (Holt et al. 1998, Ying 2006) and 0.05 to 400 μg L^{-1} (Fountoulakis et al. 2009) were also detected in sewage wastewaters and surface waters. According to (Scott and Jones 2000), 73 % of LAS were eliminated under aerobic degradation which results in their discharge at very low levels. In fact, the most widely accepted biodegradation pathway of LAS consists of the ω-oxidation of the terminal carbon atom of the alkyl chain, followed by successive β-oxidations. The sulfophenylcarboxylic acids (SPCs) formed as a result of this process constitute the degradation intermediates of LAS. In most cases, the process finishes with the desulfonation and rupture of the aromatic ring. The disappearance of SPCs indicates that LAS biodegradation has been completed (Garcia-Luque et al. 2010). However, the continuous release of LAS in surface waters increases their concentrations and threatens the life of aquatic species.

Concerns were also raised over the concentrations of PFOS and PFOA in drinking water and groundwater. Generally, PS surfactants have been detected in drinking water at concentrations typically in the low nanogram per liter with occasionally higher concentrations (lower μg L^{-1}) in some contaminated areas (Eschauzier et al. 2012). These persistent contaminants have been also detected in the groundwater in the US state of Minnesota at concentrations up to 3500 ng L^{-1} for PFOA and up to 2200 ng L^{-1} for PFOS, respectively (Xiao et al. 2013b). Based on German provisional health-based guideline values for safe lifelong exposure (determined by the German

Drinking Water Commission), the sum of PFOA and PFOS concentrations should not exceed 0.3 μg L^{-1}. The same limits were also defined by the US Environmental Protection Agency (0.4 and 0.2 μg/L for PFOA and PFOS, respectively, in drinking water) (Eschauzier et al. 2012). Due to the carbon-fluorine bond, PFOA and PFOS are highly resistant to biochemical degradation and advanced oxidation processes. Therefore, they can be incinerated at high temperature in halogen-resistant incinerators. However, the application of this treatment process is unacceptable from an economic point of view (Baudequin et al. 2011). Recent studies elaborated by Eschauzier et al. (2012) showed that PFOA and PFOS removal from drinking water was achieved using granular activated carbon and that their final concentrations were below 4.2 ng L^{-1}. At this concentration level, concerns over human health should not be taken into account.

According to Baudequin et al. (2011), electrocoagulation coupled with reverse osmosis could be also used for perfluorinated surfactants removal. Indeed, the removal of 71 % of 38 mg L^{-1} of PS was achieved using electrocoagulation followed by filtration. The coagulant (aluminum, Al^{3+}) concentration was fixed at 1.0 mg L^{-1} as long as pH did not exceed 8.

APEOs which are widely used surfactants in domestic and industrial products are commonly found in wastewater discharges and in sewage treatments plants. In the UK, concentrations of AP1EOs around 45±16 μg L^{-1} and up to 3970 ng $g^{-1}dw^{-1}$ were detected in WWTP effluents and river sediments, respectively (Montgomery-Brown and Reinhard 2003). According to Ying (2006), the biodegradation of APEOs in conventional sewage treatment plants is generally believed to start with a shortening of the ethoxylate chain, leading to short-chain APEOs containing one or two ethoxylate units. Complete deethoxylation with formation of alkylphenols (APs) has been observed only under anaerobic conditions. Regarding APE metabolites, these latter degraded more easily under aerobic than under anaerobic conditions.

NP is one of the most important APEOs metabolites (Scott and Jones 2000). Studies conducted in Spain, Japan, Germany, USA, and Canada found concentrations of NP in river water ranging from undetectable to 17.5 μg L^{-1} (Bennie et al. 1997, Buxton and Kolpin 2002, Céspedes et al. 2008, Isobe et al. 2001). Studies conducted in Spain, Japan, Germany, USA, and Canada found concentrations of NP in river water ranging from undetectable to 17.5 μg L^{-1} (Barber et al. 1988), in the vicinity of contaminated rivers 0.1–0.8 mg L^{-1} (Ahel et al. 1996), septic systems 1.2 g L^{-1} (Rudel et al. 1998) and even agricultural activities 0.16–0.38 μg L^{-1} among others (Latorre et al. 2003). NP has been also found in different sources of potable water at relatively high concentrations. Depending on the type of unit treatment process employed, the removal efficiency of NP in drinking water treatment plants (DWTPs) has been found to show wide discrepancies (from 11 to 99 %) (Berryman et al. 2004). The study conducted by Li et al. (2010) founds residual concentrations of NP (from 0.1 to 1.0 μg L^{-1}) in drinking water, whereas NP concentrations varied from 15 to 85 ng L^{-1} in the treated drinking water in Germany and Spain, respectively (Kuch and Ballschmiter 2001, Petrović et al. 2003). In WWTP, biodegradation was the main removal pathway of NP, as it was more effective in removing NP from the aqueous phase than physical treatment. A wide range of microorganisms were involved in NP biodegradation via different degradation pathways, which reduced the possible risk of NP in the environment under aerobic conditions. Removal rates of NP ranging from 13.6 to > 99 % have been reported in literature (Mao et al. 2012).

Regarding AEOs, they are used as an eco-friendly alternative to APEOs (Scott and Jones 2000). In wastewaters, AEOs are usually found in the form of a complex mixtures composed of more than 100 homologous compounds with varying alkyl chain lengths and varying numbers of ethylene oxide (EO) units (Morrall et al. 2006). AEOs concentrations in sewage wastewaters ranged between 1 and 23 μg L^{-1}. In fact, sewage wastewaters collected from eight different Canadian wastewater plants were contaminated by 1 to 22.7 μg L^{-1} of AEOs with an average of 6.8 μg L^{-1}. Ying (2006) showed that AEOs could be treated under aerobic and anaerobic conditions amended soils. The mechanism for aerobic biodegradation of AEOs was believed to be initiated by the central cleavage of the molecule, leading to the formation of PEG and FFA, followed by N- or H-oxidation of the terminal carbon of the alkyl chain, and the hydrolytic shorting of the terminal carbon of the polyethoxylic chain. In contrast to aerobic biodegradation where central prevails, the first step of anaerobic microbial attack on the AEO molecule is the cleavage of the terminal ethoxy unit, releasing acetaldehyde stepwise and shortening the ethoxy chain until the lipophilic moiety is reached.

Table 4 summarizes the concentrations of LAS, PFOA, PFOS, APEOs, and AEOs in different environmental compartments.

Generally, the presence of surfactants in biological treatment plants disturb the primary sedimentation process and decrease the capacity for the transfer of oxygen, thus rendering the biodegradation process inefficient and incomplete (Aboulhassan et al. 2006, de la Fuente et al. 2010, Koparal et al. 2006). Due to the low degradation kinetics and foam production, researchers have shown that the conventional treatment method using aerobic bacteria are suitable for treating only slightly contaminated waters (Aboulhassan et al. 2006, Mousavi et al. 2011). For cationic surfactants (QACs) and non-ionic ones (APEOs), conventional treatment processes regarding anaerobic treatment are not capable in most cases to remove these pollutants from wastewaters. Thus, the discharge of such compounds in aquatic environment at concentration ranging respectively from 0.0025 to

Table 4 Concentrations of LAS, APEOs and AEOs in different environmental compartments

Surfactants	Matrix type	Value	References
LAS	Sewage effluents	1090–1100 $\mu g\ L^{-1}$	(Holt et al. 1998, Ying 2006)
	Surface water	0.05–400 $\mu g\ L^{-1}$	(Fountoulakis et al. 2009)
	Raw wastewater	2–21 $mg\ L^{-1}$	(Fountoulakis et al. 2009)
	Untreated Sludge	400–14000 $mg\ kg^{-1}\ dw^{-1}$	(de Wolf and Feijtel 1998)
PFOA and PFOS	Ground water	>3500 $ng\ L^{-1}$ for PFOA >2200 $ng\ L^{-1}$ for PFOs	(Xiao et al. 2013b)
APEOs (NP1EO)	WWTP effluent	45±16 $\mu g\ L^{-1}$	(Montgomery-Brown and Reinhard 2003)
	River sediments	160–3970 $ng\ g^{-1}\ dw^{-1}$	(Montgomery-Brown and Reinhard 2003)
AEOs	Untreated sewage wastewater	1–22.7 $\mu g\ l^{-1}$	(Environnement Canada 1999)

300 mg L^{-1} and from 0.3 to 200 mg L^{-1} gives toxic effects to various aquatic organisms (Arslan-Alaton and Erdinc 2006).

Regarding the difficulty facing conventional WWTP (high surfactants concentration and anaerobic degradation), alternative processes are recommended for better surfactant removal.

Currently, a few alternative methods have been developed to remove surfactants from aquatic environment. Adsorption processes using a number of low-cost adsorbents have been studied to evaluate their efficiency for removal of cationic surfactants from aquatic environment (Koner et al. 2011). Owing to their abundance and lower cost, the uses of natural clay minerals such as bentonite have drawn much interest. For instance, high removal efficiency (>99 %) of a cationic surfactant (cetyltrimethylammonium bromide, CTMAB) from wastewater has been recorded in the one step process using bentonite alone (Zhu and Ma 2008). Besides, the use of silica gel waste as an adsorbent was found to be very attractive alternative for removal of cationic surfactants (362 mg L^{-1}) from industrial wastewater (Koner et al. 2011). High removal efficiency of cationic surfactants (87 %) was achieved using 10 g L^{-1} of adsorbent dose and during 30 min of treatment time. Despite the higher removal efficiency recorded using adsorption process, the fate of adsorbent used to eliminate surfactants and its regeneration ability is still unknown (Saleh 2006). Furthermore, the nature of the solid surface, the molecular structure of surfactant that is adsorbed and the nature of matrix (pH, temperature, salinity, etc.) influences the adsorption of the surfactants (Borghi et al. 2011). Another important area that deserves further investigation is the ecotoxicology of the sorbents.

Thus, additional research is needed to fill these gaps prior to the assessment of the entire process of surfactants removal from the environment. Likewise, adsorption is just a process to concentrate the contaminant and there is no transformation which raises question on the utility of the technology as a long-term method. Thus, the development of efficient technologies such as advanced oxidation processes (AOPs) replacing conventional treatment techniques becomes necessary.

AOPs are considered to be highly competitive techniques for the removal of recalcitrant organic pollutants. The principle of AOPs (O_3/H_2O_2, UV/O_3, UV/H_2O_2, H_2O_2/Fe^{2+}, UV/TiO_2, among others) is to produce the hydroxyl radicals in water (redox potential=2.8 V) capable of oxidizing a wide range of stable molecule (Andreozzi et al. 1999, Loraine 2008, Rivera-Utrilla et al. 2012). Application of AOPs for degradation of surfactants present in water and wastewater has received increasing attention in the field of environmental protection as presented in Table 5. Chemical oxidation process using either O_3 or H_2O_2 has been investigated to remove surfactants. Ozonation process using O_3 dose up to 6 mol of O_3 per mole of NP was applied by Vilve et al. (2009) to remove more than 90 % of NP, whereas only 39 % of dodecylbenzene sulfonate (SDBS) (57 μM) was oxidized after 60 min of treatment time using 60 μM of O_3. The dose of oxidant used strongly influenced the treatment efficiency. Previous research have also used Fenton process (H_2O_2/Fe^{2+}) to remove non-ionic (alkyl alcohol C_{13}–C_{15} ethoxylates) and anionic (LAS, ABS) surfactants (Mousavi et al. 2011, Vilve et al. 2009). The oxidation capacities of H_2O_2/Fe^{2+} were highly dependent on both the concentration of H_2O_2 and Fe^{2+}. Higher reduction of COD (85 %) and TOC (69 %) were achieved while treating non-ionic surfactant solution using H_2O_2 dose of 1000 mg L^{-1} and a stoichiometric ratio H_2O_2/Fe^{2+} of 2 (Vilve et al. 2009). The removal of LAS in aqueous solution was also studied by Mousavi et al. (2011) using H_2O_2 assisted to Fe^{2+} during 80 min. Fenton oxidation process (H_2O_2/Fe^{2+}) was able to remove more than 80 % of LAS (200 mg L^{-1}) at 600 mg L^{-1} and 130 mg L^{-1} for H_2O_2 and Fe^{2+}, respectively. In spite of the higher oxidation of surfactants, higher chemical consumption of oxidants (H_2O_2 and O_3) constitutes major barrier for large-scale applications.

Among different alternative treatment options, photochemical advanced oxidation processes have proved to be a good candidate for the destructive treatment of surfactants (Olmez-Hanci et al. 2011). The application of UV-C/H_2O_2 while treating non-ionic surfactants appeared to be a suitable treatment alternative and 90 % COD removal ([COD]°=

Table 5 AOPs operation conditions and removal results for anionic, non-ionic and cationic surfactants

AOPs	Surfactants	Surfactant	Operating conditions	Results and comments	References
Ozonation O_3	SDBS	Wastewater	[SDBS]=57 µM t=0–60 min; T=298 K $[O_3]$=0–60 µM; pH=7	39 % of SDBS removal	(Rivera-Utrilla et al. 2012)
	NP	Synthetic solution	Pure oxygen gas; t=1 h Room temperature 6 mol O_3 per mole NP	over than 90 % of NP removal	(Vilve et al. 2009)
Fenton (H_2O_2/Fe^{2+})	C_{13}–C_{15} ethoxylates	Laundry wastewater	H_2O_2/Fe^{2+}=2 $[H_2O_2]$=1000 mg L^{-1} pH=5; t=5 min	85 % COD reduction 69 % TOC reduction	(Kim et al. 2005)
	LAS	Synthetic solution	$[H_2O_2]$=600 mg L^{-1} $[Fe^{2+}]$=130 mg L^{-1} [LAS]=200 mg L^{-1}; t=80 min; pH=3; T=25 °C	More than 80 % of LAS removal	(Mousavi et al. 2011)
UV-C/ H_2O_2	Alkyl Polyethylene Ether	Synthetic solution	$[H_2O_2]$=10–100 mM UV length=253.4 nm Flow rate=80 ml min^{-1} Retention time=24 min Reactor volume=1900 ml; Treatment time=120 min pH=5–12	90 % COD removal (t=120 min, COD_0=490 mgL ^{1},$[H_2O_2]_0$=1000 mg L^{-1}, pH_0=9)	(Arslan-Alaton and Erdinc 2006)
UV/TiO_2	Rokafenol N_9	Synthetic solution	Reactor volume=200 ml $[N_9]_0$=50 mg L^{-1} Initial TOC=33.7 mg C/L pH=5.6; $[TiO_2]$=0.2 g/L Treatment time=5 h UV intensity=0.2 W/m^2	degradation rate=61 % TOC reduction=40 % catalyst calcinated at 600 °C with rutile 94.2 % of anatase and 5.8 %	(Mozia et al. 2005)
	NPE PAE (9-6)	Synthetic solution	Reactor volume=2000 ml [NPE]=[PAE (9–6)]=2 g L^{-1} TiO_2=0.1 % w/v UV intensity=400 W λ=365 nm	Total degradation after 250 h using 0.1 % w/v of TiO_2	(Sherrard et al. 1996)
Electro-oxidation	SDBS	Synthetic wastewater	[SDBS]=0.3 gdm^{-3} $[Na_2SO_4]$=[NaCl]=$[K_3PO_4]$= 0.1 M Current density=30–60 $mAcm^{-2}$ Flow rate=1.25 dm^{-3} min^{-1} Linear velocity=2.31 cm s^{-1}	Over 95 % COD removal ([SDBS]=0.3 gdm^{-3}, [NaCl]=0.1 M Current density=60 $mAcm^{-2}$)	(Louhichi et al. 2008)
	Sodium Dodecylbenzenesulfonate (SDBS) Hexadecyltrimethyl ammonium chloride (HAC)	Synthetic solution	[SDBS]=20–200 mg dm^{-3} [HAC]=20–200 mg dm^{-3} pH=4–10 specific energy requirement=10–20 KW h m^{-3}	83 % of TOC removal for SDBS; 68 % of TOC removal for HAC	(Lissens et al. 2003)

490 mg L^{-1}) was achieved after 120 min of irradiation and using 1000 mg L^{-1} of H_2O_2 dose (Arslan-Alaton and Erdinc 2006). The same trends have been also recorded by Olmez-Hanci et al. (2011) while treating three different commercial textile surfactants (dioctyl sulfosuccinate DOS; quaternary ammonium ethoxylate and nonylphenol ethoxylate) by UV-C/H_2O_2. Complete removal of surfactants has been recorded within 15–20 min of photochemical treatment and over 90 % of COD and TOC removals were achieved after prolonged oxidation period for an initial surfactant COD of 450 mg L^{-1} and an initial pH of 10.5. Photocatalytic process using TiO_2 photocatalyst under UV radiation represents another example of photochemical AOPs capable of generating in situ OH° radicals, among other reactive oxygen species (e.g. H_2O_2, $O_2^{\circ-}$, etc.) which ensures higher reactivity and low selectivity. Higher degradation (61 %) of non-ionic surfactant (Rokafenol N9) and higher removal of TOC (40 %) were achieved after 5 h of irradiation time (visible light illumination) using the anatase form of TiO_2 as photocatalyst (Mozia et al. 2005). Lizama et al. (2005) ensured 80 % removal of industrial-grade surfactants, sodium lauryl sulfate (SLS) and sodium dodecylbenzenesulfonate (SDDBS) after 60 min of irradiation time and using an immobilized TiO_2 as photocatalyst. In comparison, total removal of nonylphenol ethoxylate and primary alcohol ethoxylate were achieved after UV irradiation time up to 250 h and using 0.1 %*w*/*v* of TiO_2 (Sherrard et al. 1996). Although photocatalytic process seems to be very promising for the treatment of waters contaminants by surfactants, the practical applications of photocatalytic technology at large scale remain limited due to the fast recombination of photogenerated electrons/holes pairs (e^-/h^+).

Nowadays, electrochemical technologies applied for the treatment of surfactants have received considerable attention in the environmental field (Koparal et al. 2006, Lissens et al. 2003, Panizza et al. 2005). The electrochemical method combining chemistry and electronic science (electron transfer) has widely proved to be a clean, flexible, and powerful technique for water and wastewater treatment (Kim et al. 2005). Electrochemical treatment is characterized by simple equipment, easy operation, safety, selectivity, environmental compatibility, and brief retention time (Rajeshwar 1997). Compared to chemical oxidation, no addition of chemicals is necessary in the process of electrochemical degradation. In electrochemical oxidation processes, pollutant can be removed electrochemically by a direct anodic oxidation, where pollutant are firstly adsorbed on the anode surface and then destroyed through the anodic electron exchange. On the other hand, pollutants could be also degraded indirectly in the liquid bulk through reactive oxidant species (OH°, O_3, H_2O_2, chlorinated species, etc.), which act as intermediates for electrons transference between the electrode and the refractory organic compounds (Homem and Santos 2011, Panizza and Cerisola 2009). This technology has been widely applied to remove surfactants under different experimental conditions. More than 95 % of COD has been recorded by Louhichi et al. (2008) while treating synthetic wastewater polluted with sodium dodecylbenzene sulfonate (SDBS) by electrochemical oxidation process using boron-doped diamond (BDD) as anode, at 60 mA cm^{-2} of current density and 0.3 g dm^{-3} of initial organic load. Electrochemical oxidation of cationic (hexadecyltrimethyl ammonium chloride) aqueous surfactants solution has been also reached using BDD (boron-doped diamond) electrode. Removal rate of TOC up to 68 % was recorded at an applied charge of 2.5 Ah (Lissens et al. 2003).

However, electrochemical oxidation of non-ionic surfactants such as APEOs is not well documented in the literature. Despite this higher degradation of surfactants recorded using electrochemical technology, the applicability of this process for large scale remains limited. The high operating cost due to the high energy consumption is still the main drawback which limits the application of the electrochemical process.

Until date, no experiments have been conducted to exploit other AOPs, such as photosonochemical technology and photoelectrocatalytic process for removal of surfactants from water and wastewater. These technologies could offer an alternative to ensure an efficient degradation of surfactants from aqueous environment and to enhance its biodegradability in wastewater treatment plants (WWTPs).

Surfactant in sludge

The concentration of surfactant in sludge has been typically reported to be micrograms to hundreds of milligrams per kilogram (González et al. 2012). According to previous studies conducted by Lara-Martín et al. (2008), these concentrations can even reach several grams per kilogram in some cases. In fact, concentrations of LAS in raw sewage sludge are very high due to its widespread usage and strong sorption on sludge during the treatment. Sewage sludge that had been aerobically treated had LAS concentrations of 100–500 mg kg^{-1} dw, while those anaerobically treated sludge had much higher LAS concentrations ranging from 5000 to 15,000 mg kg^{-1} dw. In the same way, AFEOs concentrations detected in anaerobically treated sludge ranged from 900 to 1100 mg kg^{-1} which is much higher than in aerobically treated sludge (0.3 mg kg^{-1}) (Scott and Jones 2000).

Extremely high concentrations of QACs have been also reported in untreated municipal sewage sludge where the concentrations were around 9200 μg g^{-1}. In fact, degradation of surfactants through microbial activity is the primary transformation occurring in the environment (Ivanković and Hrenović 2010, Mungray and Kumar 2009). During biodegradation process, microorganisms can either utilize surfactants as substrates for energy and nutrients or they can co-metabolize the surfactants by microbial metabolic reactions (Mungray and Kumar 2009, Ying 2006). There are many physicochemical conditions and environmental factors that affect the biodegradation of surfactants. The most important influencing factors are the chemical structure of surfactants, the microbial population and aerobic and anaerobic environment among others.

Anionic surfactants in sludge

According to Scott and Jones (2000), a significant proportion of anionic surfactants such as LAS (10 to 35 %) adsorbs on particulate matters during sewage treatment. LAS are highly biodegraded under aerobic conditions and are completely eliminated by the activated sludge process (Ivanković and Hrenović 2010, Scott and Jones 2000). Their biodegradation is initiated by -oxidation of the alkyl chain followed by β-oxidation (Fountoulakis et al. 2009). The β-oxidation step promotes the successive cleavage of C_2 fragments. The reaction occurring during and β-oxidations generate sulfophenyl carboxylates (SPCs) resulting in the loss of interfacial activity and toxicity. The cleavage of SPCs aromatic ring generates shorter chain homologues and promotes the LAS mineralization into CO_2 and H_2O (Mungray and Kumar 2009). The rate of LAS biodegradation increased with increasing dissolved oxygen concentrations, but under low oxygen conditions (<1 mg L^{-1}) only a fraction of LAS was biodegraded (Krueger et al. 1998). According to Jensen (1999), high LAS concentrations were recorded in anaerobic digested sludge (3000–30,000 mg kg^{-1} ds) compared to lower amounts of LAS recorded in aerobic stabilized sludge (100–500 mg kg^{-1} dw) or untreated sludge (400–14,000 mg kg^{-1} ds).

Generally, the aerobic degradation of LAS requires the contribution of several species of bacteria (Hršak and Begonja 1998). Usually, the use of single bacteria has a limited capacity to degrade the alkyl chain and cannot cleave the sulfonated aromatic ring of LAS. Several bacterial strains from seawater have been used by Sigoillot and Nguyen (1992) to oxidize LAS. All the bacteria were heterotrophic, strictly aerobic of *genera Alcaligenes, Deleya, Oceanospirillum, Aquaspirillum*, and *Pseudomonas*. Under anaerobic conditions, the biodegradation process of LAS is not favored (Ying 2006). The concentration of sludge measured before and after anaerobic digestion show that the LAS degradation during anaerobic treatment is absent (McEvoy and Giger 1985). Nevertheless, the anaerobic degradation of LAS depends on alternative acceptors such as sulfate, nitrate, or carbonate. Previous studies show that LAS could be used as a source of sulfur by anaerobic bacteria under sulfur-limited conditions (Denger and Cook 1999). Under thermophilic conditions, benzene-sulfonic acid and benzaldehyde may be produced as metabolites (Mogensen and Ahring 2002). Furthermore, LAS could be partially used as a source of carbon and energy by anaerobic bacteria in the presence and absence of additional source of carbon (Sanz et al. 2003). In the presence of NO_3^- as electron acceptor, LAS could be degraded in the acidogenic step of the upflow anaerobic sludge blanket (UASB) reactor (Almendariz et al. 2001). Under mesophilic and thermophilic conditions, the biodegradation rate of LAS in a bench-scale UASB reached 40–80 % (Løbner et al. 2005). However, mechanisms other than biodegradation are also involved in LAS removal, these include adsorption, settling of suspended solids and precipitation of calcium salts (Mungray and Kumar 2009).

Cationic surfactants in sludge

Cationic surfactants having a positive charge have a strong affinity toward the surface of particulates in sewage sludge, which are predominately negatively charged (Ying 2006). Topping and Waters (1982) show that 95 % of the cationic surfactants were adsorbed on the surface of particulate matter, while Huber (1984) provides that 20–40 % of cationic surfactants in primary settling tank were associated with particulate matter. Cationic surfactants are biologically degradable under aerobic conditions. As reported by Ivanković and Hrenović (2010), cationic surfactants such as QAC could be a source of carbon and energy for some microorganisms. The biodegradation of QAC cationic surfactants was associated with an increase in bacterioplankton density, suggesting that the degradation takes place because the compound is used as a growth substrate (Garcia et al. 2001). Generally, the biodegradability of QACs under aerobic conditions decreases with the number of non-methyl alkyl groups ($R_4N^+ < R_3MeN^+ < R_2Me_2N^+ < Me_4N^+$, where Me = methyl radical) (Ying 2006). The biodegradation pathway for alkyl trimethyl ammonium (TMAC) and alkyl dimethyl ammonium (DMAC) is believed to begin with N-dealkylation, followed by N-demethylation (Ivanković and Hrenović 2010, Ying 2006). During the biological treatment using activated sludge in municipal sewage treatment, trimethylamine, dimethylamine, and methylamine were identified as the main intermediates of alkyl trimethyl ammonium salts (Ying 2006).

Initially, alkyl trimethyl ammonium salts was biodegraded to trimethylamine via N-dealkylation. Subsequently, the trimethylamine is degraded into dimethylamine and this intermediate is further degraded into methylamine. The initial oxidation of cationic surfactants cannot take place without the presence of molecular oxygen. Under anaerobic conditions, QAC exhibits limited or no biodegradation (Stasinakis 2012, Tezel et al. 2006). In addition, due to the highly reduced nature of alkyl and benzyl group, no evidence of mineralization has been noticed for QAC. For example, no biodegradation was observed for ditallow dimethyl ammonium chloride (DTDMAC) in anaerobic screening tests (Garcıa et al. 2000).

According to the previous study of Scott and Jones (2000), it can be assumed that cationic surfactants are not anaerobically biodegradable either due to the lack of appropriate metabolic pathway and/or a possible toxic effect of the surfactant upon the anaerobic microorganisms. However, recent study of Watson et al. (2012) shows that some QAC were transformed to methane, when concentrations lower that those causing inhibition to methanogens were used. An abiotic hydrolysis of target compounds was initially observed, followed by biodegradation of hydrolysis products to methane, carbon dioxide, and ammonia.

Non-ionic surfactants in sludge

Generally, non-ionic surfactants are readily biodegradable under aerobic conditions (Ivanković and Hrenović 2010). Alcohol ethoxylate (AEO) are easily biodegraded under aerobic and anaerobic conditions (Ying 2006). By using continuous flow activated sludge test, higher primary biodegradation (96 ± 0.5 %) of AEOs was achieved with the formation of a high concentrations of metabolites such as free fatty alcohol (FFA) and polyethylene glycols (PEG) (Szymanski et al. 2000). Under aerobic conditions, the biodegradation mechanism of AEOs was initiated by the central cleavage of the molecule, leading to the formation of PEG and FFA, followed by the -oxidation or the β-oxidation of the terminal carbon of the alkyl chain, and the hydrolytic shorting of the terminal carbon of the polyethoxylic chain (Ivanković and Hrenović 2010). By comparison to aerobic biodegradation, the first step of anaerobic degradation of AEO molecule promotes the cleavage of the terminal ethoxy unit, the release of acetaldehyde and the shortening of ethoxy chain until the lipophilic moiety is reached (Ying 2006). Regarding AFEOs, their anaerobic biodegradation and their breakdown products appear limited (Ivanković and Hrenović 2010, Ying 2006). The mass fractions of APEOs recorded in anaerobically digested sludge were between 900 and 1100 mg kg^{-1}, while 0.3 mg kg^{-1} of APEOs has been recorded in aerobically digested sludge (Ivanković and Hrenović 2010, Scott and Jones 2000).

In conventional sewage treatment plants, the biodegradation of APEOs is believed to start with a shortening of the ethoxylate chain, leading to short-chain APEOs containing one or two ethoxylate units. Further oxidation of the ethoxylate chain promotes mainly the formation of the alkylphenoxy ethoxy acetic acid and alkylphenoxy acetic acid (Talmage 1994). Regarding nonylphenol ethoxylate, the biotransformation under anaerobic conditions promotes the formations of nonylphenol (NP), nonylphenol monoethoxylate (NP1EO) and nonylphenol diethoxylate (NP2EO) (Lu et al. 2008). During anaerobic digestion, nonylphenol monoethoxylate and nonylphenol diethoxylate (NP2EO) are biodegraded to some extent, producing nonylphenol (NP) (Patureau et al. 2008). The removal rate of nonylphenol ethoxylate recorded in the US varied from 93 to 99 % (Naylor 1994). By comparison, in Italy, Switzerland, and Japan the biodegradation of nonylphenol ethoxylate reached 98, 89, and 99 %, respectively (Ahel et al. 1994, Crescenzi et al. 1995, Nasu et al. 2001). Overall, the nonylphenol ethoxylate are less biodegradable and only partial mineralization occurred during the biological treatment (Scott and Jones 2000). The study conducted by Manzano et al. (1999) indicates that metabolites such NPE2, NPE1, NPEC1, and NPEC2 were generated during the biodegradation of nonylphenol polyethoxylate which do not totally disappear at the end of the test (30 days). Consequently, the persistence of nonylphenol ethoxylate by-products in sludge could disrupt microbial and enzymatic activities, as biosolids will be loaded into the soil after treatment.

Future trends and perspective

This paper underlines the worldwide usage of surfactants, their fate, their aquatic and terrestrial toxicity, and the different treatment used in order to remove them from environmental compartments. Their lower cost and their favorable physicochemical properties make surfactants more suitable for industrial applications. Besides, surfactants are potentially significant as environmental contaminants due to their higher stability and their excessive occurrence. The fate of surfactants in sludge, water, and wastewater is well discussed. Nevertheless, their occurrence in soil and sediments remains an inconclusive area of investigation as this ecosystem is considered as a final sink of surfactants (Asok and Jisha 2012, Cavalli et al. 1996, González et al. 2012, Higgins and Luthy 2006). Although extensive studies have been conducted on the surfactants (anionic, cationic, and non-ionic), the fate and effect of its metabolites is still unknown and pose challenges. In order to protect human health and ecosystems, major researches focus to develop new remediation techniques for the removal of surfactants from aquatic and terrestrial media. However, the risk of its metabolites to aquatic and terrestrial environments deserves special interest. The major metabolite discussed so far is nonylphenol (NP). NP was designed as priority hazardous substances (PHS) in the EU Water Framework Directive (2000) and most of their uses are regulated (EU Water Framework Directive 2003). NP is a hydrophobic compound with a log K_{OW} value of 4.48 and low solubility in water, therefore it partitions favorably to organic matter (Soares et al. 2008). During anaerobic digestion, NP does not undergo further transformation and accumulates on biosolids at concentrations ranging from a few mg kg^{-1} to more than 1 g kg^{-1} (Stasinakis 2012). However, Wang et al. (2015) have recently shown that anaerobic biodegradation of 100 mg kg^{-1} of NP could be achieved after 90 or 110 days of incubations. The most dominant phylum groups related to NP biodegradation were *Proteobacteria*, *Firmicutes, Bacteroidetes*, and *Chloroflexi*. The use of such anaerobic microorganisms allowed 80 % of NP removal from sediments. During the anaerobic biodegradation process, NP removal was performed under either nitrate or sulfate-reducing conditions.

Even at low concentrations (micrograms per liter), NP can act as an endocrine disruptor by interfering with the hormonal system of numerous organisms. Toxicological studies of laboratory animals suggest that exposure of NP is associated with morphologic, functional and behavioral anomalies related to reproduction (Calafat et al. 2005). In fact, NP is estrogenic in vivo and in vitro (Kwak et al. 2001, Soares et al. 2008), and interferes with estrous cycle and pubertal onset in rats (Kim et al. 2002, Laws et al. 2000).

Besides, reported concentrations of surfactants in different environmental compartments are still detected in lower trace levels and ultimately depend on spatial and climatic variations. Given this fact, analytical techniques developed for the detection should have higher sensitivity, selectivity, and specificity. As reported by Gomez et al. (2011), the limited volatility of some surfactants restricts the use of gas chromatography-mass spectrometry (GC-MS). Liquid chromatography (LC) coupled to mass spectrometry (MS) has been developed and effectively implemented by several research groups for the determination of surfactants and its metabolites mainly owing to the known advantage of mass spectrometry detection over conventional detection method such as UV and fluorescence. Mass spectrometry-mass spectrometry proves to be a useful analysis technique able to identify and clarify the structure of this compound in complex environmental matrices (wastewater and sludge samples) (Evans et al. 1994, Gomez et al. 2011, González et al. 2007, Lara-Martín et al. 2012). It should be also mentioned that several questions remain unanswered for the conventional treatment processes (biological or physico-chemical treatments) generally applied to remove surfactants through wastewater treatment plants. The excessive occurrence of surfactants in the aquatic and terrestrial environmental is mainly due to the unsuccessful conventional treatment processes applied in WWTPs for the complete removal of these compounds. However, to overcome this drawback, novel qualitative and quantitative approaches that use and integrate the chemical data including AOPs have been developed and applied to remove different types of surfactants from water, wastewater, and sludge.

Until date, applications of AOPs for surfactants removal were carried out only at the laboratory scale. Future research should be focused on the development of AOPs for large-scale applications. AOPs could be effectively combined with biological processes to remove surfactants (Kitis et al. 1999, Rivera-Utrilla et al. 2012, Wang et al. 2008). Coupling a biodegradation process with physicochemical process (pretreatment step) would improve the biodegradation of surfactants and reduce the operating cost as well as a shorter retention time (Kitis et al. 1999, Wang et al. 2008). For instance, advanced oxidation pretreatment using higher oxidant dosage of Fenton's reagent was highly effective for enhancing the biodegradability of nonylphenol ethoxylate (Kitis et al. 1999). This coupling takes advantage of biological process and chemical process. Therefore, more interest for advanced oxidation process for surfactant removal should be considered.

Conclusions

This review emphasizes the widespread usage of surfactants, their occurrence and their toxicity in different aquatic and terrestrial compartments. Due to their excessive uses in different industrial applications, residual concentrations of surfactants have been detected in the environment. The introduction of these residual compounds into environment will lead to serious environmental problems including ecological risk and human health damage. Despite the extensive knowledge about surfactants, advanced studies need to be carried out to evaluate the toxicity of surfactants. More effort should be made to elucidate the toxic effects of QAC and AEOs. The available data and the risk assessment for these groups of surfactants are yet very limited. Supplementary information is also needed about the APEOs, because of their by-products biodegradation of octylphenols and nonylphenols. The exposure of such compounds in the environment can generate toxic effects for living things as humans, fish, and plants. Up to now, conventional wastewater treatment plants are not able to remove completely surfactants from waters as well as from sludge. Advanced oxidation processes have been proposed as alternative methods to ensure the higher degradation and mineralization of surfactants compounds.

Acknowledgments Sincere thanks are extended to the National Sciences and Engineering Research Council of Canada and Produits Chimiques Magnus Ltée for their financial support for this study.

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