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REVIEW

Alkylphenol and alkylphenol polyethoxylates in water and wastewater: A review of options for their elimination



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Abstract During the last 10 years, the appearance of emerging organic compounds described as endocrine disrupters in wastewaters and water resources has become a major concern for both society and public health authorities, the whole industrial world and the agricultural sector. Endocrine disrupting compounds are found in various environmental compartments such as water, sediments, soils and atmosphere, as a result of their wide usage. Numerous products are concerned including

Abbreviations: AC, activated carbon cloth; ASP, activated sludge process; AOPs, advanced oxidation processes; APs, alkylphenols; APEOs, alkylphenol ethoxylates; COD, chemical oxygen demand; EDCs, endocrine disrupting compounds; EQS, environmental quality standards; GC-MS, gas chromatography-mass spectrometry; ESMS, electrospray mass spectrometry; HPLC, high performance liquid chromatography; K_{ow} , octanol-water partition coefficient; LC-MS, liquid chromatography-mass spectrometry; MBR, membrane bioreactor; MF, microfiltration; NF, nanofiltration; NP, nonylphenol; NPEC, nonylphenoxy acetic acid; NPEO, nonylphenol ethoxylate; NMR, nuclear magnetic resonance spectroscopy; NOM, natural organic matter; OP, octylphenol; OPEOs, octylphenol ethoxylates; PEGs, polyethylene glycols; RO, reverse osmosis; SS, suspended solids; TOC, total organic content; UF, ultrafiltration; UV, ultraviolet; WWTPs, wastewater treatment plants.

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Treatment methods

surfactants, industrial additives and formulations, pharmaceuticals, and also personal care products. However, the existing conventional water treatment plants were not designed for these new contaminants. In the present study, an overview of the literature on methods for the elimination (removal and/or degradation) of emerging trace organic contaminants is presented. This review is limited to details of the treatment of one class of endocrine disrupters, namely alkylphenols and their polyethoxylate derivatives, which are suspected to interfere with the hormonal system of wildlife. The technologies proposed for alkylphenol treatment include membrane treatment using biological (membrane bioreactors) or physical processes (membrane filtration such as nanofiltration), biotechnological-based methods (biofilms, immobilized enzymes, etc.), adsorption-oriented processes using conventional (activated carbons) or nonconventional adsorbents (clays, cyclodextrin, etc.), and advanced oxidation processes (photocatalysis, photolysis, and sonochemistry). Examples are taken from the literature to illustrate various features of the technologies used in decontamination methods. Among them, photocatalytic oxidation is an interesting tool for alkylphenol treatment due to its potential to reach complete mineralization.

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1. Introduction

From the environmental point of view, the organic molecules that are of greatest current concern are those which, either by their presence or their accumulation, can have a toxic or an inhibitory effect on living organisms. Among these molecules, endocrine disrupting compounds (EDCs) have been investigated due to their adverse effects in animals and humans inhibiting the normal action of the endocrine system. The list of these xenobiotic compounds is extensive and includes for example the following families of chemicals: alkylphenols, phthalates, bisphenol A, polybromodiphenylethers, and natural and synthetic estrogens (Crini and Badot, 2007). Among these, alkylphenols (APs), and in particular their polyethoxylated derivatives (alkylphenol ethoxylates, APEOs), deserve particular attention. By far the most commercially important AP is nonylphenol (NP) which is used primarily to produce nonylphenol ethoxylate (NPEO) surfactants for a wide variety of applications and consumer products: paints and latex paints, adhesives, inks, washing agents, formulation of pesticides (emulsions), paper industry, textile and leather industry, petroleum recovery chemicals, metal working fluids, personal care products, cleaners and detergents, etc. Also commercially significant compounds are octylphenol (OP) and octylphenol

ethoxylates (OPEOs). NPEOs represent around 80% of APEOs while OPEOs make up most of the remaining 20%.

As a consequence of the use, discharge and biodegradation of NPEOs, NP occurs ubiquitously in the environment. For instance, NPEOs and also OPEOs are unstable in the environment and both undergo the same processes of degradation to yield metabolites that are generally more stable and thus more persistent. From the ecotoxicological point of view, NP is persistent in the aquatic environment, moderately bioaccumulative, and extremely toxic to aquatic organisms (Soto et al., 1991; Comber et al., 1993; Baldwin et al., 1997; Severin et al., 2003; Brian et al., 2005; Ishibashi et al., 2006; Soares et al., 2008; David et al., 2009; Lozano et al., 2012). Though less toxic than NP, NPEOs are also highly toxic to aquatic organisms, and in the environment degrade to more environmentally persistent NPs (Naylor et al., 1992; Ahel et al., 1993; Talmage, 1994; Argese et al., 1994; Servos, 1999; Maguire, 1999; Lozano et al., 2012). In addition, these emerging compounds exert endocrine disruption effects since they mimic natural hormones by interacting with estrogen receptors. Not all isomers are equally effective: the para-position of the phenolic OH-group and branched aliphatic side-chain appear to be determinant. Kim et al. (2004), Preuss et al. (2006), and Bärlocher et al. (2011) reported that the branched

NPs exhibit a higher endocrine activity than linear NP. It is important to note that not only the parent molecules but also their degradation products represent a potential ecotoxicological problem in aquatic systems (Soares et al., 2008; Rizzo, 2011) due to their widespread occurrence in surface waters and persistence in sediments. The particular case of NPs provides a good illustration of the way in which relatively inoffensive anthropogenic substances can be transformed into toxic compounds in the environment. NPEOs in domestic wastewater reach the sewage treatment plant where microorganisms progressively decompose the ethoxy chain to finally release several compounds including the NP that was initially used to synthesize the detergents (Crini and Badot, 2007).

Actually, from the analytical point of view, the methodologies for monitoring APs and APEOs are now well known and, in general, gas chromatography coupled with mass spectrometric detection is the most commonly applied analytical technique due to its simplicity, robustness, and reproducibility (Ahel and Giger, 1985; Lee, 1999; Richardson, 2002; Loos et al., 2008; Asimakopoulos et al., 2012; Selvaraj et al., 2014). Information on the applicable sample preparation techniques, the instrumental analysis and the monitoring of NP and OP can be found in the recent review of Asimakopoulos et al. (2012). Humans are mainly exposed to APs by the intake of contaminated foods and drinking water. NP and OP present in plastic containers and wrappings may migrate into foods and drinking water. Other routes of human exposure include contact with personal care products and detergents, and the use of spermicides in contraceptives (Talmage, 1994). NP has been detected in human milk, blood, and urine.

In Europe (Directive 2003/53/EC, 2003), the use of EDCs, and in particular APEs, is today restricted. The main alternatives for NPEOs include linear and branched alcohol ethoxylates, and glucose-based carbohydrates such as alkylpolyglucoside. Despite this, they are still likely to appear in many European wastewater streams, as in the case in France, a result of their frequent industrial use. In this context, it is necessary to propose and develop various efficient technologies for the elimination of alkylphenols from water and wastewater.

Several reviews dealing with different aspects of relevance for the treatment of EDCs should be mentioned. Gültekin and Ince (2007) and Belgiorno et al. (2007) discussed the treatability of EDCs in water by advanced oxidation processes. EDC removal using physical means, biodegradation, and chemical decomposition by advanced oxidation was also reviewed by Liu et al. (2009) and Bolong et al. (2009). Cabana et al. (2007a) extensively reviewed the ability of white rot fungi (WRF) and their lignin modifying enzymes, i.e., laccase, to treat EDCs from solutions. Murray and Öermeci (2012) presented recent research results on molecularly imprinted and non-imprinted polymers and evaluated their potential as a method of treatment for the removal of emerging contaminants from water and wastewater. Basile et al. (2011) critically discussed the basic principles of the advanced technologies used for EDC control in water and wastewater. Few reviews have focused on AP removal (Soares et al., 2008). The present review is limited to the methods for the removal and/or the degradation of one class of endocrine disruptors, namely alkylphenols. Among the methods reported, adsorption-oriented processes, membrane-oriented treatment, biotechnological methods and advanced oxidation processes are the most fre-

quently considered as they may be appropriate for removing trace concentrations of APs.

2. Overview of alkylphenols as emerging pollutants

Since the end of 2000s, numerous reviews and articles have reported the presence of novel chemical compounds, called emerging pollutants, not only in water, wastewater and aquatic environments, but also in sediments, soils and the atmosphere (Crini and Badot, 2007). Recent information on the so-called emerging pollutants in wastewater can be found in a review published by Deblonde et al. (2011). The definition of 'emerging' is, however, not clear (Field et al., 2006; Stasinakis, 2012). The US Environmental Protection Agency defines emerging pollutants as new chemicals without regulatory status and with an impact on the environment and human health that is poorly understood. These include polycyclic aromatic hydrocarbons (PAHs) (anthracene, phenanthrene), volatile organic compounds (VOCs) (chloroform, trichlorethylene) and endocrine disruptors such as alkylphenols, phthalates, bisphenol A, and natural and synthetic estrogens. Some trace pollutants (e.g., VOCs, HAPs) have an already recognized environmental impact while others (e.g., endocrine disruptors) are currently a subject of concern and debate (Crini and Badot, 2007). Among the emerging pollutants, numerous studies concern APs and APEOs mainly because they are suspected to interfere with the hormonal systems of wildlife. APEOs are also unstable in the environment and their degradation yields metabolites that are often more stable and thus more persistent, and that can also be more toxic. In general, the presence of APs results from the degradation of APEOs. The fate, presence, toxicity, behavior and degradation of APs in the atmosphere, sewage sludge, water, sediments and soils have been reported in numerous reviews (Table 1), and in particular in the overviews of Ying (2006), Corvini et al. (2006), Soares et al. (2008), David et al. (2009).

APs and APEOs are synthetic molecules that, in spite of their high cost, are used in numerous industrial, agricultural, and household applications. This is due to their different and important roles: they can act for instance as detergents, emulsifiers, wetting agents, dispersants, or solubilizers. From a structural chemistry point of view, these molecules include numerous isomers. In general, the term alkylphenols (abbreviated to APs in the literature) is used to refer to two groups of compounds: nonylphenols (NPs) and octylphenols (OPs). Among the nonylphenols (Fig. 1), the nine-carbon nonyl group may be linear or branched and bind at various locations around the phenol ring (ortho, meta and para), and this can be a source of confusion concerning the precise identity of the substance (Reed, 1978). NP is not a single chemical structure: it is a mixture of highly branched NPs, largely mono-substituted in the para-position, with small amounts of ortho- and di-substituted NPs. Also it includes branched C8 and C10 alkyl groups (Reed, 1978; Seidel, 2004). Other structures such as propyl-, butyl-, pentyl-, hexyl-, and octyl-phenols are also possible. Theoretically, NP consists of a mixture of 211 possible constitutional isomers with a highly branched alkyl chain and 50–80 isomers that can exist in appropriate environmental matrices (Guenther et al., 2006).

Much of the literature refers to linear or normal NPs, often the specific para regioisomer (i.e., 4-*n*-nonylphenol). This is

Table 1 Literature reviews on alkylphenol substances (selected papers).

Topic	Substance	Source
Aquatic toxicity	APs, APEOs, APnEOs	Hager (1998) Servos (1999) Sharma et al. (2009)
Analysis	APs	Bergé et al. (2012) Basile et al. (2011)
Behavior	EDCs	Langford and Lester (2002)
Bioaccumulation	APs, APnEOs	Servos (1999)
Biodegradation	APs, NP, EDCs	Hager (1998) Corvini et al. (2006) Liu et al. (2009)
Coastal and marine ecosystems	APs	David et al. (2009)
Emerging contaminants	APs, EDCs	Langford and Lester (2002) Bolong et al. (2009) Deblonde et al. (2011) Clarke and Smith (2011) Gonzalez et al. (2012) Stasinakis (2012)
Environmental activity	APEOs	Hager (1998)
Environmental fate	APs, APEOs, NP	Ying et al. (2002) Soares et al. (2008) Sharma et al. (2009)
Environmental safety	APs, APEOs	Talmage (1994) Vazquez-Duhalt et al. (2005)
Estrogenic effects	APEOs	Nimrod and Benson (1996) Servos (1999)
Human safety	APs, APEOs	Talmage (1994)
Microbial degradation	NP, AP	Corvini et al. (2006)
Monitoring	APs, APEOs, NPs, NPEOs	Ahel and Giger (1985) Lee (1999) Petrovic et al. (2003) David et al. (2009) Vincent and Sneddon (2009) Asimakopoulos et al. (2012) Bergé et al. (2012)
Occurrence	APs, APEOs, NP	Ahel et al. (1994a,b) Bennie (1999) Soares et al. (2008) Sharma et al. (2009)
Persistence	APs, APEOs	Maguire (1999) Vazquez-Duhalt et al. (2005)
Solubility	APs, APnEOs	Ahel and Giger (1985)
Toxicity	NP	Soares et al. (2008)
Treatment	APs, EDCs	Johnson and Sumpter (2001) Langford and Lester (2002) Petrovic et al. (2003) Snyder et al. (2006) Belgiorno et al. (2007) Cabana et al. (2007a) Crini and Badot (2007) Liu et al. (2009) Sharma et al. (2009) Bolong et al. (2009) Gültekin and Ince (2007) Murray and Örmeci (2012)

more problematic for APEO substances which are composed of a branched AP coupled to a polyether chain consisting of ethylene oxide units. They are manufactured by reacting branched olefins with phenol in the presence of an acid catalyst under basic conditions. NP n EO is depicted in Fig. 1 where n is the average number of moles of ethylene oxide per mole of nonylphenol, ranging from 1 to 100. The degree of ethoxylation depends on

the molar ratio of NP to olefin (ethylene oxide in this case). The NPEO most commonly used in cleaning agents uses $n = 9$ (NP9EO). In addition, for NPEO surfactants, there are also several other nomenclatures such as nonoxynol, nonylphenol polyglycol ether, nonylphenoxy[poly(ethyleneoxy)] ethanol or α -(nonylphenyl)- ω -hydroxy-poly(oxyethylene). In all cases, it is important to use the information given by the

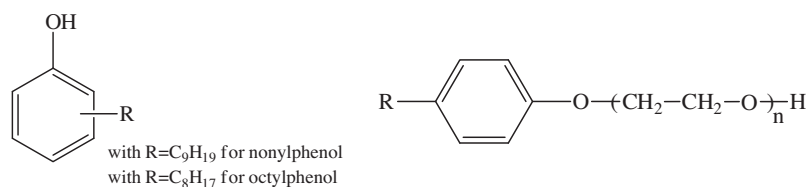


Figure 1 General molecular structure for alkylphenols abbreviated as APs (left) and alkylphenol ethoxylates abbreviated as APnEOs (right) where n is the average number of moles of ethylene oxide per mole of nonylphenol and ranges from 1 to 100.

Table 2 Chemical Abstract Service (CAS) registry names, numbers and abbreviation for several alkylphenols.

CAS Number	CA index name/other names	Abbreviation (s)	Structure	Substance	Formula
25154-52-3	Nonylphenol Nonylphenols <i>n</i> -Nonylphenol Monononylphenol	<i>n</i> -NP NP NPs	C ₉ H ₁₉ ; linear	Mixture	C ₁₅ H ₂₄ O
84852-15-3	4-Nonylphenol Branched 4-nonylphenol para-Nonylphenol p-Nonylphenols	4-NP <i>p</i> -NP NP	C ₉ H ₁₉ ; linear and/or branched	Mixture	C ₁₅ H ₂₄ O
104-40-5	4- <i>n</i> -Nonylphenol Linear para-nonylphenol <i>n</i> -para-Nonylphenol	4- <i>n</i> -NP <i>n</i> -4-NP <i>p</i> -NP	C ₉ H ₁₉ ; linear	one isomer	C ₁₅ H ₂₄ O
26027-38-3	Polyethoxylate 4-nonylphenol Nonylphenol ethoxylates Poly(oxy-1,2-ethanediyl), α -(4-nonylphenyl)- ω -hydroxynonylphenol	4-NP <i>n</i> EOs 4-NP <i>n</i> EO NP <i>n</i> EOs	C ₉ H ₁₉ ; linear	Mixture	(C ₂ H ₄ O) _{<i>n</i>} C ₁₅ H ₂₄ O
28679-36-3	Nonylphenol monethoxylate	NP1EO	C ₉ H ₁₉ ; linear	Mixture	C ₁₇ H ₂₈ O ₂
27176-93-8	nonylphenol diethoxylate	NP2EO	C ₉ H ₁₉ ; linear	Mixture	C ₁₉ H ₃₂ O ₃
104-35-8	4-Nonylphenol monethoxylate	<i>n</i> -4-NP1EO	C ₉ H ₁₉ ; linear		C ₁₇ H ₂₈ O ₂
20427-84-3	4- <i>n</i> -Nonylphenol diethoxylate	<i>n</i> -4-NP2EO	C ₉ H ₁₉ ; linear		C ₁₉ H ₃₂ O ₃
140-66-9	4-Octylphenol para-Octylphenol Octylphenol 4-tert-Octylphenol 4-(1,1,3,3-Tetramethylbutyl)phenol	t-4-OP 4-OP OP	Branched	One isomer	C ₁₄ H ₂₂ O
1806-26-4	4- <i>n</i> -Octylphenol <i>n</i> -para-Octylphenol Octylphenols	<i>n</i> -4-OP	C ₈ H ₁₇ ; linear	One isomer	C ₁₄ H ₂₂ O
2315-67-5	Octylphenol monethoxylate	t-4-OP1EO	Branched		C ₁₆ H ₂₆ O ₂
2315-61-9	Octylphenol diethoxylate	t-4-OP2EO	Branched		C ₁₈ H ₃₀ O ₂

manufacturers and the Chemical Abstract Service (CAS registry names and numbers) for a complete and clear identification of the APEs and APEO substances used. CAS number 84852-15-3 corresponds to the most widely produced nonylphenol, branched 4-nonylphenol, and referred to in the literature as NP. Table 2 and Fig. 2 show the CAS numbers for several NPs, OPs, NPEOs and OPEOs and their molecular structures.

NP is considered as a hydrophobic molecule with a high $\log K_{ow}$ (i.e., approximately 4.5), thus making it poorly soluble. As such, it preferentially associates with suspended solids. Water solubility is directly proportional to n (Ahel and Giger, 1993; Ying et al., 2002). Its value is the number of polar groups forming the hydrophilic part of the molecule. Lower oligomers (< 5) are described as water-insoluble or lipophilic whereas the higher oligomers are water-soluble or hydrophilic. The solubilities of OP1EO and OP2EO were significantly greater than those of NP1EO, NP2EO and NP (Table 3), indicating the predominant influence of the hydrophobic chain length on APnEO solubility. The $\log K_{ow}$ values for APEO

metabolites suggested that these substances may become associated with organic matter in sediments (Table 3).

3. Alkylphenols in water, wastewater and industrial discharge water

The presence of APs has been detected in all aquatic environments i.e., freshwater, coastal and marine ecosystems. NP is found in oceans, estuaries, coastal lagoons, lakes, rivers, surface waters, groundwater, and other sources of potable water. Numerous studies are in agreement that NP occurrence in aquatic environments is mainly correlated with the discharge of effluents from sewage treatment plants, with a higher incidence in those works treating wastewaters from industrialized/urban areas and with other related anthropogenic activities such as storm water discharges and run-off (Naylor et al., 1992; Ahel et al., 1994a; Corsi et al., 2003; Hale et al., 2000; Langford and Lester, 2002; Soares et al., 2008).

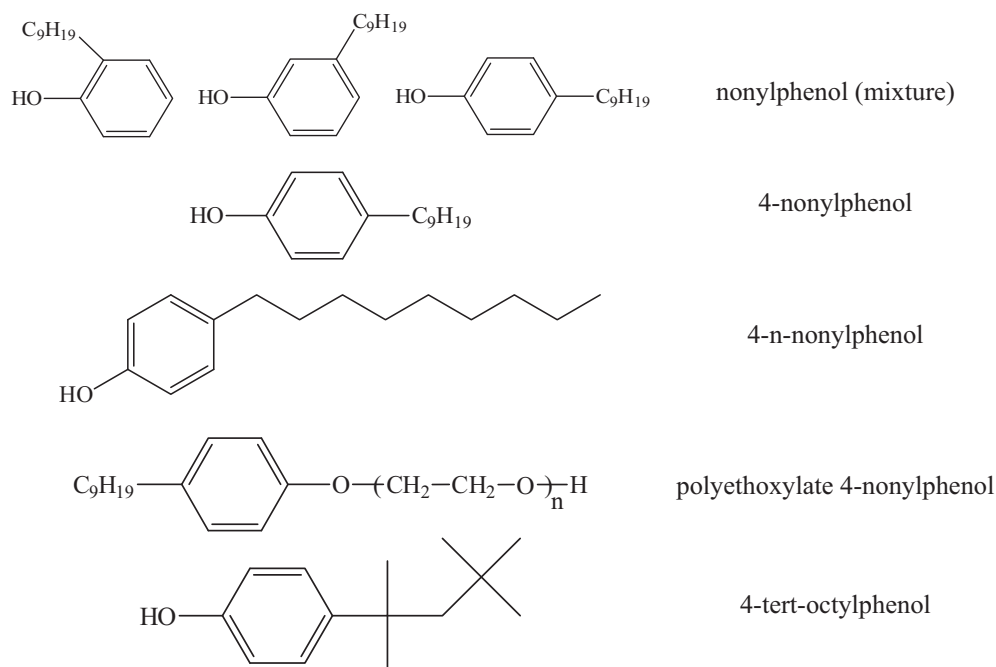


Figure 2 Molecular structures of some alkylphenols.

Table 3 Properties of some NPs and OPs (Source: Ying et al., 2002).

CAS Number	Abbreviation	Molecular weight	Water solubility ^a	Log k_{ow} ^b	Organic carbon sorption constant ^c	Half-life in river water ^d
25154-52-3	NP	220	5.43	4.48	245.470	30; 35–58
28679-36-3	NP1EO	264	3.02	4.17	288.403	
27176-93-8	NP2EO	308	3.38	4.21	151.356	
140-66-9	OP	206	12.6	4.12	151.356	8.1–51
2315-67-5	OP1EO	250	8.0	4.10		
2315-61-9	OP2EO	294	13.2	4.00		

^a In mg L^{-1} at 20 °C.

^b Logarithmic values of octanol/water partition coefficient.

^c In L kg^{-1} .

^d In days.

The European Union has included APs and their derivatives in the list of priority hazardous substances for surface waters in the Water Framework Directive (Directive 2000/60/EC, 2000) for which a drastic reduction policy is being implemented (Directive 2003/53/EC, 2003). Environmental quality standards (EQS) have been proposed for priority substances to provide a benchmark for achieving the good surface water chemical status that EU member states are required to respect. The EQS, which indicate the annual average concentration, for NP and OP in water surface were proposed at 0.3 and 0.1 $\mu\text{g L}^{-1}$, respectively (David et al., 2009). The NP concentration was close to the 90th percentile found (0.268 $\mu\text{g L}^{-1}$) by Loos et al. (2009) in 122 water samples from several European rivers. In this study, the authors reported that only about 10% of the river water samples analyzed could be classified as very clean in terms of chemical pollution. In a previous work, Loos et al. (2008), working on a laboratory and sampling intercomparison study for the chemical monitoring

of emerging pollutants including NP and OP, reported that some laboratories have problems in analyzing NP at concentrations below 100 ng L^{-1} due to the contamination of laboratory blanks. They concluded that plastic materials should not be used during extraction or sample preparation. For instance, it is difficult to compare AP concentrations reported in different studies because of the differences in sample monitoring (extraction strategies and analytical methods used) for quantification (Crini and Badot, 2007). The reader is encouraged to refer to the original articles for information on experimental conditions.

Other Environmental Protection Agencies have also adopted directives for these xenobiotic compounds listed as priority pollutants. The US EPA developed chronic criterion recommendations for NP, whereby its concentration should not exceed 6.6 $\mu\text{g L}^{-1}$ in freshwater and 1.7 $\mu\text{g L}^{-1}$ in saltwater (Brooke and Thursby, 2005). The French Water Agency has included 4-*n*-NP and 4-OP in the list of high priority

hazardous substances which must no longer be allowed to pollute and in the list of priority hazardous substances whose levels in pollution must be reduced, respectively.

A wide range of endocrine disrupters including AP have been found in sewage and output of municipal wastewater treatment plants (Gallenkemper et al., 2003; Crini and Badot, 2007). The presence of NP in wastewater treatment plants was first documented by Giger et al. (1984). The authors reported that primary degradation of APEOs in wastewater treatment plants or in the environment generates more persistent shorter-chain APEs and APs. Ying et al. (2002) and David et al. (2009) also reported that APEOs are biodegraded during the processes taking place in sewage treatment plants and partially in the environment by loss of ethoxy groups, resulting in more toxic subunits such as NPs and OP and other mono-, di- and tri-ethoxylates. NP typically occurs in the $\mu\text{g L}^{-1}$ range in effluents (Porter and Hayden, 2003; Bärlocher et al., 2011), but concentrations of up to $343 \mu\text{g L}^{-1}$ have been reported by Ying et al. (2002).

In rivers, lakes and streams, NP concentrations can range from below detection levels to highs of $> 600 \mu\text{g L}^{-1}$ (Sole et al., 2000; Shao et al., 2005; Vazquez-Duhalt et al., 2005). For example, Sole et al. (2000) measured NP values of up to $644 \mu\text{g L}^{-1}$ in a Spanish river in the vicinity of urban discharges and sewage treatment plants. NP concentrations have been reported between 0.7 and 15 ng L^{-1} in river water, also near sewage treatment plants, by Bester et al. (2001) and Petrovic et al. (2002). The results presented seasonal variations with higher concentrations in the summer due to an increase in microbial activity with warmer temperatures leading to an enhanced degradation of NPEOs. Li et al. (2004) also reported NP concentrations in a Korean river ranging from 6.8 to 190.8 ng L^{-1} with concentrations higher in the warmer season than in the colder season. Other factors such as river flow and sedimentation influence the rate of degradation (Li et al., 2004). Water samples and corresponding drinking water samples were collected seasonally at five sites of each of the two main rivers in the Chongqing Area, China by Shao et al. (2005). NPEOs and 4-NP in the two rivers were detected by LC-MS and GC-MS. The results indicated that at the five sampling points in the two rivers, NPEOs were the dominant pollutant in April and December with a similar distribution profile, and total NPEOs with different ethylene oxide lengths occurred at $6.9\text{--}97.6 \mu\text{g L}^{-1}$ in April and $2.5\text{--}52.7 \mu\text{g L}^{-1}$ in December. However, NP was the dominant pollutant in July with a concentration of $1.7\text{--}7.3 \mu\text{g L}^{-1}$. Corresponding drinking water samples derived from the river water suggested that the conventional water treatment process used in the five waterworks could remove NPEOs from the source water with a high removal efficiency ($> 99\%$). 4-NP removal efficiency, however, varied in the range of 62–95%, leaving a significantly high concentration of NP ($0.1\text{--}2.7 \mu\text{g L}^{-1}$) in drinking water in July.

Writer et al. (2010) reported concentrations in the ng L^{-1} range in Minnesota lakes without wastewater treatment effluents. NP concentrations measured for estuaries and coastal areas were much lower than those of certain freshwater sites receiving sewage inputs. David et al. (2009) reviewed NP concentrations in the range of $0.000002\text{--}4.1 \mu\text{g L}^{-1}$ found in seawater. The most contaminated sites were estuaries and coastal areas related to sewage treatment plants or industrial waste discharges. The authors concluded that the analysis of the results did not reveal considerable differences in AP con-

centration in seawater between European and Asian sites. Li et al. (2005) found NP concentrations in the Saemangeum Bay (Korea) below detection levels to $298 \mu\text{g L}^{-1}$ with high levels in the summer season. NP concentration was mainly affected by salinity and diffusion phenomena of seawater. Oros et al. (2003) and Jackson and Sutton (2011) reported the detection of NP at 0.004 ng L^{-1} in a single water sample and $0.024\text{--}6.25 \mu\text{g L}^{-1}$ in water samples from the San Francisco Bay.

A few measurements of APs in rain water have been undertaken (Bergé et al., 2012). NP concentrations in rain water and snow were found to reach between 0.03 and $1.20 \mu\text{g L}^{-1}$, suggesting that wet deposition must be considered as a major source of NP in the environment. In Europe, data show that NP concentrations in rain water are on the decline, which implies that the environment in European countries is exposed to a decreasing NP contamination (Bergé et al., 2012).

The presence of APs in industrial wastewaters is less well-documented (Berryman et al., 2008; Bergé et al., 2012; Sancey and Crini, 2012). Bergé et al. (2012) indicated industrial NP levels in the range of $0.13\text{--}200 \mu\text{g L}^{-1}$, i.e., twice as high as levels in residential wastewater.

More detailed information on the presence of APs and APEOs in river water, groundwater, coastal and marine ecosystems, can be found in the reviews of Ying et al. (2002), Ying (2006), Corvini et al. (2006), Soares et al. (2008), David et al. (2009), Bergé et al. (2012).

4. Alkylphenol elimination by existing wastewater treatment systems

Wastewater treatment plants (WWTPs) receive raw wastewater from domestic and/or industrial discharges. The objective of a wastewater treatment system is to remove mainly phosphorus, nitrogen and organic substances. The activated sludge process (ASP) is the treatment system most widely used in the world because its competitive cost and high efficiency are the two key considerations for its application. For instance, biodegradation using an ASP has proven to be the most cost-effective process as this method successfully removes the bulk of the organic contaminants that enter the works. In an ASP used in WWTPs, after pretreatment and primary physicochemical steps, the biological degradation in a secondary settling tank (the biomass concentration in the mixed liquor depends on its capacity) is used to remove 'all contaminants' from wastewater. Currently, under optimized conditions, more than 90–95% of substances can be eliminated by conventional biological-based methods used in WWTPs (Li et al., 2000; Cases et al., 2011). Treated sludge after stabilization is then often disposed of in the soil or reused for agricultural purposes: in EU-27, 53% of sludge is used in agriculture directly or after composting (Kelessidis and Stasinakis, 2012).

An important conclusion can be drawn. Although the existing conventional urban and industrial wastewater treatment plants were not designed for emerging compounds, numerous works have shown that emerging compounds such as EDCs can also be reduced by the treatment system used in the wastewater treatment plants, in particular in the WWTPs (Johnson and Sumpter, 2001; Wintgens et al., 2002; Ying et al., 2002; Gallenkemper et al., 2003; Petrovic et al., 2003; Corvini et al., 2006; Gültekin and Ince, 2007; Soares et al., 2008; Bolong et al., 2009; Liu et al., 2009; Bergé et al., 2012). It is

important to note that APs are poorly soluble hydrophobic compounds and present a strong affinity for the particulate phase (sludge). Besides biodegradation, adsorption to sludge is the most effective process. However, the majority of EDCs in wastewater is mainly regarded as removed by biodegradation and the removal efficiency was quite variable (Liu et al., 2009). For instance, it should be mentioned that even for the same compounds, significant differences are often observed between different countries or even between different WWTPs in the same country. Johnson and Sumpter (2001) previously revealed that the essential sewage treatment such as activated sludge and biological trickling filters can rapidly convert aqueous organic compounds into biomass that is then separated from the aqueous phase by settlement. However, not all compounds were completely broken down or converted into biomass. For example, the steroid estrogens found in effluent are the products of incomplete breakdown of their respective parent compounds (Johnson and Sumpter, 2001). Wintgens et al. (2002) and Gallenkemper et al. (2003), using toxicological evaluations, also indicated that WWTPs were not able to remove these novel substances sufficiently before disposing effluent into the environment. Liu et al. (2009) reported that EDCs (APs, bisphenol A, etc.) were not completely removed by existing WWTPs and remained at fluctuating concentrations in effluent, so discharge of such effluent may be the main reason for the wide distribution and occurrence of EDCs in surface waters, ground waters, and even in drinking waters. Bouki et al. (2010) reported that NP adsorption by activated sludge biomass was very fast and that there was no significant difference in the adsorptive behavior of active and inactive biomasses. NP accumulated in the biomasses reaching levels up to two orders of magnitude higher than the equilibrium water phase concentration, and this was due to the hydrophobic nature of both contaminants and biosolids. Desorption of NP from biomass was possible to a significant extent at pH 12 and above, and this may have implications for lime stabilized sludge. Data on the treatment of APs in industrial wastewaters are not documented (Sancey and Crini, 2012).

5. Alkylphenol elimination from wastewaters and water

Another important problem must also be pointed out. From the water and wastewater treatment point of view, no appropriate methods have been developed to deal with these contaminants on the urban or industrial scale. The methodology involves nothing new. For the treatment of industrial wastewater, the challenge comes rather from the optimal use and intermingling of the existing solutions with a tendency to minimize effluent discharge (Chen et al., 2013). Another problem is treatment of waters and wastewaters containing very low concentrations of substances. It should also be noted that industrial wastewaters differ significantly from WWTP and drinking water sources (usually rivers, lakes, or reservoirs) in one important way: the contaminant levels in most WWTP and drinking water sources are quite low as compared with contaminant levels in wastewaters derived from industrial-type activities. Wastewater treatment is a much more complicated process than water treatment due to highly polluted wastewater characteristics. However, the methods used for water are equally valid for wastewater, and the three main technologies proposed are membrane-, adsorption- and oxidation-based

processes. As shown in Table 4, during the last decade, several wastewater treatment methods were reported and used for the attempted removal of APs not only from synthetic solutions but also from real effluent. In general, a combination of these methods is often the best option to achieve the desired water quality.

5.1. Removal of alkylphenols by membrane-based processes

During the three last decades, membrane separation processes have evolved from simple laboratory methods to large-scale operations with a significant technical and commercial impact (Cicek, 2003). Nowadays, membrane processes are considered as an efficient technology for water treatment because of the possibility to obtain better water quality in a more compact WWTP, easier to automate with less sludge production and greater cost-effectiveness as compared to conventional processes (coagulation/flocculation/sedimentation/filtration combined with a carbon step and/or a chemical oxidation). Compared to other methods, their remarkable advantages are the high quality of effluent from a chemical point of view and the removal of microbes and viruses without chemical disinfection. Membrane filtration also provides the potential to reuse the wastewater. Drinking water is potentially the major application of membrane-based process mainly due to the recently more stringent drinking water regulations which make conventional treatments inadequate for treating emerging contaminants. However, recent studies have also shown that industrial wastewaters can also be treated efficiently using membrane technology (Crini and Badot, 2007). The technologies proposed for alkylphenol treatment include membrane treatment using biological (membrane bioreactors) or physical processes (membrane filtration such as nanofiltration).

As already mentioned, the performance of an activated sludge process is variable. An additional tertiary treatment can then be added to achieve lower pollutant levels in the liquid stream in terms of total suspended solids (SS) and chemical oxygen demand (COD). Another solution consists of using membrane bioreactor (MBR) technology and the quality of effluents obtained in these plants is similar to that obtained in a combined treatment by a conventional ASP and a tertiary step (Cicek, 2003; Cases et al., 2011). In recent years, particular attention has been paid to the impact of MBR technology on emerging pollutants. MBRs are able to operate at a higher biomass concentrations obtaining a better permeate quality due to membrane separation by filtration (microfiltration or ultrafiltration). MBR systems are also considered to be among the most promising technologies in microbiological wastewater treatment due to the fact that the long life of the sludge gives the bacteria the time to adapt to the treatment-resistant substances.

The results published by Li et al. (2000) showed that, compared to WWTPs, membrane-assisted biological treatment improved the efficiency of eliminating NP and NPEOs. Similar conclusions were recently reached by Cases et al. (2011) for 4-OP and 4-t-OP removal. Previous work in lab-scale activated sludge units by Tanghe et al. (1998) showed that NP at an initial concentration of 8.33 mg L^{-1} was almost totally removed and biodegraded. The results were temperature dependent: by lowering the temperature, elimination capacities decreased. Aeration was also a key factor in the fate of NP, and removal

Table 4 Principal processes for alkylphenol removal proposed in the literature and discussed in this review (selected papers).

Technology	Compound(s) studied	Source
Activated sludge	NP, 4-OP, 4-t-OP	Johnson and Sumpter (2001) Tanghe et al. (1998) Bouki et al. (2010) Cases et al. (2011)
Adsorption and biodegradation on microalgae	NP	Gao et al. (2011a,b)
Adsorption onto activated carbon	AP, 4-NP	Paune et al. (1998) Abe (1999) Iwasaki et al. (2002) Choi et al. (2005) Yu et al. (2008, 2009a,b) Liu et al. (2009) Xing et al. (2009)
Adsorption onto algae	NP	Gao et al. (2011a,b) Peng et al. (2012)
Adsorption onto alginate	APs	Pluemsab et al. (2007)
Adsorption onto biomass	APs	Gao et al. (2011b) Lang et al. (2009)
Adsorption onto chitosan	NP, 4-NP, 4- <i>n</i> -NP	Gao et al. (2011a) Yamada et al. (2006, 2009)
Adsorption onto clays	APs, NPEOs	Barhoumi et al. (2003) Nagasaki et al. (2003) Espantaleon et al. (2003)
Adsorption onto cyclodextrins	APs, APEOs, NP, NPEOs, 4-NP, 4-NPEO, 4- <i>n</i> -NP	Murai et al. (1996, 2006) Aoki et al. (2003, 2004) Pluemsab et al. (2007) Bonenfant et al. (2009, 2010) Sancey and Crini (2012)
Adsorption onto magnetic particles	NP	Kurinobu et al. (2007) Niu et al. (2012)
Adsorption onto silica gels	NP, NPEOs	Inumaru et al. (2000) Nikolenko et al. (2002)
Adsorption onto synthetic resins	NPEOs, NP10EO	Yang and Ren (2010) Fan et al. (2011, 2012)
Advanced oxidation processes	NP	Gültekin and Ince (2007) Liu et al. (2009) Oller et al. (2011) Rizzo (2011)
Bacterial aerobic degradation	4-NP, NPEOs	Fujii et al. (2003) Soares et al. (2003a,b, 2006) Di Gioia et al. (2004, 2008, 2009)
Biosorption on dead biomass	NP	Bertin et al. (2007) Lang et al. (2009)
Biodegradation	APs, NP	Soares et al. (2003a,b, 2006) Corvini et al. (2006) Cabana et al. (2007a,b,c) Patureau et al. (2008)
Coagulation	APs	Balabanic et al. (2012) Wada et al. (1995) Ciorba et al. (2002) Chen et al. (2013)
Combined oxidation-adsorption processes	NP	Johnson and Sumpter (2001) Tanghe and Verstraete (2001) Johnson et al. (2005) Jones et al. (2007) Liu et al. (2009) Sancey and Crini (2012)

(continued on next page)

Table 4 (continued)

Technology	Compound(s) studied	Source
Combined oxidation-biological processes	NP	Oller et al. (2011) Rizzo (2011)
Combined adsorption-biological processes	NP, NPEO	Bertin et al. (2007)
Electrocoagulation	NPEOs	Ciorba et al. (2002)
Enzymatic biodegradation	NP	Cabana et al. (2007a,b,c)
Enzymatic removal	APs	Yamada et al. (2006, 2009)
Flocculation	NPEO	Jones and Westmoreland (1998, 1999)
Membrane bioreactor	NP, NPEOs, 4-OP, 4-t-OP	Li et al. (2000) Wintgens et al. (2002, 2003, 2004) Lyko et al. (2005) Cases et al. (2011) Camacho-Munoz et al. (2012)
Nanofiltration	NP	Kiso et al. (2000) Wintgens et al. (2002, 2003, 2004) Gallenkemper et al. (2003) Jung et al. (2007) Agenson et al. (2003) Liu et al. (2009)
Ozonation	NP, 4-NP, NPEO, NP1OE, NP2OE	Ike et al. (2002) Petrovic et al. (2004) Kim et al. (2005) Ning et al. (2007a,b) Gültekin and Ince (2007) Baig et al. (2008) Zhang et al. (2008) Bertanza et al. (2010a,b) Tehrani-Bagha et al. (2012) Balabanic et al. (2012)
Photocatalysis	NP, NP1OE, NP2OE, 4-OP	Sherrard et al. (1996) Castillo et al. (2001) Ike et al. (2002) Gültekin and Ince (2007) Belgiorno et al. (2007) Yamazaki et al. (2008) de la Fuente et al. (2010) Zhang et al. (2012) Balabanic et al. (2012)
Photolysis	NPs, NPEOs	Ahel et al. (1994b) Neamtu and Frimmel (2006) Gültekin and Ince (2007) Chen et al. (2007)
Reverse osmosis	NP	Wintgens et al. (2003, 2004) Balabanic et al. (2012)
Sludge anaerobic digestion	NP	Stasinakis (2012)
Sonochemistry	NP	Yim et al. (2003) Gültekin and Ince (2007) Ince et al. (2009)

was shown to be highly dependent on the absence of anoxic zones.

Wintgens and co-workers (Wintgens et al., 2002, 2003, 2004; Gallenkemper et al., 2003; Lyko et al., 2005) carried out various studies to challenge the fact that membrane-based technology was an effective barrier to endocrine disrupting compounds including APs. The removal techniques studied were MBR, nanofiltration (NF), reverse osmosis (RO), activated carbon adsorption and ozonation (Wintgens et al., 2003, 2004). Investigations were conducted on effluents from landfill leachate treatment plants where input NP concentrations were detected in high mg L⁻¹ ranges. MBRs were capable of removing more than 80% of the NP load (Wintgens et al., 2003). RO treatment proved to be less effective in NP removal

than MBR. In another study of the removal of endocrine disrupters present in the outflow from a landfill leachate treatment plant, using an MBR system that comprises three bioreactors and an external ultrafiltration unit followed by granular activated carbon adsorption, they reported the elimination of more than 90% of NP (Wintgens et al., 2002). The MBR was the most effective process step while the carbon treatment, applied downstream, was a further polishing step. The choice of membrane type was crucial. Studying eleven different membranes with the laboratory set-up, they observed that retentions for NP and bisphenol A ranged between 70% and 100%. Gallenkemper et al. (2003) also demonstrated that NF provided high quality permeates in water and wastewater treatment containing NP and bisphenol A with similar reten-

tion. Lyko et al. (2005) reported that the characteristics of influents (landfill leachate or municipal wastewater) had an effect on the composition of the activated sludge and thus had an associated impact on the efficiency of the membrane unit on micropollutant rejection. When the MBR effluent was compared to a conventional effluent loaded with suspended matter, improved elimination can be expected due to the particle-free effluent quality. Wintgens and co-workers concluded that MBRs were a promising process combination of activated sludge and membrane filtration for wastewater treatment and reuse, and biological degradation was the most important step in the process. A vast number of options can be envisaged, e.g., artificial groundwater recharge, indirect potable reuse, and industrial process water production.

Camacho-Munoz et al. (2012) studied the effectiveness of MBRs as the advanced treatment in the removal of NP and NPEOs in WWTPs during a one-year monitoring study. The system studied operated with flat sheet and hollow fiber membranes in two parallel lines. Moreover, a RO module connected in series after the hollow fiber membrane was evaluated for one month. MBR and conventional ASP were also compared, as well as the influence of the physicochemical properties of the compounds on the removal rates achieved. No significant difference of effectiveness was found between flat sheet and hollow fiber membranes. However, an improvement was obtained with the addition of a RO module. Biodegradation has been shown to be the main route involved in the removal of organic compounds during both technologies.

Nanofiltration and reverse osmosis for AP removal were also proposed by Kiso et al. (2000), Agenson et al. (2003) and Jung et al. (2007). For example, Kiso and co-workers (Kiso et al., 2000) studied the behavior of ten kinds of APs adsorbed on the membrane polymer (polyamide). Their results showed that desalting membranes, including reverse osmosis membranes, were necessary for the effective removal of the APs. As expected, the adsorption was mainly controlled by the hydrophobic interaction.

5.2. Removal of APs by biotechnological-based methods

Another interesting biologically-based technology uses packed bed biofilm reactors which maintain a high biomass concentration and activity during the treatment minimizing, at the same time, start up operations and cell washout (Soares et al., 2003a,b, 2006). In addition, bioreactors display high tolerance versus very high and variable organic loads. Soares et al. (2003a) tested a packed bed bioreactor, with 170 ml glass bead carriers and 130 ml medium for NP removal with a *Sphingomonas* sp. The bioreactor was first continuously fed with the medium saturated with NP in an attempt to simulate the groundwater pollution. At best, nonylphenol was degraded by 99.5% at a feeding rate of 69 ml h⁻¹ and a removal rate of 4.3 mg nonylphenol day⁻¹, resulting in a 7.5-fold decrease in effluent toxicity according to the Microtox test. The bioreactor was then fed with soil leachates at 69 ml h⁻¹ from artificially contaminated soil (1 g nonylphenol kg⁻¹ soil) and a real contaminated soil (0.19 g nonylphenol kg⁻¹ soil). Nonylphenol was always completely removed from the leachates of the two soils. It was removed to 99% from the artificial soil but only 62% from real contaminated soil after 18 and 20 d of treatment, respectively, showing limitation due to NP adsorption. The authors demonstrated that it was possible to

develop a continuous biofilm reactor with a *Sphingomonas* sp. strain capable of removing 4-NP from groundwater (Soares et al., 2003b). In another study, the authors set up a mixed packed bed reactor capable of removing 4-NP mixtures at temperatures below 15 °C (Soares et al., 2006). This was the first reported case of cold-adapted microorganisms capable of mineralizing NP.

Other interesting results using biotechnological systems for NP removal have been reported. Fujii et al. (2003) developed a lab-scale packed-column reactor inoculated with a bacterial consortium for NP elimination. *Sphingomonas cloacae* S-3T was isolated from wastewater from a sewage treatment plant in Tokyo in 2000. In flask-scale experiments, S-3(T) cells immobilized on porous polypropylene carriers (beads) efficiently degraded NP to concentrations routinely measured in aquatic environments [a few parts per billion (ppb), or micrograms per liter]. The system worked properly and consistently removed several hundred ppb of NP to ecologically safe concentrations of less than 10 ppb in industrial wastewater without the addition of nutrients. The effect of wastewater pH on the system performance was also evaluated and wastewater samples with pH values of 6 or 8 were treated efficiently without pH adjustment. These results suggest that a biotreatment system using NP-degrading bacteria can efficiently remediate industrial wastewater and contribute to the preservation of aquatic environments.

Bertin et al. (2007) and Di Gioia et al. (2008) developed a set of parallel batch immobilized cell bioreactors, packed with different materials (silica beads, granular activated carbon, and glass spheres), and inoculated with a *Pseudomonas* sp. strain for the treatment of water artificially contaminated with NPEO (synthetic solutions at concentrations in the range 30–90 mg L⁻¹). The results indicated a remarkable decontamination potential and microbial stability along with biodegradation performances higher than those displayed by freely suspended cells of the same strain. The three biofilm reactors, tested under batch conditions, showed comparable degradation capabilities and specificities, being able to remove from 77% to 99% of the load after 9 days of batch treatment. Biofilm grew well and homogeneously on the packed beds of the three reactors. NPEOs were mostly removed through biodegradation, as suggested by the accumulation of two metabolites typical of NP/NPEO aerobic biodegradation, i.e., phenol and 4-nonylphenol, and by the low amounts of NPEO recovered from the reactors at the end of the study. However, NPEO degradation was not complete and trace amounts of 4-NP persisted in the reactors at the end of the treatment. In order to use more efficient biocatalysts, the same group proposed to use an aerobic bacterial consortium obtained from textile wastewater capable of degrading both 4-NP and NPEOs (Di Gioia et al., 2004, 2008, 2009). The consortium was composed mainly of Alfa and Gammaproteobacteria, with a high percentage of members of the *Pseudomonas* genus among the latter group (Di Gioia et al., 2008). Packed bed reactors were developed at the lab-scale by immobilizing the consortium on silica beads or granular activated carbon. NP concentration at 100 mg L⁻¹ was the sole carbon and energy source in the system. The consortium was able to colonize both supports and, in continuous mode, the films that formed showed a remarkable stability. Interesting degradation percentages were obtained (80–97%). Both reactors displayed comparable NP mineralization under batch and continuous conditions. The

immobilization support influenced the overall biodegradation potential of the immobilized culture. The authors concluded that biotechnological processes could represent an effective alternative to physical (adsorption) and/or chemical (ozonation, photolysis) treatments for the decontamination of effluents and solutions containing NPs and related compounds.

Cabana et al. (2007b,c) proposed cross-linked laccase aggregates for the elimination of NP, bisphenol A and triclosan. This type of immobilization involves the precipitation of the enzyme and the chemical cross-linking of the protein using bifunctional compounds. Cross-linking prevented the dissolution and possible loss of aggregates after removing the precipitating agent. This resulted in laccase stabilization against thermal and chemical denaturation and in modifications of the kinetic behavior. Their results showed that a 100-ml reactor with 0.5 mg of material operated continuously at a hydraulic retention time of 150 min at room temperature and pH 5 could remove all three EDCs from a 5 mg L⁻¹ solution. The authors noted that the use of immobilized enzymes such as laccase operating in a continuous fluidized bed reactor was an effective biotechnological way of eliminating NP from aqueous waste. In another study (Cabana et al., 2009), laccase from a strain of the white rot fungus *Coriolopsis polyzona* was immobilized covalently on the diatomaceous earth support Celite using different strategies. The first approach involved the sequential activation of the support surface with gamma-aminopropyltriethoxysilane followed by the reaction of the functionalized surface with glutaraldehyde (GLU) or glyoxal (GLY) and the immobilization of laccase on the activated surface. Another strategy tested the simultaneous internal cross-linking of the protein with GLU or GLY and the immobilization of the laccase on the silanized surface. The two strategies were modified to test the impact of the concomitant addition of bovine serum albumin (BSA) as a stabilizing agent during the immobilization steps. The highest laccase activity and the greatest degree of activity recovery (tested using 2,2'-azino-bis-(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) as the substrate) were achieved by the sequential immobilization procedure using GLU as the cross-linking agent. The solid catalysts featuring internal cross-linking of the protein showed significantly a higher stability against several denaturants. The biocatalyst formed using GLU in the sequential procedure was applied in a packed bed reactor for the continuous treatment of 5 mg L⁻¹ solutions of NP, bisphenol A (BPA) and triclosan (TCS) through repeated batch treatments. All of these EDCs were eliminated at a contact time of less than 200 min by using 3.75 units of laccase activity for BPA and TCS and 1.88 U for NP. These elimination performances were maintained over five consecutive treatment cycles using the same biocatalyst. This system was also able to remove the EDCs from 100 mg L⁻¹ solutions. Kinetic measurements showed a decreasing affinity of the solid biocatalyst for NP, TCS and BPA in that order. The authors concluded that laccase immobilization was a promising tool to increase the applicability and reusability of laccase in biotechnology for EDC removal.

Patureau et al. (2008) studied several treatment processes of mixed sludge naturally contaminated with nonylphenol ethoxylate (NPEO) in order to evaluate their efficiency for the removal of these substances. Anaerobic and aerobic treatments were carried out in continuous stirred tank reactors, operated separately or combined together, at mesophilic and thermophilic temperatures and with or without ozone

post-treatment. Anaerobic mesophilic removal of NPE led to complete removal of NP2EO, incomplete removal of NP1EO and non stoichiometric production of NP, with consequent NPEO removal of 25%. At thermophilic temperature, anaerobic digestion led to an increase in total solid removal efficiency, while improving NPEO degradation (30%). Under thermophilic aerobic conditions, the three compounds were removed simultaneously with a NPEO removal efficiency higher than under anaerobic conditions (39%). This removal was always well correlated to the removal of total solids meaning that bioavailability remained the main limiting factor. Combination of either thermophilic aerobic-mesophilic anaerobic or mesophilic anaerobic-ozonation treatments enhanced NPEO removal by comparison to single systems (45% and 48%, respectively). These results confirmed the high potential of existing and up-graded sewage sludge treatments to degrade such refractory and aged compounds.

Numerous studies reviewed by Corvini et al. (2006) concerning NP biodegradation using microbiological systems were carried out at lab scale and under real conditions. The authors discussed NP biodegradation by axenic cultures of microorganisms and complex microbial communities, with specific attention to the structure of the alkyl chain. Among the bacteria able to degrade NP, sphingomonads were very interesting microorganisms for metabolic studies due to their unusual mechanisms involved in the degradation pathway.

5.3. Removal of APs by adsorption-oriented processes

Adsorption on synthetic or natural adsorbents has also been proposed for AP removal. These include carbons (Paune et al., 1998; Abe, 1999; Iwasaki et al., 2002; Choi et al., 2005; Yu et al., 2008, 2009a,b; Liu et al., 2009; Xing et al., 2009), silica gels (Inumaru et al., 2000; Nikolenko et al., 2002), clays (Barhoumi et al., 2003; Nagasaki et al., 2003; Espantaleon et al., 2003), hypercrosslinked resins (Yang and Ren, 2010; Fan et al., 2011, 2012), cyclodextrins (Murai et al., 1996, 2006; Aoki et al., 2003, 2004; Pluemsab et al., 2007; Bonenfant et al., 2009, 2010; Sancey and Crini, 2012), biomass (Lang et al., 2009; Gao et al., 2011a), biosorbents such as chitosan (Yamada et al., 2006, 2009), alginate (Pluemsab et al., 2007; Gao et al., 2011b), and algae (Gao et al., 2011a,b; Peng et al., 2012), and magnetic particles (Kurinobu et al., 2007; Niu et al., 2012).

Iwasaki et al. (2002) studied the adsorption of APs with alkyl chains consisting of 5–9 carbon atoms onto microporous activated carbons (AC) prepared from coconut shells under different activation times. They showed that all APs were strongly adsorbed by all microporous carbons. The results indicated that adsorption ability increased mainly with activation time. The amount of 4-NP adsorbed increased with the porosity and specific surface area of the carbon used. In either APs with linear alkyl chains (heptyl > hexyl > pentyl) and those with branched alkyl chains (nonyl > octyl), the amount adsorbed increased with the number of carbon atoms. This was attributed to a molecular sieving effect. Abe (1999) and Choi et al. (2005) reported a similar efficiency of AC for NP removal. Removal performances were also studied using a lab-scale carbon fixed bed. Data showed that NP with a high K_{ow} value could be effectively removed.

Xing et al. (2009) proposed ordered mesoporous carbons with varying pore sizes synthesized using ordered mesoporous silica as hard templates for NPEO removal. As evidenced by adsorption tests, the isotherms of NPEO on material were well simulated by a Langmuir adsorption model. The surface area of a pore larger than 1.5 nm, was found to be a crucial factor for the adsorption capacity of NPEO, while the most probable pore diameter of a material was found to be vital to the adsorption rate of NPEO. Results also showed that adsorption temperature had larger effects on adsorption rate than on adsorption capacity. Theoretical studies show that the adsorption kinetics can be well depicted using a pseudo-second-order kinetic model.

Yu et al. (2008) studied the adsorption of carbamazepine and NP on activated carbon. The results showed that, at low concentrations ($10\text{--}800\text{ ng L}^{-1}$), removal of the target compounds was contrary to expectations based on their hydrophobicity. Nonylphenol ($\log K_{ow}$ 5.8) was most poorly adsorbed, whereas carbamazepine ($\log K_{ow}$ 2.45) was most adsorbable. In other works (Yu et al., 2009a,b), the same group investigated the adsorption of NP on granular activated carbons with the objective to investigate preloading effects by natural organic matter (NOM) on adsorption capacity and kinetics under conditions and concentrations (i.e., ng L^{-1}) relevant for drinking water treatment. Isotherms demonstrated that NP was significantly negatively impacted by NOM fouling. The carbon with the widest pore size distribution had considerably greater NOM loading, resulting in a lower adsorption capacity. Model predictions and experimental data were in good agreement for NP compounds, which demonstrated the effectiveness and robustness of the pore and surface diffusion model used in combination with the time-variable parameter approach for predicting removals at environmentally relevant concentrations (Yu et al., 2009b).

Inumaru et al. (2000) proposed octylsilane-grafted hexagonal mesoporous silica for low-concentration nonylphenol removal. They showed that the adsorbent exhibited high efficiency comparable to that of activated carbon.

Espantaleon et al. (2003) proposed a method of oriented-adsorption onto clays to reduce the pollution of effluents produced in tanning. Natural bentonite activated with 0.5 M H_2SO_4 was the most effective adsorbent for NPEO. The authors concluded that the process with clays could constitute a simple, selective and economical alternative to conventional physical-chemical treatments.

Nagasaki et al. (2003) studied the adsorption of NP on Na-montmorillonite using a batch experiment. They compared the results with those obtained using $\alpha\text{-SiO}_2$, $\alpha\text{-Al}_2\text{O}_3$ and gibbsite. It was found that NP adsorption on Na-montmorillonite reached the equilibrium state within 24 h, and that the interlayer width of Na-montmorillonite did not change before and after the sorption. These data suggest that NP was adsorbed on the outer surface of Na-montmorillonite. The amount of NP adsorbed on the surface of octahedral sheets of Na-montmorillonite was found to be identical to that adsorbed to gibbsite. On the other hand, adsorption on $\alpha\text{-Al}_2\text{O}_3$ was smaller, and that on $\alpha\text{-SiO}_2$ was very low. Adsorption amount was found to increase monotonously with pH. It was noted that NP was adsorbed on the broken edges of the octahedral alumina sheets of Na-montmorillonite.

Yang and Ren (2010) proposed hypercrosslinked polymers for the adsorption of NP10EO from aqueous solutions. The re-

sults showed that the amount adsorbed depends on the specific surface area, the pore size of the polymer, and also the temperature of the solution. Thermodynamic analysis indicated that the adsorption process was characterized by an interaction of the hydrophobic part of the surfactant molecule with the surface of the polymer and by the formation of micelles.

Fan et al. (2011) recently evaluated synthetic porous resins as adsorbents for phenol, bisphenol A and NPEO removal from aqueous solutions. The resins used were hypercrosslinked aminated polymers. Several interactions were proposed to explain the adsorption mechanism, namely hydrophobic effects, $\pi\text{-}\pi$ bonds, hydrogen bonding, steric effects, and electrostatic interactions. However, in the case of NP10EO adsorption onto polymeric adsorbents, the mechanism was mainly dependent on the pore size and molecular morphology. The structure, surface area and functional groups of the polymer did not appear to play a role in the adsorption process. In another work, Fan et al. (2012) showed that the adsorption of NP n EO with shorter EO chains was greater than that of molecules with longer EO chains on the surfaces of resins, and the strength of the adsorption was affected by resin surface-surfactant and surfactant-surfactant lateral interactions. Lateral interactions were endothermic, and contributed more to the adsorption process on aminated resins than on hypercrosslinked resins. The surface interactions were mainly due to bonding between the hydrophobic moiety of the surfactant and hydrophobic surfaces of the resins without electrical interactions or hydrogen bonding, even on aminated resins.

Many reports also deal with the interaction of APs in solution with cyclodextrins (CDs), natural molecules derived from starch. These substances have a remarkable capacity to form inclusion complexes in solution or in the solid state with other molecules through host-guest interactions (Morin-Crini and Crini, 2013). Murai et al. (1996) previously studied the adsorption of nonionic surfactants and ionic surfactants on cyclodextrin-based gels. They showed that one gram of material was able to adsorb 85% of APEO from a 150 ml solution containing 200 ppm of nonionic surfactant. In another work, Murai et al. (2006) showed that according to the adsorption isotherms of 4-NP and 4-NPEO, their adsorption onto cyclodextrin polymer was dependent on the length of the ethoxylates in the NPEO. As the ethoxylate chain of NPEO became longer, the efficiency of adsorption onto materials decreased. Column adsorption and desorption tests revealed that the compounds adsorbed were successfully released by various kinds of aqueous alcohol solutions.

Aoki et al. (2003, 2004) proposed an insoluble cross-linked chitosan bearing cyclodextrin moieties for the adsorption of p-nonylphenol and bisphenol A. The material proposed adsorbed bisphenol A quicker than p-nonylphenol and interesting adsorption capacities were reported (Aoki et al., 2003). Almost all of the bisphenol A and 4-nonylphenol adsorbed were released from the beads by treatment with 50% aqueous ethanol solution (Aoki et al., 2004).

Bonenfant et al. (2009, 2010) showed that NP removal by cyclodextrin was rapid and the polymer exhibited high nonylphenol 9-ethoxylate (NP9EO) adsorption capacities (1.1–6.8 mg of NP9EO per g of polymer). They concluded that cyclodextrin-based gels were interesting adsorbents for the removal of nonionic surfactants such as APEO from aqueous solutions.

There is no doubt that the use of advanced technologies based on chemical oxidation (namely AOPs for advanced oxidation processes) is considered a highly competitive wastewater treatment technology for the removal of those organic compounds not treatable by conventional techniques due to their high chemical stability and/or low biodegradability (Gültekin and Ince, 2007; Belgiorno et al., 2007; Rizzo, 2011). However, treatment for complete mineralization is generally expensive because the oxidation intermediates formed during chemical oxidation tend to become increasingly resistant to their complete chemical degradation. One attractive potential alternative is to apply AOPs in a pre-treatment to improve conventional treatment of industrial wastewater. Sancey and Crini (2012) recently showed that, an AOP pre-treatment combined with an adsorption-oriented process using a cyclodextrin derivative, was a highly efficient treatment for industrial wastewater containing recalcitrant molecules such as NP. The combined process consisting of cyclodextrin-based adsorption of pre-oxidized discharge water was interesting for the removal of recalcitrant organic compounds present in metal surface-treatment wastewaters.

Pluemsab et al. (2007) proposed calcium alginate beads covalently linked with alpha-cyclodextrin for their ability to serve as a supporting matrix for bacterial degradation of NP. The results from column chromatographic experiments showed that the material exhibited a strong affinity for NP adsorption. Although addition of cyclodextrin to the culture broth of *S. cloacae* retarded NP degradation, the bacteria immobilized on the cyclodextrin-alginate beads were effective for the degradation. Batch degradation tests using the bead-immobilized bacteria showed 46% NP recovery after a 10-day incubation at 25 °C, and recovery reached about 17% when wide shallow incubation tubes were used to facilitate uptake of the viscous liquid NP on the surface of the medium. Scanning electron microscopic photographs revealed that multiplying bacteria were present both on the surface and inside the beads but that the cyclodextrin-alginate matrix was stable and suitable for 10-day incubation.

Lang et al. (2009) studied NP biosorption on chitosan-immobilized dead fungal beads. Chitosan, a biopolymer produced on an industrial scale by the deacetylation of chitin (the second most abundant biopolymer in nature) is commonly used as support material for biomass immobilization (Crini and Badot, 2008). Biosorption is the passive uptake of substances by non-growing or non-living microbial biomass such as bacteria, fungi and algae. In general, better removal of organic compounds was obtained with dead biomass than with live biomass. Lang et al. (2009) showed that the use of fungal biomass of *Rhizopus arrhizus* immobilized on chitosan beads enabled the effective and innovative treatment of recalcitrant pollutants such as NP. A maximum monolayer capacity of the beads was over 312 mg g⁻¹ and the process was rapid (40 min of contact time). The regeneration of used dead beads with methanol was effective for at least 4 batch cycles. The technology is also interesting because the biomass could be readily prepared on a commercial scale at a very low cost.

Different *Chlorella* species presented the ability to remove NP rapidly and in large quantities as reported by Gao et al. (2011a). Among the species, *Chlorella vulgaris* enabled the highest NP elimination: nearly all NPs were removed from the medium and more than 80% of NP were degraded after a short exposure time (other conditions: 25 °C with light

illumination, initial biomass between 0.5 and 1 mg chlorophyll L⁻¹). The mechanisms included initial rapid adsorption and uptake, followed by accumulation and biodegradation. The biodegradation ability was species-specific and dependent significantly on growth conditions, particularly light. The authors concluded that, among different microalgae, the *Chlorella* genus was able to efficiently remove NP from water and degrade it. In another study, Gao et al. (2011b) demonstrated that alginate-immobilized *C. vulgaris* beads were more effective than freely suspended cells in removing NP from wastewater. The spiked NP, at an initial concentration of 1 mg L⁻¹, was almost completely removed (>98%) under an optimal algal bead concentration (4 beads ml⁻¹) after 96 h of exposure. The NP biodegradation efficiency was significantly enhanced through optimization of the cell density per algal bead and/or algal bead concentration per unit volume of medium. The method based on immobilization allows higher biomass concentrations and facilitates separation and non-destructive recovery of biomass from pollutant-bearing solutions.

Peng et al. (2012) also studied the adsorption characteristics of NP by algal *C. vulgaris* suspensions. Experimental parameters affecting the adsorption process, such as pH, contact time and the effect of solvent were studied. The results showed that the data were well described by the Langmuir adsorption model and indicated that NP adsorption by biosorbent was high during the first 30 min, and equilibrium was achieved after a contact time of 60 min. Adsorption of NP was pH-dependent: as the pH decreased, the adsorption capacity increased. The authors also showed that the fluorescence intensity of NP decreased and that the fluorescence peak of NP moved toward the infrared when algae were added.

Kurinobu et al. (2007) proposed the use of magnetic photocatalyst particles with a core-shell structure of three layers coating Fe₃O₂ core particles with SiO₂ and TiO₂ for NP removal and degradation. NP adsorption on the magnetic photocatalyst particles was found to be effective. As the photocatalyst particles were magnetic, they were easily recovered.

Niu et al. (2012) prepared core/shell structured carbon-encapsulated magnetic nanoparticles (CMNPs) with a simple method using inorganic iron salt and glucose solution as precursor substance for 4-*n*-NP and 4-OP removal. The synthesis procedure did not require the use of organic solvents. The materials were efficiently adsorbed for AP removal from water samples. The mechanism of adsorption was mainly based on π - π stacking interactions, hydrophobic interactions and hydrogen bonding between substances and graphitic carbon.

Yamada et al. (2006, 2009) proposed enzymatic removal of APs from aqueous solutions through a two-step approach conversion of APs to quinines with mushroom tyrosinase. Subsequently the enzymatically generated quinine derivatives were adsorbed on chitosan beads at pH 7 and 45 °C as the optimum conditions. This process was quite effective for 4-NP and 4-*n*-OP with removal values of 97–100%. Mushroom tyrosinase can effectively oxidize linear and branched APs into quinine derivatives (quinine conversion of branched APs was slower than that of linear compounds). The use of porous chitosan beads led to an increase in adsorption of enzymatically generated quinine derivatives, because quinine adsorption occurred heterogeneously at the solid-liquid interface. The use of *melB*

tyrosinase was interesting because it offered quinine conversion without requiring H_2O_2 .

5.4. Removal of alkylphenols by advanced chemical oxidation-based technologies

Destruction processes using various oxidation systems appear to be more interesting. They are based on chemical techniques involving oxidation reactions. Chemical oxidation is increasingly used in the treatment of water. It is necessary when the water to be processed contains non-biodegradable pollutants refractory to conventional decontamination treatment. The treatment can be carried out either by standard oxidation procedures (chemical or catalytic, electrochemical oxidation), or using advanced oxidation processes (AOPs), which have appeared in recent years. In water and wastewater treatment, oxidation is useful as it enables partial destruction with standard procedures (resulting in COD and TOC reduction) or total destruction with AOPs of the organic matter (mineralization).

Classical chemical oxidation techniques are based on the use of various powerful oxidants such as ozone, in the presence of a catalyst or not. Ozonation is commonly used in a large number of water treatment plants not only as a clarifying and disinfecting agent (Gültekin and Ince, 2007), but also as an oxidizing agent with the aim to degrade/mineralize the organic matter. For instance, ozone is a strong oxidant and reacts easily with organic molecules which have sites with high electron densities involving double bonds – the preferred sites for ozone attack. This high reactivity then leads to rapid oxidation kinetics. The mechanism in ozonated waters is either direct oxidation by molecular ozone or indirect oxidation by hydroxyl radicals that are formed by the decomposition of ozone in alkaline conditions. However, ozone-based processes have become the object of increasingly strict levels of legislation, especially their use in the final stages of mains water treatment (drinking water). Owing to its very strong oxidant activity, ozone has also become the most frequently used oxidant for the decontamination of industrial effluent - only fluorine has a higher oxidation potential. It enables the transformation of industrial compounds that are difficult to degrade into molecules much easier to deal with biologically for example. Another advantage of ozone is that it can be used to process large amounts of effluent with little or no formation of by-products (structures conjugated by ozone become non-toxic). However, the process does require a complex set-up. Ozone is an unstable oxidant with a short lifetime and as such must be used soon after it has been synthesized. It is produced on-site from oxygen using electric discharge. In addition, as ozone is expensive to produce, it is generally used on effluent that has been pre-treated in a biological or a physicochemical process. Its use can also be associated to that of other oxidants (such as H_2O_2), catalysts (metal oxides) or to other methods (UV irradiation, membrane filtration) in order to increase its oxidation throughput capacity. Hydrogen peroxide has also proved to be an excellent oxidant, without impact on the environment, and can be used in conjunction with ozone (Snyder et al., 2006).

The high efficiency of AP removal during ozonation is well documented. Petrovic et al. (2004) studied the oxidative degradation of NPEOs in water using ozonation and electron beam irradiation with and without the addition of ozone as

treatment processes. It was found that both ozonation and the two AOPs applied were able to decompose not only the NPEOs but also the polyethyleneglycols formed as by-products from NPEO degradation to residual concentrations below the limit of detection. Moreover, the treatment processes were also used to study the oxidative degradation of nonylphenoxy acetic acid (NPEC) and of NP which were formed as by-products from biodegradation of NPEOs.

Ning et al. (2007a,b) proposed that ozonation can be used to degrade NP and OP. Ozone has been found to react readily with both these APs, mainly in acid conditions ($\text{pH} = 2$). Studying the reaction mechanism between ozone and these two alkylphenols, they suggested that an initial product of ozonation was hydroxyl-alkyl phenol.

Both NP and NPEO oxidation performances and kinetics were evaluated by Hyunook et al. (2007) under different operating conditions created by varying ozone doses, solution pH and molar ratios of $\text{H}_2\text{O}_2/\text{O}_3$. For example, they demonstrated that at pH 7, more than 90% NP (initial NP concentration: 0.51 mg L^{-1}) can be removed by $4 \text{ mg L}^{-1} \text{ O}_3$. Over the pH range 5–9, NP was also effectively oxidized. NP destruction was also significantly increased when H_2O_2 was applied along with ozone. The authors concluded that ozonation could be very effective in oxidizing NP and NPEOs.

Sun et al. (2008) investigated the ozonation mechanism of 4-NP. Using GC–MS analyses, the following substances were identified: mixtures of 4-nonylbenzoquinone homologs, 4-nonylcatechol homologs and the carboxylic compounds formed. The estrogenic activity of ozonation by-products of 4-NP was studied using a recombinant yeast bioassay. The mixtures of 4-nonylcatechol homologs had a higher estrogenic activity, while mixtures of 4-nonylbenzoquinone homologs had a lower estrogenic activity than 4-NP. However, the estrogenic activity of the 4-nonylphenol ozonation solution was ultimately eliminated. The removal of the estrogenic activity of 4-NP was enhanced by the addition of humic acid, indicating the favorable effect of the presence of natural organic materials in water treatment.

Ozone oxidation was proven by Baig et al. (2008) to be an effective solution for the degradation of selected estrogenic active substances detected in secondary wastewaters such as 4-t-OP and 4-iso-NP, up to their limit of detection. The matrix-effect of wastewater was investigated performing ozone experiments under batch mode and continuous mode using drinking water and wastewater from a local plant both spiked with the non-detected substances. The results obtained indicated that the wastewater matrix greatly affected the kinetics of ozone reaction with these substances but did not really change the related reactivity scale. The ozone dose corresponding to the full conversion of target substances consequently increased as their oxidation took place competing with reactions of background pollutants represented by the COD content. However, a usual dose close to 12 mg L^{-1} was found sufficient to provide high degradation yields for all substances studied while 35% of the COD was removed.

Zhang et al. (2008) studied the ozonation of NP and OP in aqueous solutions containing acetonitrile as a cosolvent. Batch experiments were carried out to test the effects of initial pH values, ozone dosages, and initial APs concentration on degradation efficiency. At pH 9.0, the two APs were completely degraded after a period of 6 min. After 6 min for ozonation, the

degradation efficiency of NP was nearly 42% with the ozone dosage of 0.13 mg min^{-1} at pH 6.5, but with the ozone dosage of 0.38 mg min^{-1} , the degradation efficiency reached 96%. The effect of ozone dosage on degradation of OP showed that the higher the initial AP concentration, the lower the AP degradation efficiency. During the ozonation process, the rapid decrease in the pH and the sharp increase in the electrical conductivity indicated the formation of by-products with a higher polarity, which was confirmed by the HPLC analysis. The authors concluded that ozonation was a feasible process for removing APs from water.

Kim et al. (2005) compared ozonation and electrochemical degradation of NPs. Ozonation was efficient but they showed that electrochemical oxidation was also an interesting option for the treatment of NPEOs. The principal advantages were easy implementation, the possibility to operate in a wide range of treatment conditions and the fact that there was no need to store and dispense treatment reagents.

Bertanza et al. (2010a,b) reported that NP removal by conventional WWTPs is recognized but in order to reach very low concentrations, further treatment such as chemical oxidation might be required. They studied the ozonation of an effluent from an Italian WWTP (Verona, Italy) and the reaction was monitored using chemical and microbiological analyses. The authors concluded that ozonation was an economically feasible option as tertiary step.

Tehrani-Bagha et al. (2012) recently studied the efficiency of different UV-enhanced ozonation processes for degradation of a nonylphenol ethoxylate with 40 oxyethylene units (200 mg L^{-1}) in lab scale experiments at ambient temperature. The reaction was monitored by the reduction of COD and TOC and by the absorbance band of the aromatic ring of the molecule. The results showed that a combination of UV irradiation and ozonation was considerably more efficient than the individual processes (at least twice as efficient in terms of COD and TOC reductions). The synergistic effect of ozonation and UV irradiation was particularly pronounced when medium-pressure UV irradiation was used. By adding alkali to the solution, the efficiency of UV-enhanced ozonation increased with respect to COD reduction but decreased with respect to TOC reduction. This indicates partial oxidation with a lower degree of mineralization of the surfactant.

AOPs have also been widely explored for the decontamination of water polluted mainly by organic substances. These processes are used to complete the degradation initiated by biological treatment or as a pretreatment to enhance the biodegradability of recalcitrant or treatment-inhibiting compounds present in wastewaters. This enhancement is achieved by the partial oxidative degradation of the molecules to give intermediate reaction products that can be degraded by microorganisms in a biological post-treatment. AOPs can also be used as a treatment step to mineralize the compounds. For instance, in proper operation conditions, it is possible to mineralize the target pollutants to CO_2 , which is the most stable end product of chemical oxidation (Gültekin and Ince, 2007).

A wide variety of AOPs are available for wastewater treatment based on photocatalytic systems (TiO_2/UV , $\text{Fe}/\text{UV-Vis}$) or reactions that produce hydroxyl radicals by the photolysis of hydrogen peroxide and ozone ($\text{H}_2\text{O}_2/\text{UV}$, O_3/UV , $\text{H}_2\text{O}_2/\text{O}_3/\text{UV}$). Photocatalysis is an oxidation process in which a metal oxide semiconductor (e.g., TiO_2) immersed in water and irradiated by near UV light enables the formation of free hy-

droxyl radicals. TiO_2 is the most widely used catalyst because of its non-toxicity, low-cost, photo-stability and water insolubility under most environmental conditions (Belgiorno et al., 2007). Photocatalytic reactions can be divided into heterogeneous and homogeneous processes that use either catalyst particles or coatings such as TiO_2 , or soluble catalysts or redox systems like iron ions or iron complexes. The light energy necessary can either be provided by lamps or solar radiation. Photocatalysis processes have been found to be effective for the degradation of EDCs as covered in the following reviews which can be consulted (Gültekin and Ince, 2007; Belgiorno et al., 2007).

Sherrard et al. (1996) previously reported the degradation of NPE in aqueous solution (2 L of aqueous solution containing 2 g L^{-1} NPE and 0.1% w/v TiO_2 catalyst) using heterogeneous photocatalysis. From their GC-MS, ESMS and NMR data, they concluded that photocatalysis was an efficient method. Intermediates were identified and suggested that the ethylene oxide chain was more susceptible to degradation than aliphatic or aromatic moieties.

Castillo et al. (2001) investigated the photodegradation of non-ionic surfactants (nonylphenol- and alcohol-polyethoxylates, NPEO_x and C_nEO_x) in different waters (deionized water and industrial effluent) with and without a photoinductor (Fe(III)). The intermediates detected included NP2EO and nonylphenol ethoxy acetic acid (NPE2C). Much smaller amounts of NP9EO degradation products having only the alkyl chain carboxylated were also formed in the photocatalysis experiment. The C10EO6 photoproducts identified included fatty alcohols and acids. PEGs were also formed. Photodegradation in wastewater samples was more efficient than in deionized water.

Yamazaki et al. (2008) investigated photocatalytic degradation of 4-OP by recirculating the aqueous solution through a packed bed reactor with TiO_2 . The kinetics of degradation was independent of the flow rate but a decrease in TOC became smaller as the flow rate increased. Under illumination for 6 h at a flow rate of 28.5 ml min^{-1} , 83.2% of 4-OP was degraded but 60.7% of the initial TOC remained. LC-MS measurements using electrospray ionization revealed the formation of byproducts. The degradation rate was remarkably accelerated by the addition of $\text{K}_2\text{S}_2\text{O}_8$: 4-OP completely disappeared under irradiation for 2–4 h and in the presence of $\text{S}_2\text{O}_8^{2-}$, 4-OP was degraded without TiO_2 , which was attributable to reactions involving SO_4^- radicals. The $\text{UV}/\text{TiO}_2/\text{S}_2\text{O}_8^{2-}$ system was more suitable than $\text{UV}/\text{S}_2\text{O}_8^{2-}$ for the decontamination of water containing 4-OP.

The applicability of different photochemical AOPs, namely, direct UV-C photolysis, heterogeneous photocatalysis, and photo-Fenton reactions for the degradation of 300 mg L^{-1} NP9EO in water was studied by de la Fuente et al. (2010). Toxic 4-nonylphenol was never found as a byproduct of the degradation after any of the treatments. Aldehydes were formed in all of the processes, but they appeared at low levels in photo-Fenton reactions. Photo-Fenton treatments were considered to be the best degradation processes.

Zhang et al. (2012) recently studied the application of TiO_2 photocatalysis in advanced wastewater treatment to simulate the removal of endocrine disrupting compounds (bisphenol A, NP, estrone, and 17 alpha-estradiol) and estrogenic activity from secondary effluents of a municipal wastewater treatment plants, aiming to evaluate the possibility of using photocatalysis

for advanced wastewater treatment. The removal efficiencies of alkyl-hydroxybenzenes (bisphenol A, NP) by traditional processes in wastewater treatment were more sensitive to temperature than the removal of steroid hormones (estrone, and 17 alpha-estradiol), resulting in a risk of effluent insecurity. All the targeted EDCs in secondary effluent were totally degraded by TiO₂ photocatalysis within 60 min except BPA (92% removal), following pseudo first-order kinetics. The estrogenic activity was also totally removed: when EDCs reacted with hydroxyl radicals, aromatic rings were cleaved, resulting in a decreased estrogenic activity. Their findings suggested that TiO₂ photocatalysis is an effective method for the removal of certain EDCs and estrogenic activity from secondary effluents and can be used for advanced wastewater treatment.

Although photocatalysis by TiO₂ was thought to be an effective method for the degradation of organics, some researchers were concerned about the practicality of the process related to the relative difficulty of separating the catalyst powders and/or crystals from solution at the end of treatment (Gültekin and Ince, 2007). Different combined treatments have also been proposed. Ike et al. (2002) reported that the effectiveness of ozonation and ultraviolet photocatalytic treatment in the degradation of NPEO metabolites, using lab-scale reactors, follows the order: nonylphenoxy carboxylic acid > NP > nonylphenol monoethoxylate. The degradation rate of NP by UV/TiO₂ was the highest among the metabolites tested, while NP1EO showed the lowest degradation rate. Acidic metabolites were completely degraded within 4–6 min (initial concentration 0.4–1 mg L⁻¹), the NP concentrations were reduced by 75–80% in 6 min, while only 25–50% of NP1EO was eliminated at the same time. NP was efficiently degraded by ozonation, however, it was much less effective for NP1EO decomposition.

Balanic et al., 2012 evaluated the treatment performance of different wastewater treatment procedures (biological treatment, filtration, and AOPs) for the reduction of COD and seven EDCs including NP from pulp and paper wastewaters. Two pilot plants were running in parallel and the following treatments were compared: (i) anaerobic biological treatment followed by aerobic biological treatment, UF and RO, and (ii) anaerobic biological treatment followed by MBR and RO. Moreover, at the lab-scale, four different AOPs (Fenton reaction, photo-Fenton reaction, photocatalysis with TiO₂, and ozonation) were applied. The authors showed that concentrations of the EDCs studied in paper mill wastewaters were effectively reduced (100%) by both combinations of pilot plants and photo-Fenton oxidation (98%), while Fenton process, photocatalysis with TiO₂ and ozonation were less effective (70–90%, respectively).

UV irradiation (photolysis) is a common practice for drinking water treatment. Photolysis has been one of the most widely investigated AOPs of EDC degradation. Ahel et al. (1994b) previously studied the sunlight photolysis of NP and NPEOs in natural waters. The photochemical oxidation of NPEO was shown to be significantly slower than that of NP. The photochemical degradation of both NP and NPEOs was mainly due to sensitized photolysis while direct photolysis was comparatively slow. Moreover, experiments with D₂O revealed that singlet oxygen was not an important photooxidant of NP at pH values usually found in natural waters.

Neamtu and Frimmel (2006) investigated the photolysis of NP using a solar simulator in the presence/absence of dissolved organic matter (DOM), HCO₃⁻, NO₃⁻ and Fe(III) ions. The

effects of different parameters such as initial pH, initial substrate concentration, temperature, and the effect of hydrogen peroxide concentration on photodegradation of nonylphenol in aqueous solution were assessed. The results indicated that the oxidation rate increased in the presence of H₂O₂, Fe(III) and DOM with dissolved organic carbon concentrations not higher than 3 mg L⁻¹. Phenol, 1,4-dihydroxybenzene and 1,4-benzoquinone were identified using an HPLC method as intermediate products of NP photodegradation. Their results also showed a strong decrease in estrogenic activity of NP after 80 h of irradiation in the presence of hydrogen peroxide. The photolysis of NPEOs with an average oligomer length of ten ethoxylate units in aqueous solutions was also studied by Chen et al. (2007). The results showed that the degradation was effective but that the degradation pathway was complex. NPEOs with longer ethoxylate chains were degraded more easily than those with shorter chains. The performance was reduced in the presence of humic acid.

The application of sonochemistry, namely, the physical and chemical effects induced by ultrasonic irradiation in water, was also reported for the elimination of hazardous or toxic environmental contaminants in aqueous solutions. The reaction pathways proposed for the sonolytic degradation of organic compounds are the reaction with hydroxyl radicals (e.g., hydroxyl radical attack and/or addition) and a thermal reaction (e.g., pyrolysis). The hydroxyl radicals are produced by the sonolysis of water molecules inside the collapsing cavitation bubble under extremely high temperature and pressure. The behavior of the hydroxyl radicals generated may either involve the reaction with organic compounds or recombination to form hydrogen peroxide (H₂O₂) inside the cavitation bubble and at its interfacial region. Pyrolysis of volatile organic compounds occurs inside the cavitation bubble or at the interfacial region, where the temperature is sufficiently high for the induction of thermal effects.

Yim et al. (2003) investigated the sonolysis of APs in aqueous solution under a variety of conditions. In particular, the effects of added Fe(II) and Fe(III) during the sonolytic degradation of NP in aqueous solution were explored with a particular focus on degradation enhancement. Their results showed that the sonolytic degradation rate of the APs depended upon their alkyl chain length. Free radicals played a significant role in the sonolytic degradation of APs. The sonochemical effects on the addition of Fe(II) and Fe(III) as catalysts during sonication resulted in a remarkable enhancement of degradation and mineralization.

Ince and co-workers (Gültekin et al., 2009; Ince et al., 2009) also proposed sonochemistry for NP degradation. High frequency irradiation (20 kHz ultrasound) permitted the efficient decomposition of 4-*n*-NP from water in alkalized conditions. The rate of reaction increased with increasing concentrations of the substance up to a critical value above which it declined and stabilized (Ince et al., 2009). The impact of pH was such that the rate of degradation was maximum at pH = 10.8, minimum at pH = 3.0 and in between the two extremes at pH = 6.0 (Gültekin et al., 2009). The extreme rapidness of the reaction in alkaline conditions was related to the pK_a of NP (10.7) and the facilitation of the covalent bond cleavage between the phenolic and alkyl groups. The fact that the reaction was faster at more acidic pH than at pH 6 attributed to the protonation of the molecule enhancing its migration toward the negatively charged gas bubbles. The reaction rate was also

accelerated by bubbling the solution with oxygen gas and by the addition of Fenton and Fenton-like reagents. The enhancement by the latter stresses the role of OH radicals in the overall degradation process. The efficiency of sono-Fenton reactions was significantly improved by the addition of a sufficient dose of H₂O₂ into the reactor.

5.5. Removal of APs by other water and wastewater treatment methods

Wada et al. (1995) reported APS elimination by the formation of water-insoluble precipitates through the reaction of quinine derivatives enzymatically generated from APs with the amino group-containing polymers (chitosan, polyethyleneimine) in solution. Jones and Westmoreland (1998, 1999) treated nonylphenol ethoxylate residues from wool scour effluents by flocculation using a specific flocculant, and reported an uptake > 95%. The process transferred the pollutants from the wastewater stream to a spadeable sludge that was used as a starting material to produce high quality compost. During the composting process, the detergents were degraded to below detectable levels.

Ciorba et al. (2002) investigated the behavior of aluminum and carbon steel electrodes in the presence and absence of NPEO and NPEO removal by electrochemically-generated coagulants. The electrode processes were studied by potentiodynamic polarization measurements to determine the influence of surfactant addition (ethylene oxide units and organic load), inorganic composition and pH. The polarization curves showed the extent of the involvement of NPEO in the electrode processes. Their influence appeared clearly in the range of anodic activation, depending on the number of ethoxylate groups. Removal of NPEO from simulated wastewaters was carried out in electrocoagulation cells with vertical or horizontal electrodes. Removal efficiencies calculated from the COD before and after treatment were 30–50% for NP16EO and NP40EO, and 40–80% for NP4EO. The hydrophilic-lipophilic balance number for NP4EO indicated a relative ratio of polar and non-polar groups lower than that for the other two surfactants, which was in favor of a better NP4EO removal. The experiments showed that bulk processes (bridging of electrochemically-generated polymeric species and adsorption of surfactants) were predominant over the involvement of NPEO in the electrode processes, which were only responsible for the electrogeneration of coagulants.

6. Concluding and personal remarks

Alkylphenols are used to synthesize polyethoxylated derivatives, mainly nonylphenol polyethoxylates and octylphenol polyethoxylates, essential in numerous applications. For instance, technical grade nonylphenol is produced on a large scale from phenol for the synthesis of alkylphenol polyethoxylates, a large family of nonionic surfactants often used in domestic detergents, dispersing agents, and industrial and institutional cleaners. These compounds are found in various environmental compartments as a result of their wide usage and this presence in the environment is entirely due to human activity. These molecules can find their way directly into the environment, for instance through industrial effluent, or they can transit via municipal sewage treatment plants. Effluent

from treatment plants is in fact considered to be the largest source of NPs in the environment (Soares et al., 2008; Sabik et al., 2003; Giger et al., 1984). Numerous articles report the contamination of various compartments of the environment: water, soil, sediment, atmosphere (Table 1). Although legislation concerning the use of APs and their derivatives has become increasingly strict over recent years, e.g., the EU, Switzerland and Canada, these molecules are still found in the environment, especially in the aquatic environment.

Many studies have also focused on methods, mostly at the laboratory scale, for the elimination of APs. However, little is known about the efficiency of these techniques for the removal of APs and their derivatives when applied to actual domestic and industrial effluents. It can be noted that the existing conventional water and wastewater treatment plants were not designed for these new contaminants and also that no appropriate methods have been developed to deal with them at the industrial or urban scale. In addition, the removal success of APs can vary greatly from one treatment plant to the next. A non-negligible part of the AP and their derivatives entering the plant thus finds its way to the outlet and into the environment without having been degraded. The few studies published on the subject show that the best levels of degradation are achieved with plants using the most complete treatment processes, involving treatment with ozone, active carbon, or both (Berryman et al., 2004; Jones et al., 2007; Soares et al., 2008). A treatment process composed of ozonation and subsequent activated carbon filtration with chlorination was able to remove 95% of NP (Soares et al., 2008). Likewise, very few data are available on the treatment of industrial effluent (Berryman et al., 2004; Jones et al., 2007). The small number of studies tends to support the widespread trend to look for substitutes for these products, particularly in Europe, in the framework of the REACH program which concerns the regulation of chemicals and their safe use.

As already mentioned, sewage treatment plants do eliminate part of these substances, mainly through degradation processes occurring in the activated sludge. The mechanisms involved in the degradation have been clarified for a number of years. Elimination by adsorption to the sludge is a removal mechanism that is enhanced with the time spent in the sewage treatment plants, the type of treatment and the temperature (Soares et al., 2008; Maguire, 1999). Degradation is then only partial and occurs through dissociation of each of the ethoxylated moieties. An aerobic sequence during the treatment of the waste water produces carboxylated NPs while an anaerobic sequence generates the ethoxylated counterparts (Mayer et al., 2007). The endpoint of the degradation of nonylphenol ethoxylates is nonylphenol itself (Corvini et al., 2006; Ying et al., 2002; Bennie, 1999; Servos, 1999).

The question remains as to the method or combination of methods best suited for the efficient treatment of these molecules often present as traces in complex industrial effluent or urban wastewater. Several types of treatment involving physical, biological or chemical processes have been proposed following laboratory studies and can be envisaged at the urban/industrial scale (Table 5). A certain number of problems must be born in mind: (i) the ability to treat complex effluent, especially industrial waste of highly diverse origins, (ii) heterogeneous pollution outflow – not only variable concentrations but also variable types of pollutants with different levels of toxicity, and (iii) and of course rapidly changing volumes of

Table 5 A summary of advantages, disadvantages and remarks concerning the main methods used for AP removal from water and wastewater.

Process	Main characteristic	Advantages/Disadvantages/Remarks
<i>Adsorption</i> : active carbons, non-conventional materials	non-Destructive process	<ul style="list-style-type: none"> • efficient treatment with COD and TOC reduction • excellent quality of the treated solution/effluent • rapid saturation of the reactors • elimination of the adsorbent • combined with a biological step, adsorption may be an interesting process • for water and wastewater treatment applications
<i>Biological</i> : biodegradation, membrane bioreactor, activated sludge process, biotechnology	Use of biological cultures and/or membranes	<ul style="list-style-type: none"> • well accepted by the public as 'natural' degradation • efficient treatment • management and maintenance of the microorganisms • biotechnology through the use of different types of microorganisms and biocatalysts is an economical approach compared to other techniques and an ecologically favorable process • mainly for water treatment applications
<i>Oxidation</i> : photocatalysis, photolysis	<i>In situ</i> production of reactive hydroxyl radicals	<ul style="list-style-type: none"> • efficient emerging process: lab-scale • mineralization of the APs with COD and TOC reduction • interesting results with TiO₂-photocatalytic processes • no or few chemicals added • no production of sludge • economically non-viable (WWTPs) • possible formation of byproducts • potential water reuse applications (photocatalysis) • photocatalysis may be envisaged in an integrated approach • mainly for wastewater treatment applications
<i>Ozonation</i>	Use of an oxidant	<ul style="list-style-type: none"> • efficient process • generation of ozone on-site • increased biodegradability of the effluent • disinfection • high energy requirements • possible formation of intermediates • for water and wastewater treatment applications
<i>Membrane filtration</i> : NF, RO	non-destructive process	<ul style="list-style-type: none"> • rapid and efficient, and no chemicals required • high investment and energy costs • problematic: membrane clogging, elimination of the concentrate • mainly for water treatment applications

effluent to process. Taking into account each of these characteristics, four methods are often quoted for the treatment of an effluent presenting different contaminations – including APs - namely adsorption on active charcoal, membrane filtration, biotechnology and advanced techniques of oxidation.

Active-carbon technology in adsorption-oriented processes could be a valid solution owing to its simplicity and chemical efficiency. Activated carbons are known for being very broad spectrum adsorbents, able to remove not only metals, dyes and pesticides, but also novel organic molecules such as endocrine disrupting compounds (Paune et al., 1998). Another major advantage of treating water with activated carbon is that no by-products are formed, unlike chemical treatment or chemical oxidation. In addition, microporous carbons can be used as supports for bacteria which degrade part of the adsorbed organic material (biological elimination) and thus operate *in situ* regeneration of the adsorbent. However, although the high absorbing power of activated carbon no longer needs to be proved, it does pose the problem of elimination after use, especially since it becomes rapidly saturated: the efficiency of the filters decreases with time. They must then be changed or regenerated. Regeneration is carried out with heat or chemicals and is rather costly in energy, leading to real economic issues.

An alternative solution is to use the so-called non-conventional carbons, i.e., carbons obtained from low-cost resources such as agricultural bagasse, husks, etc., which are simply incinerated as soon as they become saturated. AP adsorption onto non-conventional adsorbents (cyclodextrins, biopolymers, biomass, etc.) has also been proposed with interesting results although these processes are basically at the stage of lab scale.

As a result of the development of recycling and reutilization policies, membranes, which were originally devoted to the production of drinking water, are now progressively gaining ground in the treatment of industrial effluent. This type of technology enables the separation of not only colloidal particles, but also of dissolved substances. Membrane filtration (NF, RO, etc.) provides high quality abatement of APs but its main disadvantage is its relatively high cost. Membrane bioreactor systems are considered to be among the most promising technologies in microbiological wastewater treatment for the removal of emerging compounds from urban wastewaters (Cases et al., 2011). Much work is also necessary to demonstrate the possibilities of membrane bioreactors for industrial wastewater treatment. Biotechnological processes based on the use of (immobilized) microorganisms could also represent an effective alternative to conventional treatments.

Another solution, which presents advantages from the point of view of chemical efficiency, is the technique of advanced oxidation. The aim of this process is to modify the state of novel refractory toxic organic molecules, particularly by biodegradation, (i) to render them insoluble for elimination by precipitation, (ii) to transform them to yield new substances that are soluble but not or less toxic, and (iii) to eliminate them completely by mineralization. Advanced oxidation processes are very efficient for the treatment of effluent containing refractory compounds that are toxic and/or non-biodegradable and are reported to give excellent results in particular in COD and TOC reduction due to mineralization of organic compounds. Based on a substantial number of relevant studies, photocatalysis, among the wide variety of AOPs, is an interesting tool for AP treatment due to its potential to render mineralization complete. In association with biodegradation or adsorption, advanced oxidation would appear to be the technique of the future, although its cost is still preventing its generalization. Gültekin and Ince (2007) reported that the main advantage of AOPs over all chemical and biological treatments was their environmental friendliness as they neither transfer pollution from one phase to the other as in chemical insolubilization and adsorption nor produce large amounts of hazardous sludge as in ASP. However, despite these advantages, AOPs can also lead to the formation of harmful by-products in the effluent. A list of identified oxidation by-products can be found in a review by Gültekin and Ince (2007), where phenol and p-hydroquinone were the most commonly observed molecules regardless of the AOP technique. In general, research has mainly focused on the technical performances of AOPs, while their environmental impact is usually ignored. On this point, Belgiorno et al. (2007) reported that, the effluent produced by various AOPs though not toxic itself, might after final disinfection be transformed into toxic compounds. Rizzo (2011), reviewing recent developments in bioassays used it as a tool to quantify AOPs in water and wastewater treatment effluent, comprehensively discussed the effects of AOPs on the toxicity of aqueous solutions of different classes of contaminants such as endocrine disrupting compounds and the toxicity-biodegradability dualism that occurs when AOPs are used in a pretreatment step to improve industrial wastewater biodegradability. Rizzo (2011) concluded that bioassays were extremely useful tools to evaluate the dangerousness of AOPs.

In WWTPs, several studies have shown that removal of NP from wastewater can be enhanced by adding activated carbon filters, UV treatment and ozonation to existing treatment processes (Paune et al., 1998; Johnson and Sumpter, 2001; Tanghe and Verstraete, 2001). AOPs and membrane-based technologies are also an option to treat urban sewage. These methods are efficient from a chemical point of view and could complete the currently used sequences of treatment (Johnson and Sumpter, 2001). However, many are not exploitable for technological but especially economic reasons. Between 2005 and 2010, the United Kingdom conducted a demonstration program to evaluate technologies to remove endocrine disrupting compounds from urban wastewater (Jones et al., 2007). Advanced treatment techniques undoubtedly reduce the discharge of micropollutants, however, they inevitably exacerbate costs, and entail environmentally undesirable increases in energy consumption and CO₂ emission. In addition, the costs involved may only be justifiable in the event of waste water recycling (as in agro-food or pharmaceutical industries) or to make

water suitable for consumption, where the aim is not to reduce pollution of the natural environment but to preserve the food chain from contamination or to preserve particularly vulnerable aquatic systems such as lakes. Moreover, except for oxidation techniques, the elimination of alkylphenols implies their transfer into the sludge, and once there, very little is known of their fate although some recent studies do tend to show that composting of the sludge is an efficient means of attenuating the levels of nonylphenols. For instance, these methods do not resolve one of the main problems which is their accumulation in the sludge due to the high hydrophobicity of APs. Most of the sludge disposal routes including recycling to land, disposal in landfill, biological stabilization and incineration have drawbacks such as high costs and contamination of the environment. Alternative methods for treating NP contaminated sludge have been proposed such as composting (La Guardia et al., 2001) and aerobic stabilization (Giger et al., 1984).

Finally our literature survey showed that research has been and continues to be conducted in the areas of combined oxidation-adsorption, oxidation-biodegradation or adsorption-biological treatments in order to improve the removal, degradation and/or biodegradation of APs (Oller et al., 2011). Combined methods are interesting because they take advantage of synergistic effects. However, the large majority of the works published focus on the behavior of a single chemical tested in much higher concentrations than those detected in the water environment, whereas APs exit in complex mixtures rather than as a single product. Future research needs to look into this aspect.

Now what remains to be done is to find novel solutions for the elimination of alkylphenols – not only from water but also from real wastewaters – that are chemically efficient, technically feasible, economically viable, and ecologically friendly. To achieve this aim, it will be necessary to adopt a multidisciplinary approach with chemists, biologists, microbiologists, polymerists and engineers working together toward a common goal.

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