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Advanced Treatments for the Removal of Alkylphenols and Alkylphenol Polyethoxylates from Wastewater

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Abstract Since the 2000s, among organic contaminants, alkylphenols and alkylphenol polyethoxylates have been listed as hazardous substances by several national, European and international agencies because they are considered endocrine disruptors. Among the molecules classified as priority substances in terms for monitoring and action, nonylphenols and octylphenols and their polyethoxylated derivatives receive particular attention, especially in developing countries. Effluents from treatments plants are considered to be the largest source of alkylphenols in the environment. Although legislation concerning their use has become increasingly strict, these substances are still found in the environment, especially in water resources.

The existing water and wastewater treatment plants have not been designated for these emerging contaminants. Conventional treatments such as biodegradation, sand filtration, carbon adsorption and/or chemical oxidation in place are not effective in their elimination removal. No appropriate methods have been developed to deal them at the urban or industrial scale. Thus, alkylphenols have become a relevant research topic for scientists interested in water engineering issues related to

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their treatment. However, the challenge is not simple, as it is difficult to remove trace contaminants from complex mixtures of substances in a way that is chemically effective, technologically simple, economically viable, and environmentally friendly.

The main objective of this chapter is to summarize recent trends in proposed advanced treatment methods for the removal of alkylphenols and alkylphenol polyethoxylates from wastewater. After general and brief considerations on these emerging contaminants, this chapter focuses on adsorption-oriented processes, biotechnological methods, and advanced oxidation processes. Among the advanced methods described and discussed are removal of alkylphenols and alkylphenol polyethoxylates by adsorption onto cyclodextrin polymers, clays or molecularly

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imprinted polymer, biodegradation using microalgae or constructed wetlands or by sequential anaerobic-aerobic digestion processes, treatments based on ozone-carbon coupling, electrochemical degradation, photocatalysis, zero-valent iron-activated persulfate coupling and catalytic ozonation. Among these technologies, advanced oxidation processes, in association with biodegradation and/or adsorption, seem to be the technique of the future, although their costs still prevent their widespread use.

Keywords Alkylphenols · Alkylphenol polyethoxylates · Wastewater · Removal technologies · Advanced treatments · Ozonation · Adsorption · Granular activated carbon · Cyclodextrin polymers · Clays · Molecularly imprinted polymer · Biodegradation · Sequential anaerobic-aerobic digestion · Microalgae · Constructed wetlands · Phenolic root exudates · Advanced oxidation processes · Electrochemical degradation · Photocatalysis · Zero-valent iron · Catalytic oxidation · Nanomaterials

4.1 Introduction

Alkylphenols and mainly their polyethoxylate derivatives, alkylphenol polyethoxylates, are used in a variety of applications and consumer products, e.g. paints and latex paints, adhesives, inks, formulation of pesticides, paper industry, textile and leather industry, petroleum recovery chemicals, metal working fluids, personal care products, washing agents, cleaners and detergents. By far the two most commercially important alkylphenols are nonylphenol and octylphenol, which are used primarily to produce nonylphenol polyethoxylates and octylphenol polyethoxylates, respectively. Due to their widespread use, alkylphenols and alkylphenol polyethoxylates, particularly nonylphenol, are ubiquitous in the environment (Ying et al. 2002; Gultekin and Ince 2007; Soares et al. 2008) and are found in various compartments such as rivers, freshwater, coastal and marine ecosystems, sediments, soils, sewage sludge, and the atmosphere (Corvini et al. 2006; Soares et al. 2008; David et al. 2009; Bergé et al. 2012). The occurrence of these substances in aquatic environments is mainly correlated with the discharge of effluents from sewage treatment plants and from industry (Langford and Lester 2002; Corsi et al. 2003; Soares et al. 2008). The literature on alkylphenols and alkylphenol polyethoxylates is extensive (Table 4.1).

Nonylphenol is persistent in the aquatic environment and extremely toxic to aquatic organisms. Its dominant source in the environment is (partial) biodegradation of nonylphenol polyethoxylates rather than direct discharges, as industrial discharges are strictly controlled from a regulatory point of view (Soares et al. 2008). Nonylphenol ethoxylates in domestic wastewater reach the sewage treatment plant where microorganisms progressively decompose the ethoxy chain to finally release several compounds including the nonylphenol that was initially used to synthesize the detergents. These substances are readily biodegradable under aerobic or

Table 4.1 Literature papers on alkylphenols and alkylphenol polyethoxylates published in the last decade

Topic	References
Aquatic toxicity	Kovarova et al. (2013), Derco et al. (2017), Priac et al. (2017), Watanabe et al. (2017), Zhang et al. (2017), Abd-Elkareem et al. (2018), Ahmadpanah et al. (2019) and Olaniyan et al. (2020)
Ecotoxicity	
Aquatic environment	Pradyot (2010), Kovarova et al. (2013), Priac et al. (2017), Salgueiro-Gonzalez et al. (2018), Skrbic et al. (2018) and Salomon et al. (2019)
Water resources	
Aquatic compartments	
Costal and marine ecosystems	
Analysis	Basile et al. (2011), Bergé et al. (2012), Lu and Gan (2014a), Czech et al. (2016), Jardak et al. (2016), Tuan Omar et al. (2016), Martin et al. (2017), Priac et al. (2017), Salgueiro-Gonzalez et al. (2017, 2018), Acir and Guenther (2018), Salomon et al. (2019) and Xie et al. (2019)
Sample handling	
Determination	
Quantification	
Detection	
Matrices	
Biodegradation	Mao et al. (2012), Lu and Gan (2014b), Karci (2014), Salomon et al. (2019) and Dan et al. (2020)
Degradation	
Transformation products	
Biological effects	Bergé et al. (2012), Gonzalez et al. (2012), Tuan Omar et al. (2016), Cahyanurani et al. (2017), Salgueiro-Gonzalez et al. (2018), Cheng et al. (2019) and Xie et al. (2020)
Bioaccumulation	
Biota species	
Emerging contaminants	Pradyot (2010), Deblonde et al. (2011), Clarke and Smith (2011), Bergé et al. (2012), Gonzalez et al. (2012), Stasinakis (2012), Kovarova et al. (2013), Tuan Omar et al. (2016) and Priac et al. (2017)
Endocrine disrupting compounds	Mao et al. (2012), Lu and Gan (2014a), Hart et al. (2016), Shirdel and Kalbassi (2016), Tuan Omar et al. (2016), Sharma and Chadha (2017), Watanabe et al. (2017), Guo et al. (2019), Salomon et al. (2019), Sayed et al. (2018, 2019), Saravanan et al. (2019) and Olaniyan et al. (2020)
Estrogenicity	
Environmental behavior	Pradyot (2010), Bergé et al. (2012), Kovarova et al. (2013), Lu and Gan (2014a), Cavalheiro et al. (2017), Priac et al. (2017) and Janousek et al. (2020)
Environmental contamination	
Impact	
Environmental fate	
Persistence	
Industrial wastewater	Pradyot (2010), Deblonde et al. (2011), Jardak et al. (2016), Derco et al. (2017), Ho and Watanabe (2017), Chokwe et al. (2017), Priac et al. (2017) and Salomon et al. (2019)
Sources	
Monitoring	Asimakopoulos et al. (2012), Bergé et al. (2012), Priac et al. (2017) and Tousova et al. (2017)

(continued)

Table 4.1 (continued)

Topic	References
Municipal wastewater	Pradyot (2010), Derco et al. (2017), Deshayes et al. (2017), Chokwe et al. (2017), Priac et al. (2017) and Lu et al. (2019)
Sources	
Occurrence	Mao et al. (2012), Kovarova et al. (2013), Lu and Gan (2014a), Cavalheiro et al. (2017), Chokwe et al. (2017), Priac et al. (2017), Acir and Guenther (2018) and Cheng et al. (2018)
Regulation	Acir and Guenther (2018)
Sludge	Pradyot (2010), Clarke and Smith (2011) and Stasinakis (2012)
Sediments	Pradyot (2010), Lu and Gan (2014b), Liu et al. (2016), Salgueiro-Gonzalez et al. (2018) and Shiu et al. (2019)
Toxicity	Karci (2014), Lu and Gan (2014a), Chokwe et al. (2017), Priac et al. (2017), Acir and Guenther (2018), Ivey et al. (2018), Kim et al. (2019) and Olaniyan et al. (2020)
Exposure pathways	
Human safety	
Treatment	Basile et al. (2011), Murray and Öermeci (2012), Karci (2014), Rao et al. (2014), He et al. (2016), Jardak et al. (2016), Peng et al. (2016), Temiz et al. (2016), Armijos-Alcocer et al. (2017), Derco et al. (2017), Gao et al. (2017), Priac et al. (2017), Abargues et al. (2018), Bjorklund and Li (2018), Crini and Lichtfouse (2018), Flanagan et al. (2018), Maza-Márquez et al. (2018), Bodzek (2019), Gupta and Bux (2019), Hung et al. (2019), Musaev et al. (2019), Tomei et al. (2019), Xie et al. (2019), Zaytseva and Medvedeva (2019), Dan et al. (2020) and Kaur et al. (2020)
Removal technologies	
Advanced treatments	
Innovative methods	
Non-conventional methods	

anaerobic conditions in the environment. They are then found in water or adsorbed on sediment. Though less toxic than nonylphenol, nonylphenol polyethoxylates are also highly toxic to aquatic organisms. More generally, alkylphenol polyethoxylates are unstable and both undergo the same processes of degradation to yield metabolites that are generally more stable and thus more persistent. It is known that not only the parent molecules but also their degradation products or metabolites represent a potential ecotoxicological problem in aquatic systems. In addition, these emerging compounds exert endocrine disruption effects since they mimic natural hormones by interacting with estrogen receptors (Naim et al. 1994; Claisse and Alzieu 1993; Cocchieri et al. 1993; Smith and Jaffe 1994; Ginsberg 1994). Humans are exposed to alkylphenols by the intake of contaminated foods and drinking water. Nonylphenol and octylphenol present in plastic containers and wrappings may migrate into foods and drinking water. Another route of human exposure includes contact with personal care products and detergents. Nonylphenol has been detected in human milk, blood, and urine (Table 4.1).

Because of their ubiquitous occurrence in the environment and their high toxicity, alkylphenols and their derivatives constitute a major concern for all the national (e.g., French Water Agency), European (European Agency) and international (US EPA) institutions involved in water management. Over the last 20 years, European legislation on wastewater discharges has become increasingly strict, particularly in

France, where nonylphenols and octylphenols and their polyethoxylate derivatives are the target of action campaigns (e.g., in France with RSDE action – Research and Reduction of Substances in Water; first circular of May 7, 2007). These substances are among the 70 priority substances and their use has been restricted since 2013 (Directive 2003/53/EC, 2003). In the European Water Framework Directive (2013/39/CE), nonylphenols (in particular 4-(*para*)-nonylphenol) and octylphenols (*para-tert*-octylphenol) are classified as priority hazardous substances and priority substances, respectively (Soares et al. 2008). Thus, these substances have been monitored in industrial discharge waters with the aim of reducing or eliminating them (with an elimination target for each industrial company for November 2021, December 2028 or August 2033, depending on the concerned substance). The industrial sector must therefore mobilize to eliminate or reduce these substances. However, the problem is not simple because it is difficult to remove trace contaminants from complex mixtures of substances (Crini and Badot 2007, 2010). Moreover, their elimination is not systematically targeted in industrial treatments. Domestic discharges are also affected but the existing conventional water treatment plants used to treat these discharges have not been designated for these emerging contaminants. In this context, it is necessary to propose and develop various efficient technologies for the elimination of alkylphenols from water and wastewater that are efficient, economically viable, technologically simple, and without environmental impact. This is what has motivated the scientific community for the past 20 years. The European Union has also established maximum concentrations at 0.3 µg/L for 4-(*para*)-nonylphenol and 0.1 µg/L for *para-tert*-octylphenol in inland waters. For nonylphenol, the US EPA guide on quality of drinking water recommends a maximum concentration of 28 µg/L for fresh water.

After general and brief considerations on alkylphenols and alkylphenol polyethoxylates, this chapter presents recently proposed advanced technologies for their removal including adsorption-oriented processes, biotechnological methods, membrane bioreactor technology, and advanced oxidation methods. Selected works have been highlighted to present research and discuss these technologies.

4.2 General Considerations on Alkylphenols

4.2.1 Applications

Alkylphenols and alkylphenol polyethoxylates 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, antistatic agents, demulsifiers, (heat) stabilizers, or solubilizers. They were used primarily as surfactants in detergents. These substances can also be used as curing agents or as

chemicals to make phenolic resins or to produce plastics (Möbius et al. 2001; Lorenc et al. 2003; Kayama et al. 2003; Pradyot 2010; Kovarova et al. 2013).

Indeed, alkylphenols and alkylphenol polyethoxylates have been used for more than 50 years, being important for industrial activities such as the cleaning industry, textiles, coatings, metallurgical industry, adhesives, pesticide formulation, pulp and paper, oils and fuels, construction materials, and the plastic industry (Priac et al. 2017). They also found use in cosmetics and personal care products, the synthesis of flavors and antioxidants, the production of fragrances and stabilizers, the processing of rubber for the manufacture of tires, printing inks, the paint industry, electrical insulation varnishes, veterinary medicine formulations, the civil engineering and construction industry, and leather auxiliaries. However, international bans on the use of certain substances and/or restrictions are now in place, particularly in the Europe. Indeed, European legislation (directive 2003/53/EC), in force since 2005, now prohibits the use of nonylphenol and its polyethoxylate derivatives as dispersing agents. Specific exceptions are still granted for certain applications. Despite strict regulations, alkylphenols continue to be found in European rivers and streams, as well as in industrial discharges (Crini et al. 2016).

4.2.2 Chemistry

In general, the term of alkylphenols (abbreviated to APs in the literature) is used to refer to two groups of compounds: nonylphenols (NPs) and octylphenols (OPs). Figure 4.1 gives their general molecular structure. From a structural chemistry point of view, these molecules include numerous isomers. Among the nonylphenols, 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. Nonylphenol is not a single chemical structure (Fig. 4.2): it is a mixture of highly branched nonylphenols, largely mono-substituted in the *para*-position, with small amounts of *ortho*- and di-substituted nonylphenols. 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, technical nonylphenol 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 nonylphenols, often the specific *para* region-isomer, i.e. 4-*n*-nonylphenol or *para*-nonylphenol (Fig. 4.1).

The term of alkylphenol polyethoxylates (APnEOs) also refers to two groups of substances, nonylphenol polyethoxylates (NPnEO) and octylphenol polyethoxylates (OPnEO). However, their structure is more complicate because these substances are composed of a branched alkylphenol (nonylphenol or octylphenol) coupled to a polyether chain consisting of ethylene oxide units (Vazquez-Duhalt et al. 2005; Guenther et al. 2006; Gultekin and Ince 2007; Soares et al. 2008; Vega Morales et al. 2009). Alkylphenol polyethoxylates are manufactured by reacting

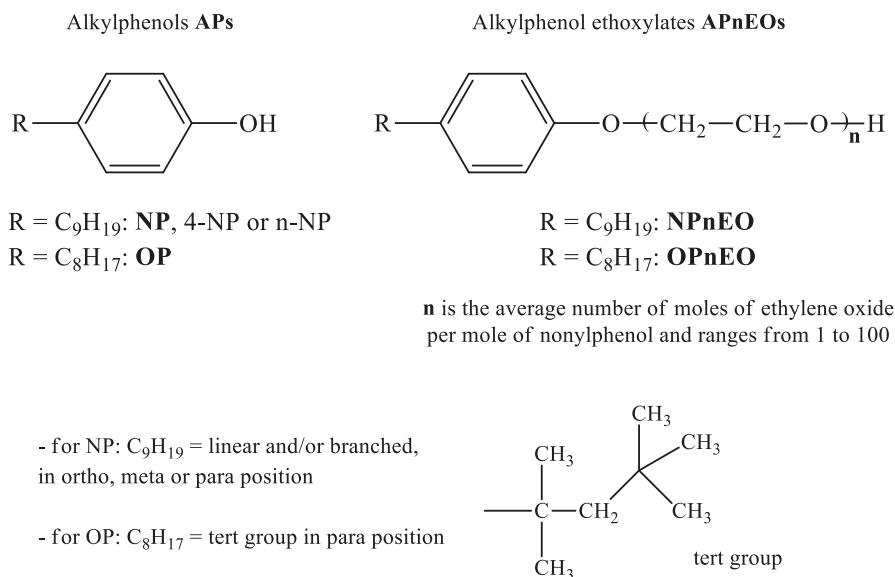


Fig. 4.1 General molecular structure for alkylphenols abbreviated APs and alkylphenol polyethoxylates abbreviated APnEOs (*NP* nonylphenol, *OP* octylphenol, *NPnEO* nonylphenol ethoxylates, *OPnEO* octylphenol ethoxylates)

branched olefins with phenol in the presence of an acid catalyst under basic conditions. The structure of NPnEO is depicted in Fig. 4.1 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 nonylphenol to olefin (ethylene oxide in this case). The nonylphenol polyethoxylate most commonly used in cleaning agents uses *n* = 9 (NP9EO). In addition, for nonylphenol polyethoxylates surfactants, there are also several other nomenclatures such as nonoxynol, nonylphenol polyglycol ether, nonylphenoxy[poly(ethylenoxy)] ethanol or α -(nonylphenyl)- ω -hydroxy-poly(oxyethylene). In all cases, it is important to use the information given by the manufacturers and the Chemical Abstract Service (CAS registry names and numbers) for a complete and clear identification of the substances used. CAS number 84852-15-3 corresponds to the most widely produced nonylphenol, branched 4-nonylphenol, and referred to in the literature as 4-nonylphenol, para-nonylphenol or p-nonylphenol. Table 4.2 and Fig. 4.2 show the CAS numbers for several nonylphenols, octylphenols, nonylphenol polyethoxylates and octylphenol polyethoxylates, and their molecular structures, respectively (Priac et al. 2017).

Nonylphenol is considered to be a hydrophobic molecule with a relatively high partition coefficient compared to others (Table 4.2), making it poorly soluble. As such, it preferentially associates with suspended solids. Water solubility is directly proportional to *n* (Ahel et al. 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

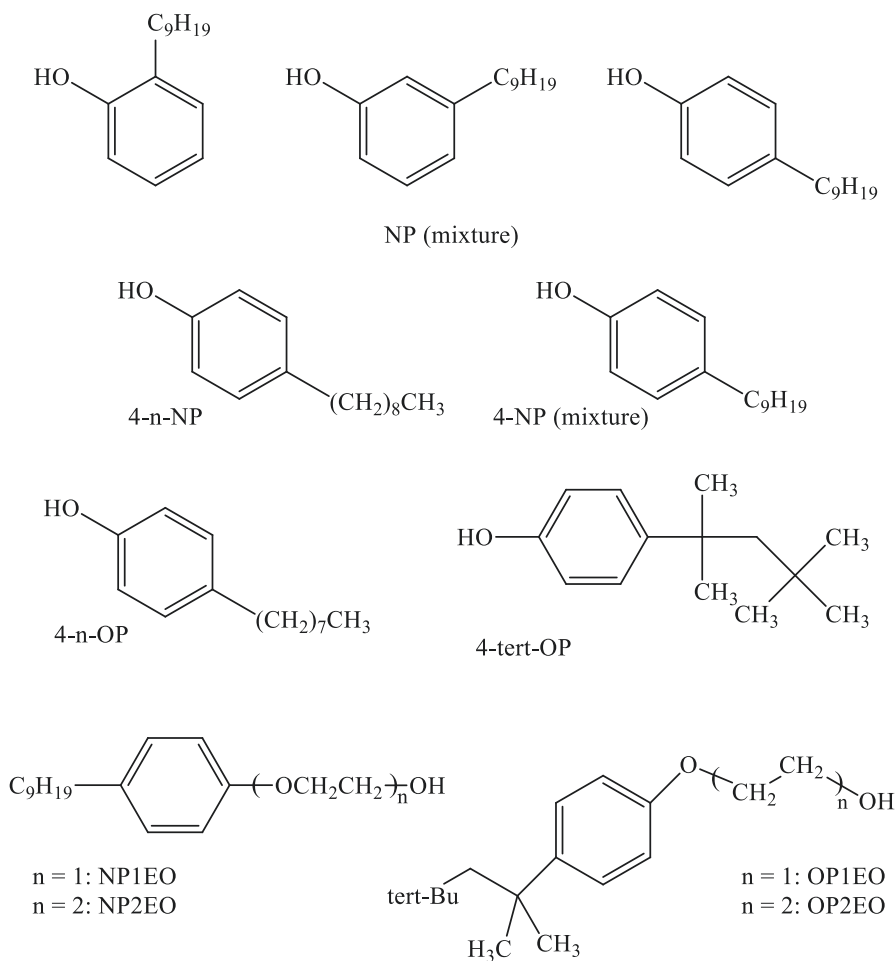


Fig. 4.2 Molecular structures of some alkylphenols (*NP* nonylphenols, *4-n-NP* linear para-nonylphenol, *4-NP* para-nonylphenols, *4-tert-OP* para-octylphenol, *NP1EO* nonylphenol monoethoxylates, *NP2EO* nonylphenol diethoxylates, *OP1EO* octylphenol monoethoxylates, *OP2EO* octylphenol diethoxylates)

water-soluble or hydrophilic. The solubilities of octylphenol monoethoxylate and octylphenol diethoxylate are significantly greater than those of nonylphenol monoethoxylate, nonylphenol diethoxylate and nonylphenol (Table 4.2), indicating the predominant influence of the hydrophobic chain length on alkylphenol polyethoxylates solubility. The low partition coefficient for alkylphenol polyethoxylate ($\log K_{ow}$ values in Table 4.2) suggests that these substances may become associated with organic matter in sediments. For this reason, alkylphenol polyethoxylates and their degradation products (including alkylphenols and/or metabolites such as

Table 4.2 Chemical Abstracts Service (CAS) registry names, numbers, abbreviation and properties for several alkylphenols

CAS Number	CA index names	Abbreviations	Structure	Substance	Formula	Water solubility ^a	logK _{ow} ^b
25154-52-3	nonylphenol nonylphenols <i>n</i> -nonylphenol monononylphenol	NP NPs <i>n</i> -NP	C ₉ H ₁₉ : linear	mixture	C ₁₅ H ₂₄ O	5.43	4.48
84852-15-3	4-nonylphenol branched 4-nonylphenol <i>para</i> -nonylphenol <i>p</i> -nonylphenol	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 <i>para</i> -nonylphenol <i>n</i> - <i>para</i> -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-NPnEOs 4-NPnEO NPnEOs	C ₉ H ₁₉ : linear	mixture	(C ₂ H ₄ O) _n C ₁₅ H ₂₄ O		
28679-36-3	nonylphenol monethoxylate	NP1EO	C ₉ H ₁₉ : linear	mixture	C ₁₇ H ₂₈ O ₂	3.02	4.17
27176-93-8	nonylphenol diethoxylate	NP2EO	C ₉ H ₁₉ : linear	mixture	C ₁₉ H ₃₂ O ₃	3.38	4.21
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 <i>para</i> -octylphenol octylphenol 4- <i>tert</i> -octylphenol 4-(1,1,3,3-tetramethylbutyl) phenol	<i>t</i> -4-OP 4-OP OP	branched	one isomer	C ₁₄ H ₂₂ O	12.6	4.12

1806-26-4	4- <i>n</i> -octylphenol <i>n-para</i> -octylphenol octylphenols	<i>n</i> -4-OP	C ₈ H ₁₇ : linear	one isomer	C ₁₄ H ₂₂ O	
2315-67-5	octylphenol monethoxylate	<i>t</i> -4-OP1EO	branched		C ₁₆ H ₂₆ O ₂	4.1
2315-61-9	octylphenol diethoxylate	<i>t</i> -4-OP2EO	branched		C ₁₈ H ₃₀ O ₂	4

^ain mg/L at 20 °C

^blogarithmic values of octanol/water partition coefficient

alkylphenoxy carboxylic acid) have been found in a range of abiotic and biotic matrices worldwide.

4.2.3 Alkylphenols and the Aquatic Environment

Since the late 2000s, numerous reviews and articles have reported the presence of nonylphenol and octylphenol in all aquatic environments, i.e. in oceans, estuaries, coastal lagoons, lakes, rivers, surface waters, groundwater, and other sources of potable water (Table 4.1). Their occurrence in these environments is mainly correlated with the discharge of effluents from sewage treatment plants and from industry (Langford and Lester 2002; Corsi et al. 2003; Soares et al. 2008). Numerous studies evaluating the presence and concentrations of alkylphenol polyethoxylates and their metabolites have also been published on their ubiquitous distribution in sewage treatment plant discharges, industrial discharge waters and living organisms (Gultekin and Ince 2007). Although partial elimination or degradation/biodegradation is observed in sewage treatment plants and industrial treatment plants, these discharges are nevertheless an important source of contamination. It is also recognized that industrial discharge waters (surface treatment industry, textile sector, etc.) are another important input of these substances into the aquatic environment. Following input into receiving waters, the more persistent alkylphenols tend to accumulate in sediments (Ying et al. 2002). An input to the environment was the direct application of pesticide formulations containing nonylphenol. Alkylphenols can also be bind strongly to soil following applications of sewage sludge to agricultural land. In indoor air, a source of alkylphenols was building materials, due to their use as antioxidants for polymer resins.

In Europe (European Commission 2013, 2015, 2018), environmental quality standards 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 environmental quality standards for nonylphenol and octylphenol in water surface were proposed at 0.3 µg/L and 0.1 µg/L, respectively (David et al. 2009). However, environmental quality standards are still not harmonized worldwide. The US EPA developed chronic criterion recommendations for nonylphenol, whereby its concentration should not exceed 6.6 µg/L in freshwater and 1.7 µg/L in saltwater (Brooke and Thursby 2005). Much higher values were found not only in the European aqueous compartments but also in North America and Asia (Sole et al. 2000; Bester et al. 2001; Petrovic et al. 2002; Oros et al. 2003; Li et al. 2004; Shao et al. 2005; Vazquez-Duhalt et al. 2005; Jackson and Sutton 2008; David et al. 2009; Bergé et al. 2012; Kovarova et al. 2013; Crini et al. 2016).

In rivers, lakes and streams, nonylphenol concentrations can range from below detection levels to highs of >600 µg/L, depending on various factors such as season, river flow and sedimentation, which influence the rate of (bio)degradation. In general, the results for surface waters present seasonal variations with higher concentrations in the summer due to an increase in microbial activity with warmer

temperatures leading to an enhanced degradation of nonylphenol ethoxylates. It was suggested that a microbial activity at warmer temperatures leads to an enhanced biodegradation of nonylphenol and octylphenol as well as photolysis induced by sunlight can influence alkylphenol concentration in the surface layer of natural waters during summer (Kovarova et al. 2013). Li et al. (2005) found nonylphenol concentrations in Saemangeum Bay (Korea) below detection levels to 298 $\mu\text{g/L}$ with high levels in summer season. Song et al. (2020) recently reported a value of 1100 ng/L in seawater in Tokyo Bay (Nagasaki City, Japan). Oros et al. (2003) and Jackson and Sutton (2008) reported detection of nonylphenol at 0.004 ng/L in a single water sample and 0.024–6.25 $\mu\text{g/L}$ in water samples from San Francisco Bay. Concentrations in the ng/L range in Minnesota lakes without wastewater treatment effluents were reported. Xu et al. (2018) reported concentrations of nonylphenol in a Chinese river water and sediment (Pearl River Delta Guangzhou) of 5.05 $\mu\text{g/L}$ and 14.40 $\mu\text{g/L}$, respectively. Nonylphenol concentrations measured for estuaries and coastal areas were much lower than those of certain freshwater sites receiving sewage inputs (David et al. 2009). Saeed et al. (2017) reported concentrations of alkylphenol in coastal waters and sediments in Kuwait with levels of a few ng/L and ng/g , respectively. A few measurements of alkylphenols in rain water have been undertaken (Bergé et al. 2012). Nonylphenol concentrations in rain water and snow were found to reach between 0.03 and 1.20 $\mu\text{g/L}$, suggesting that wet deposition must be considered as a major source of nonylphenol in the environment. The presence of alkylphenols in industrial wastewaters is less well-documented (Berryman et al. 2004; Bergé et al. 2012; Sancey and Crini 2012; Crini et al. 2016). Bergé et al. (2012) indicated industrial nonylphenol levels in the 0.13–200 $\mu\text{g/L}$ range, i.e., twice as high as levels in residential wastewater. Crini et al. (2016) reported nonylphenol concentrations in the <0.1–102 $\mu\text{g/L}$ range discharge waters from surface treatment industries. Following an inter-laboratory study, the authors highlighted the high variability of the results and the difficulty of analyzing these molecules in complex matrices. In Europe, if an industry is confronted with alkylphenols and alkylphenol polyethoxylates in its discharges, it must put in place actions to eliminate or reduce them, but there are not yet specific regulations.

From an ecotoxicological point of view, the estrogenicity of alkylphenols such as nonylphenol and octylphenol has been highlighted in fish (Ahmadpanah et al. 2019; Sayed et al. 2019), aquatic invertebrates (Hart et al. 2016; Guo et al. 2019) and plants (Cahyanurani et al. 2017; Cheng et al. 2019). For example for fish, nonylphenol is hepatotoxic (Abd-Elkareem et al. 2018), hemotoxic (Ahmadpanah et al. 2019), histopathological (Shirdel and Kalbassi 2016), genotoxic (Sharma and Chadha 2017; Sayed et al. 2018), immunotoxic (Sayed et al. 2019), and reproductive toxic (Watanabe et al. 2017; Saravanan et al. 2019).

4.3 Adsorption-Oriented Processes to Remove Alkylphenols from Wastewater

Due to their widespread use in our everyday applications, chemicals, including so-called emerging substances, are ubiquitous in the environment. The list of emerging substances is particularly long and includes pesticides, pharmaceuticals, cosmetics, personal care products and industrial products such as alkylphenols and alkylphenol polyethoxylates. In recent years, many substances have been classified as priority or priority hazardous substances because of their potential effects on human health (Ribeiro et al. 2015). The problem is not only the variety of these compounds and their harmful and toxic effects, but also their low concentrations in the environment and the fact that most substances are recalcitrant and persistent. These facts pose new challenges for the scientific community (Luo et al. 2014). From a water engineering perspective, however, the challenge is not simple, as it is difficult to remove trace contaminants from complex mixtures of substances (co-occurrence of multi-contaminants in mixed wastes, variability of the pH of the effluents, important salinity, etc.) by conventional methods used in municipal wastewater treatment plants, drinking water treatment plants and industrial water treatment plants. However, the water treatment industry has to deal with these substances and integrate these problems into their management, due to increasingly strict regulations.

The most common process in municipal wastewater treatment plants is biological treatment using activated sludge (Qiang et al. 2013; Priac et al. 2017). This conventional treatment is often insufficient to remove most organic pollutants. Indeed, published research results have shown that municipal wastewater treatment plants are the largest local source of release of priority substances and pollutants to the environment due to the low removal efficiency of many of these compounds (Shao et al. 2005; Priac et al. 2017; Eggen et al. 2014; Qiang et al. 2013). Shao et al. (2005) have previously reported that only half of the total amount of pollutants is removed in conventional wastewater treatment plants by removal or adsorption on sludge. Currently, the purification performance is >90%, but the discharges still contain a cocktail of substances.

Among publications focusing on the practical application of pollutant removal technologies, work to extend existing municipal wastewater treatment plants to other tertiary processes or final treatments dominates (Vazquez-Duhalt et al. 2005; Soares et al. 2008; Basile et al. 2011; Garcia-Rodríguez et al. 2014; Ribeiro et al. 2015; Grandclement et al. 2017). The concept is to use a final or tertiary treatment to remove the remaining pollutants produced during secondary biological treatment. The concept is to use final or tertiary treatment to remove the remaining pollutants produced during secondary biological treatment. The technology involves the implementation of integrated processes that are a combination of two or more treatment methods that are intended to be complementary (Grandclement et al. 2017). For example, the addition of activated carbon can increase the removal of poorly biodegradable organic compounds through adsorption (Alvarino et al. 2016). This addition of a final treatment step can optimize the efficiency of biological

treatment plants and significantly reduce the release of pollutants into the environment. However, the use of tertiary treatment in Europe is not yet widespread for reasons of economic viability, although it may be necessary in the future if further restrictions are applied. In fact, there are two main policies with regard to water pollution control: the first is to focus on reducing pollutant emissions at source (e.g., France) and the second is to focus on downstream reduction at treatment plants (e.g., Switzerland, Germany).

The main tertiary treatments used to date at some industrial sites are activated carbon adsorption, advanced oxidation such as ozonation, and membrane filtration (ultrafiltration, reverse osmosis) (Jones et al. 2007; Hollender et al. 2009; Cases et al. 2011). Each treatment has its own constraints not only in terms of cost, but also in terms of feasibility, efficiency, practicability, reliability, environmental impact, sludge production, operation difficulty, pre-treatment requirements and the formation of potentially toxic byproducts. For example, the advantages for membrane filtration often cited are: large range of commercial membrane available from several manufacturers, small space requirement, simplicity and efficiency, production of a high-quality treated wastewater, no chemicals required and well-known separation mechanisms. The main disadvantages are: investment costs, high energy requirements, high maintenance and operation costs and rapid membrane clogging. Another problem of membrane processes is the formation of separate contaminant concentrates (retentate), which needs to be further investigated. The advantage of chemical oxidation processes, including ozone-based processes, is that they can lead to total mineralization of organic matter into carbon dioxide and water, or to the transformation of hydrophobic organic compounds into more polar, biodegradable compounds (Kralchevska et al. 2010). The processes are also integrated physico-chemical methods, simple, rapid and efficient. Another advantage is the fact that ozone is generated *on-site* (no storage-associated dangers). The main disadvantages are: chemicals required, pretreatment indispensable of the effluent, formation of (unknown) intermediates, no significant diminution of chemical oxygen demand, and generation of sludge.

4.3.1 Alkylphenol Removal onto Activated Carbons

Activated carbons are one of the oldest and most widely used adsorbents for adsorbing contaminants from drinking water sources (e.g. rivers, lakes or reservoirs) and for removing pollutants from wastewater streams (e.g. effluents from the textile, pharmaceutical, food and beverages, and petroleum refining industries). Activated carbon technology is indeed widely used on an industrial scale to eliminate pollution in order to obtain water quality that meets regulatory requirements. For example, in a drinking water treatment plant, the large-scale treatment sequence consists of coagulation/flocculation, flotation clarification, sand filtration, disinfection, activated carbon filtration and post-chlorination. In industrial wastewater treatment,

carbon technology is used either in secondary treatment or in tertiary treatment after chemical and/or biological operations.

The wide use of activated carbons in industry for liquid phase applications is due to their relatively low cost compared to other materials, their specific characteristics (inert nature, hydrophobic and organophilic, stable in a wide pH range), their high availability, their versatility (products in granular, powdered or fiber forms) and above all their high efficiency (in the >90–99% range) in adsorption-oriented processes. This capacity is mainly due to their structural characteristics and porous texture which gives them a large surface area (500–1500 m²/g for liquid phase applications), and their chemical nature which can be easily modified by chemical or thermal treatment in order to vary their properties. Activated carbon technology is also simple and flexible and can be easily integrated into a water treatment plant (Dąbrowski et al. 2005; Crini and Badot 2007; Çeçen and Aktaş 2012; Morin-Crini and Crini 2017).

At the industrial scale, they are used to eliminate organic matter, inorganic and organic contaminants (dyes, metals, pesticides, aromatics, rare earth elements, radionuclides, etc.), to decrease chemical oxygen demand and biochemical oxygen demand, to discolor water, and to treat substances that cause a taste or smell. Since the 1980s, activated carbons have also been proposed to remove alkylphenols and alkylphenol ethoxylates (Singer and Yen 1980). Abundant data have been published on this topic (Iwasaki et al. 2001; Tanghe and Verstraete 2001; Dąbrowski et al. 2005; Crini and Badot 2007; Yu et al. 2009; Çeçen and Aktaş 2012; Tsytsarski et al. 2014; Katsigiannis et al. 2015; Mailler et al. 2016; Jeirani et al. 2017; Priac et al. 2017; Vatankhah et al. 2019).

Iwasaki et al. (2001) reported that alkylphenols had very high adsorbability by microporous activated carbon having high specific surface area (carbon prepared from coconut shell, powder with specific surface area ranging from 500 to 1800 m²/g). The amount of 4-nonylphenol adsorbed at equilibrium concentrations above 20 µg/L increased with activation time as prolongation of the latter increases micropore volume and specific surface area. The amount adsorbed at 1 µg/L increased with activation time from 0.5 to 2.5 h, but decreased from 2.5 to 4.5 h. This decrease under prolonged activation was attributable to the effect of decreased dispersion force through pore enlargement being greater than the effect of increased specific surface area. The authors observed that, in both alkylphenols with linear alkyl chains and those with branched alkyl chains, the amount adsorbed increased with the number of carbon atoms. The amount of alkylphenols adsorbed at equilibrium concentrations above 10 µg/L was higher for alkylphenols with linear alkyl chains of 5–7 carbon atoms than for those with branched alkyl chains of 8–9 carbon atoms due to the molecular sieving effect of the latter. Iwasaki et al. (2001) concluded that activated carbons were effective materials to remove alkylphenols and alkylphenol ethoxylates from effluents at lab-scale, even at very low concentration. Tanghe and Verstraete (2001), studying adsorption of nonylphenol onto granular activated carbon, reported similar conclusion. The maximum adsorption capacity of granular activated carbon for nonylphenol was 100 mg/g (contact time of 4 d or 24 h depending on the carbon dosage used, 1 and 0.1 g/L, respectively). These authors

also reported that the influence of temperature (4 °C and 28 °C) on performance was negligible and a full-scale carbon filter unit will be sufficient to remove environmentally relevant nonylphenol concentrations of 10 µg/L. Later, Tsytsarski et al. (2014) demonstrated that the amount of carbon had no significant influence on performance. Yu et al. (2009) evaluated the adsorption of nonylphenol on granular activated carbons, with a particular focus to adsorption mechanism. The authors demonstrated that film diffusion was the primary controlling mass transfer mechanism for very low concentrations of nonylphenol, and therefore must be accurately determined for good breakthrough predictions. However, film diffusion was difficult to predict with a correlation due to the complexity of carbon particle topography and system hydrodynamics. A discussion on adsorption mechanism and relationship between chemical and physical surface properties of carbons on alkylphenol removal can be found in Çeçen and Aktaş (2012).

Activated carbon technology is used at industrial scale not only for removing alkylphenols but also for other emerging substances (Altmann et al. 2014; Nam et al. 2014; Katsigiannis et al. 2015; Mailler et al. 2016; Morin-Crini and Crini 2017; Jeirani et al. 2017; Crini et al. 2019; Vatankhah et al. 2019). However, it presents several disadvantages. The adsorption efficiency depends on the type of carbon used, and the higher the quality, the greater the cost. Commercial activated carbons are also non-selective (Dąbrowski et al. 2005; Crini and Badot 2010; Rivera-Utrilla et al. 2011; Vatankhah et al. 2019). Another problem is the rapid saturation of filters, and thus their regeneration. This regeneration step of saturated carbon is difficult and expensive, not straightforward, and results in loss of the adsorbent (the powdered form in particular poses a challenge from aqueous stream). For these reasons, their widespread use is restricted, in particular small and medium-size enterprises.

Over the past two decades, a new approach has been developed the development of composite adsorbents incorporating activated carbon. Another approach is to replace conventional activated carbons by other adsorbents, called non-conventional materials, such as, for example, cyclodextrin polymers, molecularly imprinted polymer and clays, which will be presented below. These adsorbents used to selectively remove alkylphenols have their own advantages and disadvantages (Crini and Badot 2010; Morin-Crini and Crini 2017; Crini et al. 2019). They are effective in treating emerging substances, but are basically at the laboratory stage despite undeniable progress.

4.3.2 Cyclodextrin Polymers for Sequestration of Alkylphenols

Cyclodextrins are natural oligosaccharides obtained by enzymatic degradation of starch. They have the ability to form inclusion complexes with a wide range of hydrophobic molecules. This property has, for example, been used by the pharmaceutical industry since the 1980s to complex active pharmaceutical ingredients. Cyclodextrins also find many applications in our daily lives, from cosmetics to food, textiles, agrochemicals, chromatography, catalysis, in the packaging industry and in

the veterinary field. In recent years, cyclodextrin polymers have been proposed as innovative materials for their ability to selectively complex pollutants substances present in complex effluents, such as dyes, aromatic compounds, chlorophenols, pesticides and metals. It's a growing sector. These commercial polymers are also becoming very popular for the tracking and removal of trace emerging substances such as pharmaceuticals, personal care products, surfactants and other industrial products (Morin-Crini and Crini 2013; Cova et al. 2018; Crini et al. 2018; Morin-Crini et al. 2018; Fenyvesi et al. 2019, 2020; Fernández et al. 2019; Sikder et al. 2019).

The hydrophobic cavity of cyclodextrin molecules allows the formation of host-guest inclusion complexes with suitable guest molecules through numerous interactions including van der Waals forces, hydrophobic interactions and hydrogen bonds (Fig. 4.3). Thus, this molecular encapsulation *via* cyclodextrin can be used to form a functional material for separating, anchoring and removing organic contaminants from harmful matrices (Morin-Crini and Crini 2013; Crini et al. 2018; Morin-Crini et al. 2018). Incorporation of cyclodextrin into materials can be achieved by a facile chemical cross-linking reaction and among the materials, the most popular is an O-alkylated polymeric resin produced by reaction of cyclodextrin molecules with epichlorohydrin used as cross-linked (Crini and Morcellet 2002; Romo et al. 2004; Crini 2005; García-Zubiri et al. 2006; Mohamed et al. 2012; Morin-Crini and Crini 2013). A commercial analog of cyclodextrin-epichlorohydrin polymer is Sephadex® using dextran instead of cyclodextrins (Fig. 4.4).

Cyclodextrin polymers are suitable materials for several reasons. Their one-step synthesis in water is simple, easy to set up in a lab, requires only mild reaction conditions (water-based chemistry, mild temperatures at atmospheric pressure), where the reagents involved are easy to find. Epichlorohydrin is not expensive and its mode of action is well understood. It is the most frequently used cross-linking agent in polysaccharide chemistry. Various types of materials can be obtained with physical, textural, mechanical and chemical properties that can be varied giving different forms such as gels, powders, beads, nanoparticles, foams and sponges. The materials can be porous or non-porous with hydrophilic and hydrophobic properties. Their properties are strictly related to their 3D macromolecular structure. The most remarkable property of cyclodextrin polymers is their ability to generate both inclusion complexes (Fig. 4.5) and association complexes (cooperation between

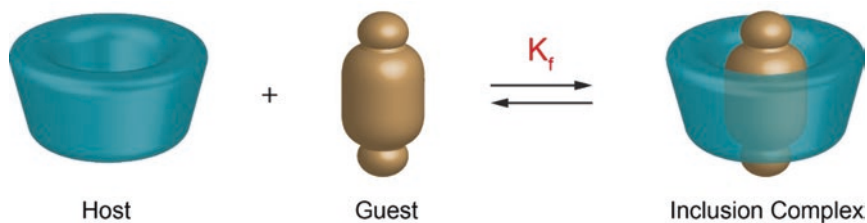


Fig. 4.3 Representation of the inclusion phenomena between a cyclodextrin molecule (the host) and a contaminant (the guest) to form inclusion complexes (K_f is a constant of formation)

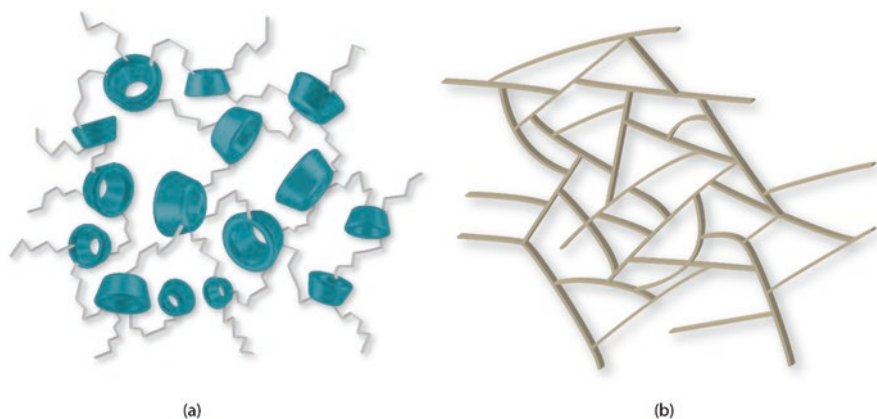


Fig. 4.4 Comparison of the structure of (a) a cross-linked epichlorohydrin cyclodextrin polymer and (b) a cross-linked epichlorohydrin dextran resin (Sephadex®)

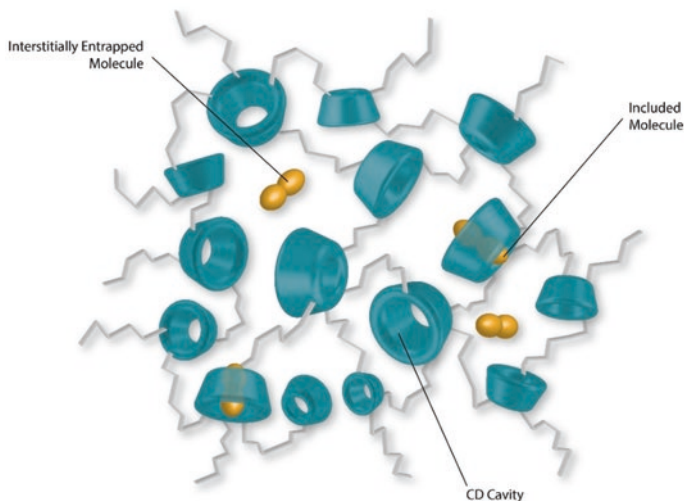


Fig. 4.5 Illustration of the role of cyclodextrin cavities and the 3D polymer network during the complexation of a pollutant by a cyclodextrin polymer

cyclodextrin cavities). In general, the performance in terms of pollutant removal can be explained not only by these two phenomena but also by the 3D network of polymer that allows the material to trap pollutants through additional interactions that complement complexation. This is why pollutants are more efficiently sequestered by cyclodextrin polymers than by native cyclodextrins, regardless of the complex structure of the pollutant. In addition, another advantage of these polymers is that, compared to commercial materials such as activated carbons and organic resins, cyclodextrin polymers are able to specifically interact with pollutants present as

traces in complex mixtures. Their regeneration is also easier and more environmentally friendly.

Cyclodextrins have long been studied in the field of separation science (mainly chromatography) and have received considerable attention over the last two decades for their performance in environmental remediation-based applications, particularly in wastewater treatment (Fourmentin et al. 2018; Barbosa et al. 2019; Celebioglu et al. 2019; Crini et al. 2019; Murcia-Salvador et al. 2019; Pellicer et al. 2019; Qin et al. 2019; Romita et al. 2019; Xiao et al. 2019; Xu et al. 2019; Fenyvesi et al. 2020). Cyclodextrin polymers are used as sorbents in liquid-solid sorption processes to remove a fairly broad list of contaminants, ranging from benzene- and phenol-based substances to volatile organic compounds, dyes, pharmaceuticals, pesticides, and metals. Over the past decade, these polymers have been proposed to eliminate endocrine disruptors and other emerging pollutants such as non-steroidal anti-inflammatory drugs, estrogens, hormones, bisphenol A, and perfluorinated alkyl substances. These polymers may also interact with non-ionic and ionic surfactants (Cserhati et al. 1992; Murai et al. 1996, 1997, 2006) and detergents but studies on the removal of alkylphenols are rare (Takeda et al. 2000; Murai et al. 2006; Bonenfant et al. 2009, 2010, 2012; Sancey and Crini 2012; Charles et al. 2014, 2016).

Murai et al. (1996, 1997) were the first to suggest that cyclodextrin polymers can retain different alkylphenols by forming inclusion complexes with cyclodextrin molecules. The performances were high: 1 g of material was able to adsorb 85% of alkylphenol ethoxylate from a 150 mL solution containing 200 ppm of nonionic surfactant. However, kinetics were relatively slow. The authors demonstrated that the materials could be used in batch or column adsorption experiments with surprisingly similar performances. Another interesting feature was the fact that the sorbents proposed can be easily regenerated. At the end of the 2000s, Hausler's group also showed the efficiency of cyclodextrin polymers for the removal of alkylphenol monoethoxylates (Bonenfant et al. 2009, 2010, 2012). The experiments were performed using synthetic solutions containing 500 mg of material and aqueous alkylphenol mono- and diethoxylate solutions at concentrations of 12–82 mg/L. The abatement performance of the material was between 1.1 and 6.8 mg of pollutant adsorbed whatever the initial concentration. The data indicated a relationship between the chemical structure of the organic pollutant and the performance of the materials. Later, Crini's group also demonstrated that the adsorptive uptake of such materials depended on their textural properties and surface chemistry (Sancey et al. 2011; Sancey and Crini 2012; Charles et al. 2014, 2016). Their results also demonstrated that cyclodextrin polymers presented a facility of regeneration, and after this treatment, the performance remained unchanged showing both the chemical stability of the polymers and the reproducibility of the values.

Figure 4.6 compares the performance of five materials on the removal of several alkylphenols, (see Figs. 4.1 and 4.2 for their structure), present in synthetic solution at a concentration of 100 µg/L. The alkylphenols are a mixture of nonylphenol (NP, CAS number 25154-52-3), a mixture of 4-nonylphenol (4-NP, CAS number 84852-15-3), the linear *para*-nonylphenol (4-*n*-NP, CAS number 104-40-5), the linear *para*-octylphenol (4-*n*-OP, CAS number 1806-26-4), and the *para*-octylphenol

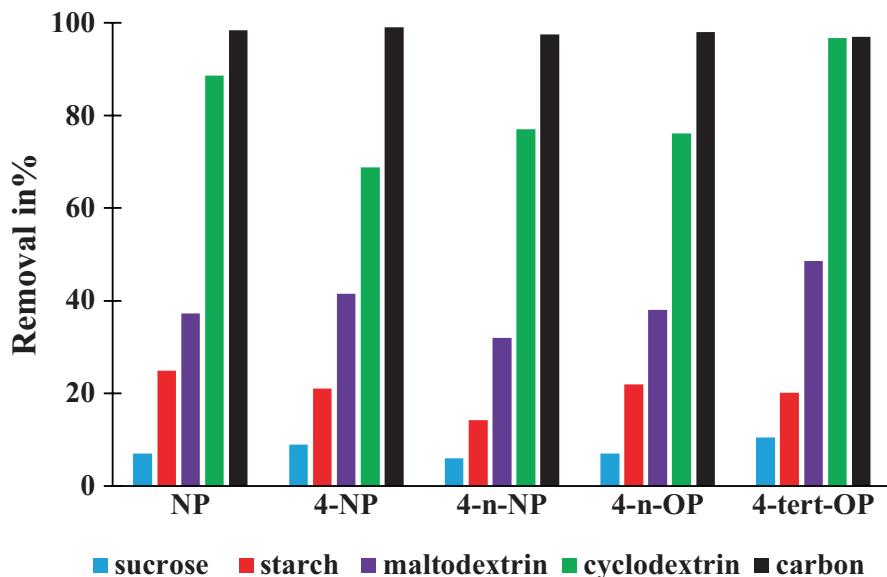


Fig. 4.6 Comparison of different materials for the removal (in %) of several alkylphenols (NP: nonylphenol, mixture, CAS number 25154-52-3; 4-NP: 4-nonylphenol, mixture, CAS number 84852-15-3; 4-n-NP: linear *para*-nonylphenol, CAS number 104-40-5; 4-n-OP: linear *para*-octylphenol, CAS number 1806-26-4; 4-*tert*-OP: *para*-octylphenol, CAS number 140-66-9; adsorbent dose 2 g/L; initial concentration 100 µg/L; contact time 4 h; agitation 250 rpm; T 25 °C; pH 6; n = 2)

(4-*tert*-OP, CAS number 140-66-9). It clearly shows that the cyclodextrin polymer and commercial activated carbon have the best performance relative to the other materials, regardless the contaminant studied. As expected, conventional carbon had the highest levels of alkylphenol removal (close to 100%). This result also indicates that adsorption onto carbon is non-selective. For cyclodextrin polymer, the order of sorption is as follows: 4-*tert*-octylphenol > nonylphenol > 4-n-nonylphenol ~ 4-n-octylphenol > 4-nonylphenol. If the values obtained for 4-*tert*-octylphenol and 4-nonylphenol are compared, an important decrease is observed, suggesting that the difference in the chemical structure between these two substances may explain the different obtained values. On the contrary, sucrose- and starch-based polymers were not able to remove alkylphenols (<10% and <20% respectively), suggesting that for cyclodextrin polymer, the main mechanism for adsorption of alkylphenols in these materials was inclusion within the cyclodextrin cavities. It is interesting to note that, although it does not have the type of cavity that participates in inclusion complexes, cross-linked maltodextrin has an adsorption capacity towards alkylphenols (the performances obtained are nevertheless inferior to those of cross-linked cyclodextrins). This result shows that the macromolecular structure of the material must also be taken into account to explain the adsorption mechanism.

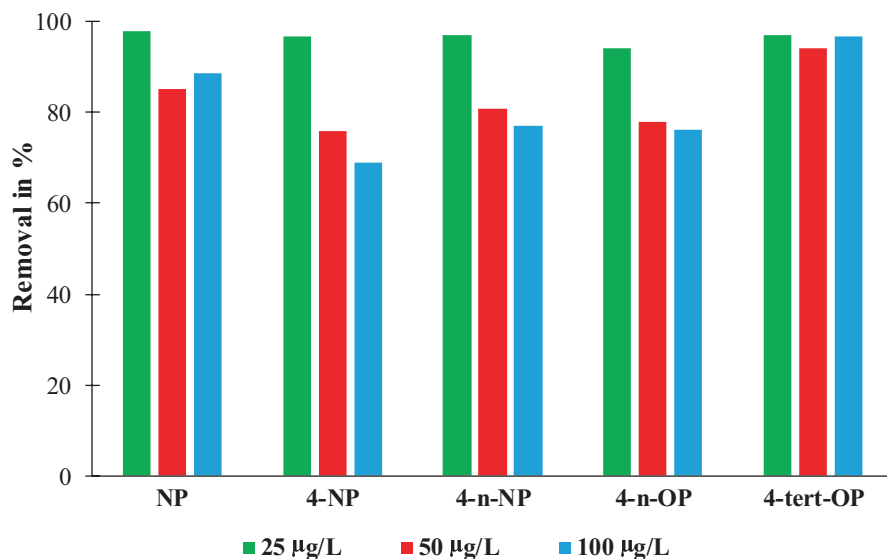


Fig. 4.7 Effect of initial alkylphenol concentration on the removal (expressed as % abatement) of five alkylphenols present in a mono-contaminated solution by a cyclodextrin polymer (NP: nonylphenol, mixture, CAS number 25154-52-3; 4-NP: 4-nonylphenol, mixture, CAS number 84852-15-3; 4-*n*-NP: linear *para*-nonylphenol, CAS number 104-40-5; 4-*n*-OP: linear *para*-octylphenol, CAS number 1806-26-4; 4-*tert*-OP: *para*-octylphenol, CAS number 140-66-9; conditions: adsorbent dose 2 g/L; contact time 4 h; agitation 250 rpm; T 25 °C; pH 6; n = 2)

Figure 4.7 reports the effect of the initial alkylphenol concentration on the performance of a cyclodextrin polymer to remove five alkylphenols from mono-contaminated solution. At any concentration, the same order of abatement was obtained for all alkylphenols studied. The affinity was independent of alkylphenol concentration between 25 and 100 µg/L. For a concentration below 25 µg/L, all the alkylphenol present in each solution is adsorbed (values below the quantification limit). For the concentration range studied (25–100 µg/L), the 4-*tert*-octylphenol substance showed the highest affinity. For other compounds, when the alkylphenol concentration was increased, sorption efficiency decreased, due to the saturation of the site on the material and/or steric effects. For example, for 4-nonylphenol, when the initial concentration was increased from 25 to 100 µg/L, the removal decreased from 97 to 69%.

Figure 4.8 compares the removal of five alkylphenols in a mixture at three concentrations by a cyclodextrin polymer (fixed conditions: adsorbent dose, contact time, T 25 °C). These results show that the performance obtained changed for each alkylphenol alone or in the presence of the others, suggesting the presence of competition effects between contaminants. Differences in the degree of sorption can be attributed to the chemical structure of each alkylphenol (Fig. 4.2). Indeed, it is known that the size of each molecule can determine its accessibility to the cyclodextrin-based network. Thus, steric effects can also be advanced to explain the

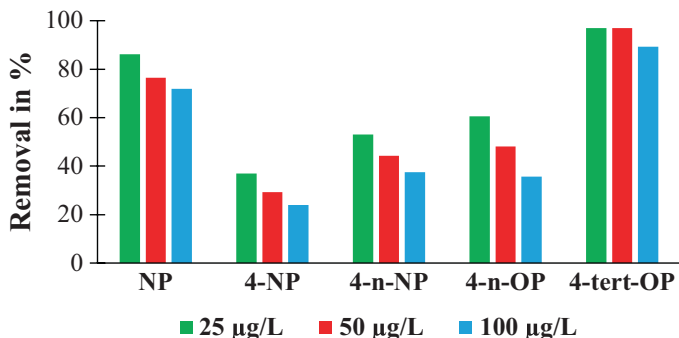


Fig. 4.8 Effect of initial alkylphenol concentration on the removal (expressed as % abatement) of five alkylphenols present in a mixture by a cyclodextrin polymer (NP: nonylphenol, mixture, CAS number 25154-52-3; 4-NP: 4-nonylphenol, mixture, CAS number 84852-15-3; 4-n-NP: linear para-nonylphenol, CAS number 104-40-5; 4-n-OP: linear *para*-octylphenol, CAS number 1806-26-4; 4-*tert*-OP: *para*-octylphenol, CAS number 140-66-9; adsorbent dose 2 g/L; contact time 4 h; agitation 250 rpm; concentration 25, 50 or 100 µg/L for each alkylphenol in mixture; T 25 °C; pH 6; n = 2)

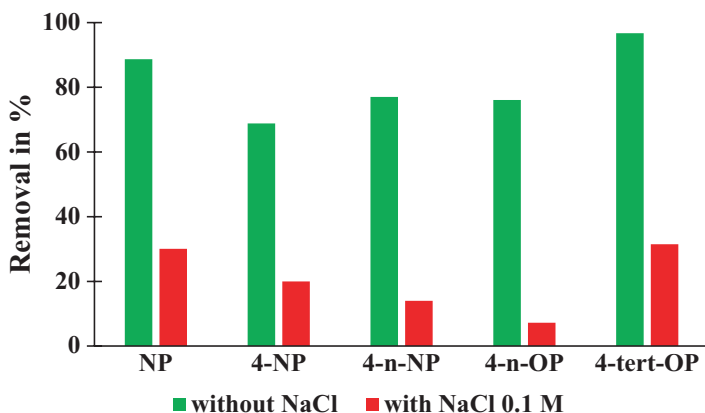


Fig. 4.9 Effect of NaCl on the removal (expressed as % abatement) of five alkylphenols present in solution by a cyclodextrin polymer (NP: nonylphenol, mixture, CAS number 25154-52-3; 4-NP: 4-nonylphenol, mixture, CAS number 84852-15-3; 4-n-NP: linear para-nonylphenol, CAS number 104-40-5; 4-n-OP: linear *para*-octylphenol, CAS number 1806-26-4; 4-*tert*-OP: *para*-octylphenol, CAS number 140-66-9; adsorbent dose 2 g/L; contact time 4 h; agitation 250 rpm; concentration 100 µg/L for each alkylphenol in synthetic solution; T 25 °C; pH 6; n = 1)

differences of adsorption observed for cyclodextrin polymer between alkylphenols when they were in a mixture. Figure 4.9 shows the effect of the presence of NaCl on the performance of cyclodextrin polymer for five alkylphenols. Their removal was significantly decreased in the presence of NaCl for all substances. Probably, NaCl maximizes electrical charge on the surface of the material by masking of adsorption sites, thus decreasing attraction interactions that negatively affect complexation.

Table 4.3 Concentrations (in $\mu\text{g/L}$) of alkylphenols present in three industrial effluents before and after sorption on cyclodextrin polymer (NP: nonylphenol, mixture, CAS number 25154-52-3; 4-NP: 4-nonylphenol, mixture, CAS number 84852-15-3; 4-*n*-NP: linear para-nonylphenol, CAS number 104-40-5; 4-*n*-OP: linear *para*-octylphenol, CAS number 1806-26-4; 4-*tert*-OP: *para*-octylphenol, CAS number 140-66-9; adsorbent dose 2 g/L; contact time 4 h; agitation 250 rpm; T 25 °C; pH 6.5; n = 1)

Alkylphenol	Effluent 1		Effluent 2		Effluent 3	
	Before treatment	After treatment	Before treatment	After treatment	Before treatment	After treatment
NP	45.9	2.3	120	<0.5	49.2	1.23
4-NP	<0.5	<0.5	85.2	2.31	26.5	0.78
4- <i>n</i> -NP	13.5	<0.5	50.3	7.2	<0.5	<0.5
NP1EO	<0.1	<0.1	<0.1	<0.1	7.11	<0.1
NP2EO	5.1	<0.1	2.98	<0.1	10.5	1.25
4- <i>n</i> -OP	12.3	<1	32.1	1.32	5.99	0.99
4- <i>tert</i> -OP	7.9	<0.5	44.2	4.44	1.23	<0.5
4- <i>tert</i> -OP1EO	6.12	1.05	<0.1	<0.1	<0.1	<0.1
4- <i>tert</i> -OP2EO	<0.1	<0.1	<0.1	<0.1	0.99	<0.1

With the exception of a few very recent works (Charles et al. 2014, 2016), studies of real concrete cases are rare. Table 4.3 shows the values obtained before and after treatment for three industrial effluents. Analytical monitoring of these effluents showed that nine alkylphenols were found at least once. Of these, nonylphenol, nonylphenol diethoxylate, 4-*n*-octylphenol, 4-*n*-octylphenol and 4-*tert*-octylphenol systematically occurred at detectable concentrations. Others alkylphenols and alkylphenol polyethoxylates were below the limit of quantification. The data shows that the real effluents before treatment contained a variable load of alkylphenols not only in quality (number of substances detected) but also in quantity (measured concentrations). After treatment by sorption onto a cyclodextrin polymer, high levels of alkylphenol removal are achieved using cyclodextrin materials (Table 4.3).

Numerous studies demonstrated that cyclodextrin polymers are a promising alternative in the treatment of wastewater containing a cocktail of emerging trace substances, mostly at lab-scale. Recently, a company has developed new eco-friendly cyclodextrin polymers (Dexsorb® adsorbents of Cyclopure company; Cyclopure 2020), which can quickly and safely remove from water hundreds of emerging substances. These commercial adsorbents are produced in varying formats, allowing for use in analytical, household and municipal water treatment applications. Industrialists will now have to be convinced to use cyclodextrin polymers in their municipal wastewater treatment plants.

4.3.3 *Molecularly Imprinted Polymer for Selective Removal of Alkylphenols*

Molecularly imprinted polymers are commercial synthetic materials in various forms to suit the target desired application, obtained by polymerizing functional monomers and cross-linked them in the presence of a template (Alexander et al. 2006). When the template is then removed, it leaves a cavity capable of recognizing and selectively binding to the imprinted compound. These new class of materials combine the robustness of cross-linked polymers with the attractive properties of natural receptors, mimicking molecular recognition by biological receptors (Huang et al. 2015; Cantarella et al. 2019).

Molecularly imprinted polymers are used as separation and extraction materials and as sensors in many applications, including solid-phase extraction, chromatography, analytical chemistry, food separation, medical applications, drug delivery, protein recognition and purification, biomarkers and molecule detection (BelBruno 2019). Many recent studies have reported novel results on the use of molecularly imprinted polymers as selective adsorbents for the removal of pharmaceuticals, personal care products and pesticides (Murray and Öermeci 2012; Alvarez-Lorenzo and Concheiro 2013; Chen et al. 2015, 2016; Huang et al. 2015; Madikizela et al. 2018; Cantarella et al. 2017, 2019). For water applications, the main advantages of these polymers are their ease of preparation, available in a wide variety of shapes and sizes, their relatively low cost, their physical and chemical stability, and their effectiveness in removing chemicals and pathogens. Another important feature is that molecularly imprinted polymers are easily regenerated and reusable several times.

Molecularly imprinted polymers could also be a promising adsorbent for the removal of alkylphenols (Murray and Öermeci 2012; Alvarez-Lorenzo and Concheiro 2013; Matějčiček et al. 2013; Gryshchenko and Bottaro 2014; Huang et al. 2015; Xie et al. 2019). For example, Xie et al. (2019) reported that molecularly imprinted polymers had remarkable adsorption capacity, kinetics and reusability compared to other adsorbents. The maximum adsorption capacities of the MIP for 4-*tert*-octylphenol and 4-nonylphenol were 35.97 and 61.73 mg/g, respectively, which were significantly higher than those of the non-molecularly imprinted polymer due to the imprinting effect and other adsorbents. Alkylphenol adsorption reached equilibrium within 30 min, and could be reused five times. The polymers also showed high selectivity towards alkylphenols and real water samples gave satisfactory results. Gryshchenko and Bottaro (2014) also reported that molecularly imprinted polymers could be a promising adsorbent for separation and analysis of alkylphenols.

Based on data from the literature, there is no doubt that molecularly imprinted polymers have high adsorption capacities. However, studies on these materials in the field of water treatment are at the laboratory stage and pilot studies need to be conducted.

4.3.4 Adsorption of Alkylphenols onto Clays

Adsorbents such as clay minerals and modified clays are efficient for the removal of contaminants from wastewater and drinking water sources, even at trace levels. These materials have high specific surface area, porous structures and defined particles sizes, which facilitates physical and chemical interactions with dissolved species. In addition, natural clays are abundant and low-cost resource, and the technological process is simple. Numerous studies have been published on the removal of dyes, metals and organics (phenol, chlorophenols) present in industrial wastewaters, with high levels of performance (the maximum efficiency can reach 100%). The mechanisms such as ion-exchange, surface complexation and direct bonding of contaminants to the clay surface are also well-known (Espantaleon et al. 2003; Nagasaki et al. 2003; Priac et al. 2017). A survey of data literature shows that clays can also be used as efficient adsorbents for the removal of alkylphenol using clays. However, in the field of water data are rather rare, whereas studies on alkylphenol-clay interactions in soils or alkylphenol-sludge interactions are more numerous.

To reduce the pollution of effluents produced in tanning, Espantaleon et al. (2003) proposed a simple, selective and economical alternative to conventional physical-chemical treatments based on modified clays using batch experiments. These materials, obtained using the activation of natural bentonite by a 0.5 M H_2SO_4 solution, were used as effective adsorbent for alkylphenol ethoxylates removal. Nagasaki et al. (2003) also proposed a simple method of oriented-adsorption onto clays to reduce the contamination of solutions by nonylphenol. The authors studied the adsorption of nonylphenol on Na-montmorillonite. The results of a series of batch experiments were compared to those obtained using $\alpha\text{-SiO}_2$, $\alpha\text{-Al}_2\text{O}_3$ and gibbsite. It was found that nonylphenol 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 adsorption. These data suggest that nonylphenol was adsorbed on the outer surface of Na-montmorillonite. The amount of nonylphenol 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 nonylphenol was adsorbed on the broken edges of the octahedral alumina sheets of Na-montmorillonite.

Another interesting topic in the literature is the study of interactions of alkylphenols and soils. Alkylphenols and alkylphenol ethoxylates occurrence in soil is related to anthropogenic activities such as sewage sludge application, land filling and accidental spills. As already mentioned, tons of nonionic surfactants are produced in Europe every year. In municipal wastewater treatment plants, alkylphenol ethoxylates are partly degraded to alkylphenols by shortening the hydrophilic chain of the ethoxylates. These compounds are then degraded in anaerobically stabilized sewage sludge to yield fully diethoxylated 4-nonylphenol, a more lipophilic and toxic substance that resists to further microbial degradation.

Alkylphenols can be found not only in aqueous compartments (surface water, groundwater, sediment) and sludge, but also in soils and even in the air (Kovarova

et al. 2013; Salomon et al. 2019). They have also detected in drinking water and milk. Indeed, these substances can end up in the environment, for example when sewage sludge is spread in agriculture (this activity is regulated in Europe, although there are no limit values set for sludge). The presence of substances in sewage sludge is a growing concern for farmers, and for society in general, because alkylphenols, such as nonylphenol, are considered to be endocrine disruptors, affecting the reproductive capacity of animals and humans (Naim et al. 1994; Claisse and Alzieu 1993; Cocchieri et al. 1993; Smith and Jaffe 1994; Ginsberg 1994). From a scientific point of view, adsorption and desorption of alkylphenols and alkylphenol ethoxylates in sewage sludge and soils is a hot topic. For example, an interesting challenge is to understand the uptake of alkylphenols by plants from sludge-amended soils because this depends on its bioavailability, which is determined by sorption behavior. In this context, it is important to understand how alkylphenol compounds are bound by the soil components and how they migrate. As most of them have a very low solubility, it may be interesting to consider that their transport in groundwater as well as their binding to soil components could be enhanced by their parent molecules, i.e. the nonionic surfactants, from which they are derived. A detailed study of the coadsorption of alkylphenol compounds, such as paramethylphenol, parapropylphenol and para-nonylphenol, with nonionic surfactants has been published by Barhoumi's group (Barhoumi et al. 2003a, b, 2006; Barhoumi and Saïd 2017).

Small hydrophobic molecules such as phenol can be solubilized by surfactant micelles. These provide an environment in which these compounds can find a more stable state than in aqueous solution. The hydrocarbon core of the micelles gives them the ability to solubilize hydrophobic compounds. As a result, numerous studies have shown that surfactant micelles significantly improve the apparent solubility of hydrophobic organic compounds in water (Abdul et al. 1990; Fountain et al. 1991; Pennell et al. 1993, 1994; Shiau et al. 1994). Hydrophobic molecules may also interact with adsorbed surfactants. This is due to the structure of surfactants adsorbed phases. The adsorption mechanism of surfactants onto minerals is now well known. At low equilibrium concentrations, surfactants may be adsorbed as isolated molecules. Surfactant surface aggregates can solubilize hydrophobic molecules as do bulk micelles. The consequence may be an apparent increase in the adsorbed amount of the solute when a surfactant molecule is present in the system. Two situations may be encountered. Firstly, the solute molecule is not adsorbed by the solid surface when alone, but is adsorbed when a surfactant molecule is adsorbed: this process is often called "adsolubilization". Secondly, the solute is adsorbed by the solid surface when it is alone and its surface concentration is increased in the presence of a surfactant: this is a coadsorption process.

The adsorption of alkylphenols from aqueous solution onto kaolinite was first studied and compared to the case of phenol (molecular weight MW 94.1 g/mol; solubility 85 g/L at 25 °C). *para*-Methylphenol (MW 108.1 g/mol; solubility 19 g/L at 25 °C), *para*-propylphenol (MW 136.1 g/mol; solubility 3 g/L) and *para*-nonylphenol (MW 220.3 g/mol; solubility 0.005 g/L) were chosen as test solutes (Barhoumi et al. 2003a, b, 2006). Adsorption of alkylphenol was studied in the presence of an alkylphenol polyethoxy nonionic surfactant, and isotherms were

determined by the solution depletion method. As the alkylphenol and the surfactant molecules had very similar UV spectra, a specific method was used to determine the phenol function content of the solutions.

Phenol, like alcohol, is only weakly adsorbed by oxide surfaces, as water is preferentially adsorbed. The adsorption isotherms indicate the amount of mole of alkylphenol per unit area as a function of its equilibrium solution concentration. Barhoumi et al. (2003a) previously reported that phenol had only a low affinity for this type of surface. Its plateau surface concentration was $0.06 \mu\text{mol}/\text{m}^2$ and the adsorption isotherm is L-shaped (Langmuir type), suggesting that only a limited number of surface sites are adsorption sites for phenol molecules and that no lateral interaction effects are visible between adsorbed molecules. The behavior of alkylphenols was completely different (Barhoumi and Saïd 2017): the curves showed S-shaped adsorption isotherms that were very similar to the adsorption isotherms of surfactants. Each of these adsorption isotherms had a clear plateau which corresponded to a high surface concentration compared to that of phenol. This behavior may indicate an aggregation of alkylphenols at the interface, as do surfactants. These molecules are not considered to be surfactants due to an unfavorable size ratio of the hydrophilic and hydrophobic parts of the molecule, alkylphenols are not subject to micelle formation. Nevertheless, they are so hydrophobic that it is easy to imagine that once a few of them are attached to the surface, they can become anchor points for the others. Their structure is close to that of non-ionic surfactants, which may explain why they can have similar properties at the interface (Barhoumi and Saïd 2017).

The adsorption isotherms of paramethylphenol in the presence of Triton™ X-100 (an octylphenol ethoxylate with 9.5 ethylene oxide units) were also carried out together with the evolution of the surface concentration of Triton™ X-100. The critical micelle concentration of Triton™ X-100 is $0.27 \text{ mmol}/\text{L}$. Isotherms were also determined by solution depletion methods. Other results showed that the longer the alkyl chain, the lower was the adsolubilization part in the adsorption process. Since the surfactant is not displaced by the adsorption of alkylphenols, it is possible that the adsorption sites of the alkylphenol molecules (when alone) are different from the adsorption sites of the surfactant. In this case, the adsorption of surfactant and solute is therefore not competitive. In summary, alkylphenols can be adsorbed by kaolinite with a mechanism close to that of surfactants. If a non-ionic surfactant is added to the medium, the adsorbent properties are modified according to the length of the alkyl chain. The longer the length of the alkyl chain of alkylphenol derivatives, the smaller the influence of the surface aggregates Triton™ X-100 on their adsorption behavior. The total capacity is increased in all cases, but in the range of low solute concentrations, the initial slope is less and less modified as the length of the chain increases. This unexpected behavior, depending on the relative hydrophobicity of the molecules, may be due in part to the adsorbent properties of alkylphenols that are capable of aggregating alone at the kaolinite/water interface and in part to the limited swelling capacity of the surface micelles of Triton™ X-100.

4.4 Remediation of Alkylphenols Using Biotechnological Processes

4.4.1 Alkylphenol Removal Using Microalgae

Algae-based technologies are alternative options for treating wastewater and generating useful products at low cost and high efficiency (Biris-Dorhoi et al. 2016; Hwang et al. 2016; Molazadeh et al. 2019; Wollmann et al. 2019). Indeed, the cultivation of microalgae offers a chemically efficient step for wastewater treatment plants, combined with the production of potentially valuable biomass. For water treatment applications, microalgae have the following high adsorption capacity, high surface area/volume ratio, wide distribution range, rapid metabolism, low cost, and abundant availability. Algae-based technologies can be easily integrated into a wastewater treatment plant as secondary or final treatment. Data from the literature show that algal-based treatments appear to work well compared to chemical processes, which are generally too expensive to be implemented in most places and may result in secondary pollution. In addition, the algal biomass produced during treatment can be used for methane production, composting, production of fuels or fine chemicals, and as animal feed or in aquaculture.

Algae-based technologies can treat human sewage, livestock waste, agro-industrial waste, pig farm effluents, agricultural waste and wastewater from food processing. Microalgae have the potential to effectively remove not only nutrients (they use nitrogen and phosphorus for growth) and coliform bacteria from wastewater and reduce conventional water parameters such as chemical and biochemical oxygen demand (Biris-Dorhoi et al. 2016; Wollmann et al. 2019), but also pollutants (metals) and emerging substances (Abdel-Raouf et al. 2012; Biris-Dorhoi et al. 2016; Delrue et al. 2016; Maza-Márquez et al. 2018; Gupta and Bux 2019). Indeed, they have been known for many years for their ability to degrade/eliminate toxic organic substances such as chlorophenols, polycyclic aromatic compounds, hormones (progesterone, norgestrel), antibiotics (tetracycline), triclosan and pesticides (α -endosulfan) (Mara and Pearson 1986; De la Noüe and De Pauw 1988; Redalje et al. 1989; Muñoz and Guieysse 2006). They biodegrade or biotransform pollutants through metabolic action, and mechanisms include accumulation and degradation, which includes adsorption, transformation and mineralization. Microalgae also produce oxygen and have a disinfectant effect due to the increase in pH during photosynthesis (Mara and Pearson 1986).

The great advantage of this biotechnology is that most of the algal species with proven efficacy are readily available, especially in countries that lack infrastructure for wastewater treatment. As photosynthesis is a key process for the cultivation of microalgae, these systems are ideal for regions with high temperatures and exposure to sunlight. In addition, when combined with conventional activated sludge systems, algal-bacterial symbiosis can reduce the electrical energy requirements for aeration (Redalje et al. 1989). For all these reasons, these biological processes develop (Biris-Dorhoi et al. 2016; Hwang et al. 2016; Molazadeh et al. 2019; Wollmann et al. 2019).

Recent studies have also been reported the removal, biosorption and biodegradation of alkylphenols by microalgae (Zhou et al. 2013, 2014; Delrue et al. 2016; He et al. 2016, 2020; Maza-Márquez et al. 2018; Gupta and Bux 2019; Wang et al. 2019). For example, Zhou et al. (2013, 2014) studied the removal of nonylphenol and octylphenol by the freshwater green microalga *Scenedesmus obliquus* in cultures exposed to different concentrations of alkylphenols for 5 days. At concentrations below 1 mg/L, the parameters growth, fluorescence transient, photosynthetic pigments and cell ultrastructure of *Scenedesmus obliquus* are not affected. This green microalga is commonly found in most types of freshwater, and plays an important part in the functioning of aquatic ecosystem. After 5 days of culturing, >89% nitrophenol and >58 octylphenol were eliminated by *Scenedesmus obliquus*. The dissolved concentrations for alkylphenols in the medium decreased rapidly: within one day, nonylphenol and octylphenol were rapidly eliminated with efficiencies of 70.9–90.4% for nonylphenol and 37.8–82.2% for octylphenol, depending on the initial concentration. The authors also showed that algae biomass yield decreased with increasing concentrations of nonylphenol and octylphenol. Algal growth was significantly inhibited at 4 mg/L for both compounds. The removal of alkylphenols was due to algal degradation and was primarily attributed to the process of cell biotransformation of the algae rather than simple adsorption and accumulation in the cells. Similar findings were previously reported by Gao et al. (2011) and Wang et al. (2007) for other algal species, *Chlorella fusca* and *Microcystis aeruginosa*, respectively. Zhou et al. (2013) concluded that technology based on the use of *Scenedesmus obliquus* was a potential approach for the removal of multi-contaminants, including alkylphenols, in addition to nutrients and metals. Further examples can be found in the review published by Wang et al. (2019).

The use of microalgae for wastewater treatment and the use of the resulting biomass for energy production is a two-pronged approach. Algae-based processes are already used on an industrial scale to treat so-called conventional pollution and there is no doubt that these green processes will continue to develop. However, the effect of these treatments on the monitoring of emerging substances such as alkylphenols is not yet systematically realized. There is also a need for research into degradation mechanisms.

4.4.2 Constructed Wetlands for the Removal of Alkylphenols

Constructed wetlands in combination with the use of plants are capable of removing conventional contaminants and emerging substances due to the interaction between plants and microorganisms (García-Rodríguez et al. 2014; Gorito et al. 2017; Herrera-Melian et al. 2018; Osei et al. 2019; Dan et al. 2020; Kaur et al. 2020). In many countries of the world, they are considered to be an effective alternative to conventional biological treatments for municipal wastewater treatment to treat suspended solids, chemical oxygen demand, biological oxygen demand, nutrients (nitrogen, phosphate) and metals, which is why they have developed strongly

(Gorito et al. 2017; Schultze-Nobre et al. 2017). Constructed wetland technology is also being applied on a large scale for the treatment of industrial effluent from olive mills, wineries, coffee processing, and the pulp and paper industry (Schultze-Nobre et al. 2017). They may also be considered for the treatment of agricultural runoff, animal wastewater, leachate, sludge and mine drainage. The advantages cited are simplicity, low operation/maintenance costs and environmental friendliness. Constructed wetland technology is a complex system containing water, solids (substrate, soil, plants) and microorganisms. Their design (wetland configuration, soil/substrate matrix, plant species, hybrid systems, etc.) and operational factors (operating mode, hydraulic residence time, etc.) affect its performance. In this system, physical, chemical and biological processes may occur simultaneously, such as volatilization, adsorption, sedimentation, photodegradation, plant uptake and microbial degradation. The occurrence of these processes depends on various factors such as the physical and chemical characteristics of pollutants (hydrophobicity, vapor pressure, pKa, etc.), the properties of soil/substrate (e.g. important for the growth of plants and microorganisms), the conditions used (pH, temperature, ionic strength, oxygen, etc.), the seasonal variation, etc. A challenge for constructed wetland technology is the question of the presence of so-called emerging substances such as alkylphenols and their polyethoxylated derivatives. The increasing occurrence of organic pollutants in wastewater poses indeed a new challenge (Kaur et al. 2020).

A great deal of research has been carried out on this topic, showing promising results for the removal of emerging substances. It is demonstrated that the establishment of vegetation-based wastewater treatment systems, such as wetlands, is a potential approach to address contaminants of emerging concern. The presence of vegetation such as *Phragmites australis* in constructed wetlands can improve contaminant removal. The effect of plants is related to the release of root exudates, which may enhance the biodegradation of contaminants by recruiting specific microorganisms. In addition, vegetation makes the process more resistant to hydraulic changes. Several authors have also pointed out that some root exudates are linked to improved contaminant removal in planted constructed wetlands. It is already known that in terrestrial ecosystems, plant root exudates play a crucial role in the underground ecosystem. Plant roots create hotspots of biological activity in the soil by interacting with a diverse community of microorganisms, invertebrates and nearby plants. However, there is a lack of knowledge regarding the removal percentage attributable to plants and how plants affect this removal improvement.

Constructed wetlands have been investigated for the elimination/degradation of organic pollutants. Phenolic root exudates released from plants are potentially effective for the degradation of pharmaceuticals (de la Paz et al. 2019) and aromatic compounds such as dimethylphenols (Schultze-Nobre et al. 2017) and alkylphenols (Hoang et al. 2010; Dan et al. 2020). Schultze-Nobre et al. (2017) studied the removal of dimethylphenols and ammonium in laboratory-scale horizontal subsurface flow constructed wetlands planted with *Juncus effusus*. Removal efficiencies of dimethylphenol was dependent on the inflow loading of the contaminant and was higher in the planted systems. Both planted systems yielded 99% removal efficiency up to loads of 240 mg/d, compared to only 73% for the unplanted constructed

wetland. Highly efficient dimethylphenol removal was determined for inflow loads up to 240 mg/d (40 mg/L), whereas loads of 600 mg/d (100 mg/L) resulted in a decrease in treatment efficiency. Removal efficiency was also found to be higher in planted systems, as compared to unplanted wetlands, although the presence of a gravel bed, as well as the density of the above-ground plant biomass, did not significantly influence the efficiency of dimethylphenol removal between the two planted constructed wetlands. Higher amounts of surplus organic carbon were detected in the hydroponic constructed wetland, suggesting incomplete dimethylphenol transformation and/or a more intensive release of organic substances from the plant roots as a response to possible toxic stress. Both aerobic and anaerobic processes should be responsible for carbon and nitrogen transformation and methane generation, which is of greatest importance in the inflow sections of both planted constructed wetlands. Ammonium removal was found to be highly efficient in the planted constructed wetland and insufficient in the unplanted counter-part. The authors concluded that horizontal subsurface flow constructed wetlands planted with *Juncus effusus* were a promising alternative system for the treatment of effluents contaminated with dimethylphenol isomers.

p-tert-Butylphenol is an important industrial chemical that is widely used in the production of phenolic resins and surfactant. However, it is recognized as an important hazardous contaminant because of its acute and chronic toxicities and estrogenic activity. This emerging substance is frequently detected in the environment (0.003–64 µg/L) as a result of water and sludge discharges from wastewaters treatment plants. Recently, Dan et al. (2020) studied the accelerated biodegradation of *p-tert*-butylphenol in the *Phragmites australis* rhizosphere by phenolic root exudates. Their results showed that *p-tert*-butylphenol was initially adsorbed to root surface (56–83%), and subsequently degraded (17–44%) by rhizosphere microbes of *Phragmites australis* (conditions: 300 mL of solution containing 6.2–8.6 g of *Phragmites australis* and 10 mg/L of butylphenol; 25 °C; 70% humidity; 12 h/day light; experimental period of 16 days). The presence of certain phenolic root exudates (*p*-hydroxybenzoic acid, *p*-coumaric acid, caffeic acid and ferulic acid) at the same identical concentration (50 mg/L) is beneficial for the enrichment of *p-tert*-butylphenol degrading bacteria and then accelerates the biodegradation of the substance, the performances being classified in the following order: unit 2 (+ *p*-coumaric acid) > unit 1 (+ *p*-hydroxybenzoic acid) = unit 4 (+ ferulic acid) > unit 3 (+ caffeic acid) > unit 6 (sterile). Dan et al. (2020) demonstrated the ability of phenolic root exudates with functional structures to accelerate the biodegradation of specific aromatic compounds by co-metabolism in the plant rhizosphere. However, the inherent process and mechanism remain insufficiently elucidated.

The removal of emerging contaminants by constructed wetlands is a recent area of study. Publications are numerous for pharmaceutical compounds but rarer for surfactants such as alkylphenols. This technology requires more research to achieve feasibility in terms of large-scale application to treat emerging substances. Further research is also necessary to evaluate the toxicity of the emerging pollutants to the plants and the respective carbon and nitrogen transformations that occurs in these complex root/solid/biofilm systems.

4.4.3 Alkylphenol Removal in Sequential Anaerobic-Aerobic Digestion of Sewage Sludge

Alkylphenol ethoxylates entering wastewater treatment plants are subjected to biotransformations producing alkylphenols (mainly nonylphenol) and their short chained ethoxylates (monoethoxylate and diethoxylate). These substances have been detected in effluents or adsorbed onto solids, but due to their hydrophobic-lipophilic nature, proved by the high octanol-water partition values coefficient values (K_{ow}), they tend to accumulate in sewage sludge. Similar behaviour was also detected for their biodegradation products, which were found to be more persistent, lipophilic, and bioaccumulative than their parent compounds (Venkatesan and Halden 2013). The prevalent distribution of alkylphenol ethoxylates and related intermediates in sludge has a positive effect on the quality of wastewater treatment plant effluent, but raises serious concerns about sludge disposal practices, particularly for agricultural reuse. Enrichment of the resulting solid fraction occurs at concentrations several orders of magnitude higher than those of the influent wastewater (Mailler et al. 2017). Accurate characterization of alkylphenol ethoxylates and their derivative compounds in sludge is therefore crucial to assess the environmental impact and safety of the agricultural reuse practice. Despite the relevance of the presence of these compounds in the solid fraction, previous studies in wastewater treatment plants were mainly focused on liquid streams and less attention was paid to their fate in the sludge treatment chain. Only recent studies have considered specific characterization of digested sludge for micropollutants and alternative processes in sludge treatment lines to improve their removal (Braguglia et al. 2015; Mailler et al. 2017).

The environmental impacts of alkylphenol ethoxylates and their metabolites when sludge is reused in agriculture include direct uptake by crops and subsequent transfer into the food chain, raising serious concerns for human health and negative effects on plant growth. Their persistence and recalcitrance amplify and extend these effects over time, with long-term consequences that are difficult to predict. In addition, metabolites such as nonylphenol are capable of mimicking natural hormones and inducing endocrine disruption in aquatic and terrestrial organisms (Soto et al. 1991), which, through cultivation, can be recycled in the food chain.

The relevance of the alkylphenol ethoxylate content in the assessment of the environmental impact and safety of agricultural reuse of sewage sludge has been recognized by the European Union in the Working Documents on Sludge 3rd draft (EU-WDS, EU 2000) and on Sludge and Biowaste (EU-WDSB, EU 2010). They suggest for alkylphenol ethoxylates the limit value of 50 mg/kg_{dw}, which is also applied in Sweden (Rule et al. 2006) and Turkey (Ömeroğlu et al. 2015), while Denmark prescribes a lower limit of 10 mg/kg_{dw} (Inglezakis et al. 2014).

Efficient sludge digestion is the key step in the sludge treatment chain to reduce the solid fraction and, at the same time, to improve the quality of the digested sludge in terms of content of toxic contaminants such as alkylphenol ethoxylates, pathogens and virus. The combination of two sequential, anaerobic-aerobic digestion

steps has been proposed and investigated as effective strategy to improve the performance of the single anaerobic digestion process. The rationale behind this approach is that different reaction environments (anaerobic and aerobic) offer complementary and therefore optimal biodegradability conditions for the different solids fractions and contaminants in sludge (Kumar et al. 2006). In order to improve the performance of the process in terms of reduction of solids content and removal of persistent contaminants, a modification of the sequential process has been proposed, namely the operation of the post-aerobic stage under mesophilic conditions ($T = 37\text{ }^{\circ}\text{C}$) (Tomei et al. 2016). Since anaerobically digested sludge is at mesophilic temperature ($T = 37\text{ }^{\circ}\text{C}$) and exothermic reactions occur in aerobic digestion, little external energy input is required for the sequential digestion process.

In a recent comprehensive study on the fate of micropollutants in the anaerobic-aerobic digestion process, Tomei et al. (2019) analysed the fate of conventional and emerging substances, including alkylphenol ethoxylates. Experiments were conducted on real secondary sludge sampled in the aeration basin of a large-scale wastewater treatment plant (serving about 780,000 equivalent inhabitants). The sludge characterization in terms of classical parameters is reported in Table 4.4. The mean concentration of alkylphenol ethoxylates and related metabolites in secondary sludge throughout the experimental campaign was $2.66 \pm 1.88\text{ mg/kg}_{\text{dw}}$, while the concentration range of the alkylphenol ethoxylates and related metabolites analysed (referring to the period when the tests were performed) is shown in Table 4.5 (Tomei et al. 2019).

The experimental apparatus consisted of two 7.4 L digesters operated in semi-continuous mode and in series: waste sludge was introduced into the anaerobic reactor (working volume 7 L) once a day and an equivalent volume of anaerobically digested sludge was fed to the next aerobic reactor (working volume 4.5 L). Both reactors were equipped with mechanical stirrers and a thermostatic jacket to maintain the process temperature. The anaerobic reactor was operated under mesophilic conditions ($T = 37\text{ }^{\circ}\text{C}$) and with a sludge retention time of 15 days. The dissolved oxygen concentration in the aerobic reactor was controlled at $\sim 3\text{ mg/L}$ and the aerobic sludge retention time was 12 days. A scheme of the sequential process, with additional detailed information on the laboratory-scale installation, is given elsewhere (Tomei and Carozza 2015). Tests were conducted for both configurations:

Table 4.4 Characterization of the sludge (values are reported as average value and standard deviations in parentheses; dw dry weight)

Parameter	Concentration	Unit
Total solids	39.71 (3.47)	g/L
Volatile solids	27.44 (1.95)	g/L
Chemical oxygen demand	39.87 (9.32)	g/L
Total organic carbon	309.44 (28.51)	g/kg _{dw}
Total N	60.35 (2.14)	g/kg _{dw}
Total P	19.01 (5.36)	g/kg _{dw}
Total S	10.48 (2.74)	g/kg _{dw}

Table 4.5 Range of concentration in $\mu\text{g}/\text{kg}_{\text{dw}}$ of the analysed alkylphenol ethoxylates and related metabolites, abbreviation (*LOD* limit of detection in $\mu\text{g}/\text{kg}_{\text{dw}}$; *dw* dry weight)

Alkylphenol ethoxylates and related metabolites	Abbreviation	LOD	Concentration
4- <i>tert</i> -octylphenol monoethoxylate	OP1EO	1.86	24–2280
4- <i>tert</i> -octylphenol diethoxylate	OP2EO	0.75	6–11
Nonylphenol monoethoxylate	NP1EO	0.75	197–312
Nonylphenol diethoxylate	NP2EO	0.75	124–346
4- <i>n</i> -octylphenol	n-OP	0.75	26–41
4- <i>tert</i> -octylphenol	t-OP	3.7	<LOD-17
4-nonylphenol	NP	0.75	238–1166
4- <i>tert</i> -nonylphenol	t-NP	0.75	<LOD

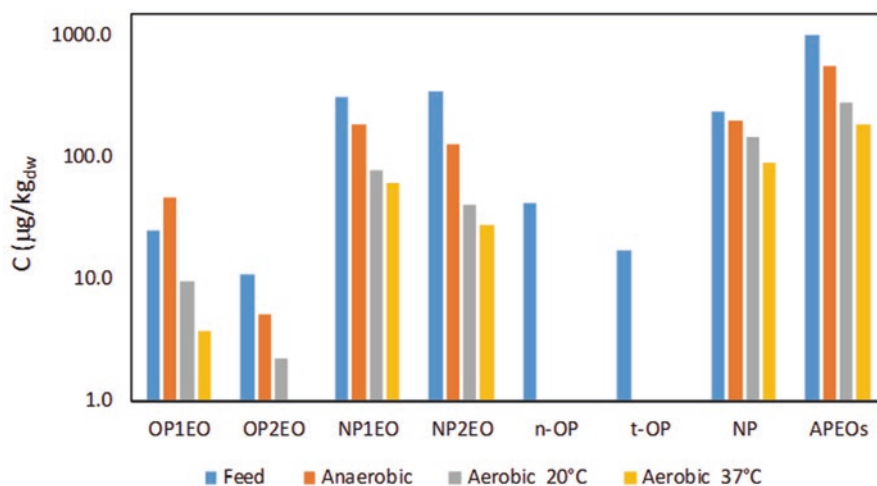


Fig. 4.10 Concentration pattern of alkylphenol ethoxylates and related metabolites in the fed sludge and in the digested sludge after the anaerobic and aerobic digestion for the two operating conditions: anaerobic mesophilic-aerobic at $T = 20\text{ }^{\circ}\text{C}$ (AA20) and anaerobic mesophilic-aerobic at $T = 37\text{ }^{\circ}\text{C}$ (AA37)

anaerobic mesophilic-aerobic at $T = 20\text{ }^{\circ}\text{C}$ (AA20) and anaerobic mesophilic-aerobic at $T = 37\text{ }^{\circ}\text{C}$ (AA37).

The overall performance of the sequential process showed very good results in terms of volatile solids reduction with an average removal of 40–43% in the anaerobic phase and an additional aerobic removal of 18–30% for AA20 and AA37 respectively. Extensive data on the performance parameters of the sequential digestion in terms of solids and micropollutant removal are available in Tomei et al. (2019). With respect to the removal of alkylphenol ethoxylates and their metabolites, Fig. 4.10 shows the concentration pattern in the feed sludge and in digested sludge after anaerobic and aerobic digestion for the two operating conditions AA20 and AA37, while Table 4.6 shows the corresponding removal efficiencies. Despite the high removal of volatile solid, no accumulation is observed in the digested sludge

Table 4.6 Removal efficiencies (%) in the anaerobic unit and in the aerobic units operated at 20 °C (anaerobic mesophilic-aerobic: AA20) and 37 °C (anaerobic mesophilic-aerobic: AA37)

Alkylphenol	Anaerobic	Aerobic (AA20)	Aerobic (AA37)
4- <i>tert</i> -octylphenol monoethoxylate	98.5	81.4	93.6
4- <i>tert</i> -octylphenol diethoxylate	41.9	60.8	87.5
Nonylphenol monoethoxylate	34.6	61.1	73.2
Nonylphenol diethoxylate	28.7	71.6	82.8
4- <i>n</i> -octylphenol	~100	–	–
4- <i>tert</i> -octylphenol	~100	–	–
4-nonylphenol	88.3	32.1	63.8
4- <i>tert</i> -nonylphenol	–	–	–

for all compounds, but a steady decrease in concentration is detected in all stages of digestion process. Post-aerobic treatment provides additional removals that are more evident at higher temperature.

Of the alkylphenol ethoxylates analysed, 4-*tert*-nonylphenol remained below the limit of detection during the sequential process, while 4-*n*-octylphenol and 4-*tert*-octylphenol were completely removed during the anaerobic step. High anaerobic removals of 98.5 and 88.3% were also detected for 4-*tert*-octylphenol monoethoxylate and 4-nonylphenol, respectively. For ethoxylates compounds, a progressive decrease in anaerobic removal according to the complexity of the molecule was observed, reaching values of 29% for nonylphenol diethoxylate. In respect to the single anaerobic digestion, the post-aerobic step at 20 °C allowed significant additional removal in all cases, with values ranging from 32 to 81% for 4-nonylphenol and 4-*tert*-octylphenol monoethoxylate, respectively. Aerobic removals were improved by operating the digester at 37 °C with values varying from 64% for the less degradable 4-nonylphenol to 94% for 4-*tert*-octylphenol monoethoxylate. In the aerobic phase, there is not clear evidence of the correlation between removal efficiency and molecule complexity for the two temperatures studied.

The results of this study showed that the post-aerobic digestion step (after the conventional anaerobic digestion process) could improve the removal of alkylphenol ethoxylates and their metabolites with better results at the higher aerobic temperature (37 °C vs. 20 °C). Alkylphenol ethoxylates are characterized by high lipophilicity, which leads to their marked accumulation in sewage sludge. The high removal obtained in the sludge matrix by the sequential digestion process has therefore demonstrated the feasibility of this treatment strategy to obtain “cleaner” sludge suitable for safe agricultural reuse.

4.5 Removal of Alkylphenols by Advanced Oxidation-Processes

4.5.1 Removal of Alkylphenols from Municipal Wastewater Using Ozone/Granular Activated Carbon

For downstream reduction in treatment plants, the proposed tertiary treatment for wastewater treatment is often the use of an ozonation step combined with an activated carbon adsorption step. Treatment using ozonation and adsorption on activated carbon is already used for the treatment of drinking water (ozone disinfection for the potabilization of surface or ground water). The oldest use of ozone is as a biocide in drinking water (it is currently known as one of the most efficient and fastest microbiocides). Ozone can also be used as the only technology or in combination with other processes with the aim, for example, of improving coagulation/flocculation, biodegradability, or as a primary or secondary treatment in association with biological wastewater treatment.

Ozonation and adsorption processes differ fundamentally in the way they work: with ozone (generated *on-site* because it is unstable and decomposes to elemental oxygen in a short amount of time after generation), the substances are transformed by chemical processes, whereas the substances are adsorbed onto the coals by mainly physical mechanisms. Ozone as a strong oxidant can also be used in wastewater treatment to remove organic pollutants that are refractory to other treatments (Rodríguez et al. 2008). However, although the number of works on the efficiency of ozone to eliminate organics is important, the use of ozone is less extended in wastewater treatments than in disinfection or in natural water treatments.

In a municipal wastewater treatment plant, the ozonation stage consists of using the oxidation capacities of ozone to destroy all organic molecules, including alkylphenols. It exploits the indirect radical reactions that take place during ozonation. In fact, the injection of ozone does not completely eliminate the pollutants present in the wastewater, but causes them to oxidize, which facilitates their further removal. Combined with activated carbon and/or sand filters, which traps the molecules that are refractory to ozonation, this treatment allows an overall organic pollutant reduction of 80%. The ozonation technology integrates well into existing municipal wastewater treatment plants and can be easily managed by its staff. Despite significant investments, this technology is already widely applied, e.g. in Switzerland and Germany. Indeed, the ozonation process is beginning to become widespread because it effectively removes many of the substances that threaten drinking water quality, fish reproduction and/or the survival of sensitive aquatic organisms, while having reasonable operating costs. Ozonation is also attractive for new developments, for example, in the water management, particularly in those where the objective is the reuse of wastewater. The important parameter of ozonation is the time period during which the ozone must remain in contact with the water in order to neutralize the pollutants. This time period is not without financial consequences (the faster the ozone treatment, the smaller the reactor). Ozone is an expensive oxidant and the

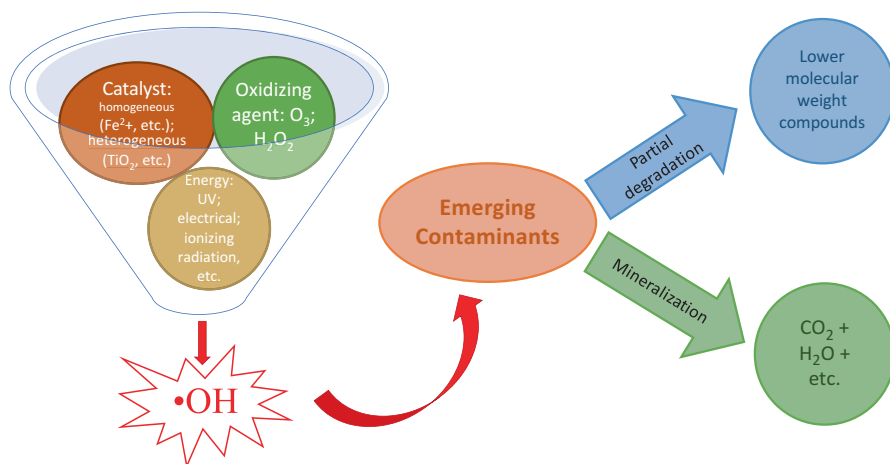


Fig. 4.11 Advanced oxidation processes for degradation of water emerging contaminants. (Source: Corina Bradu, Bucharest, Romania)

necessary doses in wastewater treatments are higher than in surface or ground water, thus increasing operational cost (Rodríguez et al. 2008).

Ozone is a strong oxidant and a virucide that is capable of reacting through well-known reaction mechanisms (it attacks electron rich structures in molecules), that depends on process parameters such as pH, presence of other substances and type/structure of the pollutants (Hoigne and Bader 1983; Sánchez-Polo et al. 2005). Ozonation may take place by the direct reaction of the ozone molecule with the target substance or by means of hydroxyl radicals produced during the decomposition of ozone in aqueous media. In practice, both direct and indirect reactions take place simultaneously, excepted when an oxidation process is specifically designed to enhance the concentration of hydroxyl radicals in a solution (case of an advanced oxidation process). Several significant works demonstrated that ozonation efficiently reduced the concentrations of many trace organic compounds present in secondary wastewater effluents, including pharmaceuticals and alkylphenols (Ternes et al. 2003; Huber et al. 2005; Hollender et al. 2009; Wert et al. 2009; Zucker et al. 2015) through direct and indirect oxidation reactions. Ribeiro et al. (2015) summarized data published over the last decade on the application of advanced oxidation processes for the elimination of priority substances and certain other pollutants defined in the European Directive. Advanced oxidation processes generate highly oxidizing and non-selective species such as hydroxyl radical, being particularly interesting for the treatment of effluents containing emerging pollutants (Fig. 4.11).

The application of the ozonation process to improve the biodegradability of alkylphenol ethoxylates began in the late 1970s (Narkis et al. 1985). Although ozonation itself reduced chemical oxygen demand by only 39% and total organic carbon by 16%, it significantly improved the biodegradability of nonylphenol

ethoxylates by altering their molecular structure. The elimination of chemical oxygen demand was as high as 70% and the removal of total organic carbon was 62.5% by biodegradation after the ozonation process, while the reduction without ozonation was 25% of chemical oxygen demand and 23% of total organic carbon. The optimum pH for the degradation of alkylphenol ethoxylates by ozone was 9 (indirect radical reactions favored), and it appears that the primary attack takes place on the polyethoxylate chain and not the aromatic ring.

Ning et al. (2007a, b) showed that the ozonation process was an appropriate tool for the degradation of nonylphenol and octylphenol. They investigated the degradation of these two alkylphenols in an acidic environment, i.e. a direct reaction of ozone. Studied contaminants were relatively easily degraded by ozonolysis. Based on the results of the study on the reaction mechanism of the nonylphenol oxidation with ozone, it is assumed that the aliphatic chain of the alkylphenols no longer has a significant effect on the behavior of these compounds during ozonation. The primary product is hydroxyl-alkylphenol, which is formed by attacking the aromatic ring in the ortho position with ozone and then by the addition of hydroxyl groups. Based on the reaction mechanism study, the initial product of ozonation appears to be hydroxyl alkylphenol. Kim et al. (2005b) previously reported that the dominant ozonation products of nonylphenol were acetaldehyde and formaldehyde.

Zhang et al. (2008) also studied the degradation of nonylphenol and octylphenol in aqueous solutions containing acetonitrile to improve the solubility of alkylphenols by ozone. The authors conducted experiments to test the effects of initial pH, alkylphenol concentrations and ozone dosage on removal efficiency. Complete removal of nonylphenol and octylphenol was obtained after 6 min of ozonation at pH 9. Experiments at pH 6.5 showed that the amount of ozone required for degradation is higher when the degradation efficiency of nonylphenol was nearly 42% with an ozone dosage of 0.13 mg/min, whereas with an ozone dosage nearly three times higher, the degradation efficiency increased to 96%. It was concluded that the higher the initial alkylphenol concentration, the lower the degradation efficiency of alkylphenol.

Baig et al. (2008) examined the matrix effect of wastewater during ozonation of octylphenol and nonylphenol. The data obtained indicated that the wastewater matrix significantly affected the ozonation kinetics, but did not change the corresponding reactivity scale. The dose of ozone required for complete degradation of these substances was increased, but a usual dose of 12 mg/L was sufficient for sufficient degradation. The ozonation process proved to be an effective solution to treat secondary waste water containing the mentioned oestrogenic active substances.

The study by Bertanza et al. (2010) on the removal of nonylphenol from wastewater treatment plants showed that these conventional systems cannot achieve the very low concentrations required, and therefore additional treatment such as ozonation was necessary. The authors carried out experiments with wastewater from an Italian wastewater treatment plant in Verona and concluded, that ozonation was an economically viable solution as a tertiary step and a promising technology to reduce pollutants emissions. Similar conclusion was reported by Schaar et al. (2010) and Ibáñez et al. (2013). Schaar et al. (2010) reported a significant reduction in toxicity

and pollutant emissions at the outlet of an actual wastewater treatment plant by ozonation. Grandclement et al. (2017) considered promising hybrid biological processes to remove pollutant as well as a combination of biological and physicochemical or chemical processes.

In Switzerland, a new law to reduce the discharge of pollutants from wastewater treatment plants came into force in 2016 to protect ecosystems and sources of drinking water (Böhler et al. 2017; Bourgin et al. 2018). The Neugut wastewater treatment plant (equivalent to 150,000 people, Dübendorf) was the first wastewater treatment plant in Switzerland to implement long-term ozone treatment. The following treatment steps are used: mechanical treatment with preliminary clarification, biological treatment, ozonation, and sand filtration with possible post-precipitation. Sewage sludge is then treated by mesophilic anaerobic digestion, dewatered and transported to an incineration plant. Among filtration methods, the most effective is sand filtration which removes dissolved organic carbon, assimilable organic carbon and total suspended solids. However, filtration with fresh activated carbon is a better treatment as finishing step after ozonation, resulting in a significant reduction of organic compounds (Bourgin et al. 2018). Monitoring of 550 substances including alkylphenols confirmed that an average reduction of >80% (up to >84% for a shortlist of 12 indicator substances established by the Swiss Federal Office for the Environment which requires an elimination performance of 80% for these substances) was achieved through a combined advanced treatment. The process uses a low ozone concentration of 3.5 mg/L, which is sufficient to effectively remove emerging substances and meet regulatory requirements, while also keeping operating costs low. After ozonation (the system is installed in the filtration reactor), additional filtration treatment is necessary to avoid possible negative ecotoxicological effects due to oxidation by-products (e.g. bromate, nitrosamines, metabolites). Positive effects of ozone treatment have indeed been demonstrated by *in vivo* and *in vitro* bioassays. The authors concluded that ozonation and activated carbon adsorption is a recommended technology that lead cost-efficiently to a significant abatement of the pollutant load and toxicity.

So, it has been proven that the removal of nonylphenol from wastewater could be improved by adding supplementary steps such as activated carbon filtration, ultraviolet treatment and ozonation to existing treatment processes (Johnson et al. 2005). Attention is paid to these potential solutions, although these could be expensive and did not provide always a final solution due to the accumulation of pollutants in the sludge (Jones et al. 2007). However, additional ozonation of surplus sludge could also results in increased removal of endocrine disrupting compounds absorbed in the sludge (Shao et al. 2005; Qiang et al. 2013). Qiang et al. (2013) reported that ozonation was an effective means for excess sludge reduction. Indeed, sludge-bound pollutants were effectively removed during sludge ozonation. Ozone treatment was suitable for the degradation of endocrine disrupting compounds, such as 4-nonylphenol, estrone, estriol, 17 α -ethynylestradiol, and bisphenol A. Results indicated that the emerging substances present in activated sludge could be effectively removed by ozone even though the apparent rate constants in sludge were 3–4

orders of magnitude lower than those in water. This technology was considered as environmentally friendly.

A drawback of ozonation is the insufficient mineralization of pollutants. However, total mineralization with ozone is very expensive. Thus, newly developed processes use ozone only for the removal of toxic compounds and/or partial oxidation of resistant organic pollutants from wastewater. Controlled ozonation processes which are applied can inactivate inhibitory compounds in biological wastewater treatment and improve the biodegradability of recalcitrant organic matter by modifying its chemical structure. The extent of this partial oxidation should only be sufficient to facilitate subsequent biodegradation of the transformed organic matter. The combination of ozonation with homogeneous or heterogeneous catalysis which can increase the production of hydroxyl radicals can be one of the solutions. Another possibility is to use ozone in combination with other techniques such as ultrasonic/UV radiation, hydrogen peroxide, or other hybrid methods (Fujita et al. 2004; Gogate and Pandit 2004; Johnson et al. 2005; Li et al. 2006; Jones et al. 2007; Rodríguez et al. 2008; Alvarez et al. 2006; Poyatos et al. 2010; Vatankhah et al. 2019). Many examples can be found in two comprehensive reviews published by Rodríguez et al. (2008) and by Poyatos et al. (2010).

The performances of O_3 - H_2O_2 couple on the biodegradability of nonylphenol ethoxylates was investigated by Adams et al. (1996). The results showed that these substances were oxidized to shorter polyethoxylate chains, although biodegradability was not improved with a low dosage of ozone and hydrogen peroxide. In order to achieve a reduction of at least 80% of dissolved organic carbon, 7 mg of absorbed ozone per mg of nonylphenol ethoxylates was required. The possibility of the formation of toxic oxidation byproducts was not excluded but was not explicitly investigated.

The study on oxidation kinetics of nonylphenols and nonylphenol ethoxylates carried out by Hyunook et al. (2007) showed that the degradation efficiency increased significantly when ozone and hydrogen peroxide were combined. The authors demonstrated that nonylphenol and its derivatives can be effectively oxidized over a pH range of 5 to 9. At pH 7, the efficiency was even greater than 90%.

Wastewater at the outlet of the municipal wastewater treatment plant has been treated using several ozone-based processes by Rivas et al. (2009). The application of ozone as the sole oxidizing agent was capable of halving the initial chemical oxygen demand (35 mg/L at a flow rate of 40 L/h) with a degree of mineralization of approximately 40%. The ozone/hydrogen peroxide system significantly improves the performance of the oxidation process, increasing the degree of mineralization up to 70% (35 mg/L ozone at a flow rate of 40 L/h in the presence of 0.01 M hydrogen peroxide). The simultaneous application of ozone and UV radiation showed beneficial effects on both the chemical oxygen demand removal rate and total organic carbon conversion compared to ozone alone. However, compared to the ozonation alone, no improvement was observed for combination of ozone with commercial activated carbon. On the contrary, Li et al. (2006) showed that the presence of granular activated carbon during ozonation (ozone/activated carbon) improved oxidation efficiency through increased conversion of ozone to hydroxyl radicals.

Alvarez et al. (2006) studied the effect of ozone/activated carbon at pilot-scale on the removal of pollutants from municipal wastewater. The results showed that the simultaneous use of ozone and granular activated carbon initially improved the removal of ozone-refractory pollutants. However, the promoting effect of ozone and activated carbon decreased over time. The technology uses the advantage of the high adsorption capacity of activated carbon for pollutant removal (Rivera-Utrilla et al. 2011). Activated carbon also serves as an initiator of ozone decomposition (a role that can also occur with other types of catalysts), which increases the formation of hydroxyl radicals (Hoigne 1998; Alvarez et al. 2006). The mechanism of this catalytic ozonation is not completely elucidated (Jans and Hoigne 1998; Sánchez-Polo et al. 2005; Alvarez et al. 2006). Jans and Hoigne (1998) reported that the reaction of ozone with activated carbon was a catalytic reaction. However, the work of Sánchez-Polo et al. (2005) showed that activated carbon acted more like a classical initiator during ozonation. The overall efficiency of the ozone/activated carbon depended largely on the characteristics of the activated carbon and the wastewater matrix.

The role of carbon as a catalyst, promoter or initiator is still a subject of debate. Vatankhah et al. (2019) investigated the effectiveness of simultaneous ozone and granular activated carbon in removing environmentally relevant substances from wastewater. In contrast to previous publications, which provided the results of short-term experiments (1–3 h), this work focused on evaluating the robustness of ozone/granular activated carbon in a long-term experiment (up to 20 h). The results showed that this combination improved the reduction of some pollutants compared to ozone in only 20 h of operation. However, its overall efficiency decreased significantly after prolonged exposure to ozone, indicating that granular activated carbon did not contribute as a catalyst. The use of ozone initially resulted in an increase in the BET surface area of the granular activated carbon (mainly micropores), which improved the adsorptive removal of the pollutants studied. However, exposure to ozone eventually caused structural damage to the surface of the granular activated carbon leading to a reduction of the BET surface area in the later stages and to a significant decrease of overall efficiency.

An alternative ozonation process using zeolite-based adsorbents has been proposed by Fujita et al. (2004). Organic pollutants and ozone can be adsorbed in the zeolite micropores. As a result, concentrations in micropores become much higher than those in the mass phase and the apparent reaction rate may be increased.

Derco et al. (2015, 2017) studied the removal of nonylphenol, octylphenol and alkylphenol ethoxylates from industrial and municipal wastewater treatment. The main objective of the work was to investigate an alternative wastewater treatment process in the event of a production expansion and a consequent increase in alkylphenol releases. In this purpose, the capacity of the municipal wastewater treatment plant (which include secondary treatment) located closest to the industrial facility releasing alkylphenols was assessed. And ozonation and combined ozone/granular activated carbon processes were investigated as possible tertiary treatment step for the municipal wastewater treatment plant, or as end-of-pipe industrial wastewater treatment. It must be noted that before discharge to municipal sewers, industrial

wastewater containing alkylphenols is subject of a pre-treated by coagulation with FeCl_3 and zeolite adsorption. Higher efficiencies were obtained when the ozonation is applied in industrial wastewater treatment (before discharge to municipal sewers), with target pollutants conversions greater than 90% for 2 h treatment time, except for 4-*tert*-octylphenol. The highest conversion, 98% was obtained for octylphenol ethoxylates. However, a great variability in ozonation performance was observed for both industrial and municipal wastewaters, depending on sampling time. For example, nonylphenol ethoxylates showed the highest variability of the removal efficiency values (3.0–92.7%). Significantly higher volumetric ozone consumption was observed for industrial treatment compared to ozonation of municipal wastewater due to higher organic pollution. Negligible differences were observed for the removal of nonylphenol and nonylphenol ethoxylates when comparing ozone and ozone/granular activated carbon processes carried out under the same conditions. On the other hand, a significantly higher removal/degradation rate of octylphenol ethoxylates was observed with the ozone/granular activated carbon process compared to the ozone alone. A lower toxicity impact of ozonation treatment intermediates and products on *Vibrio fischeri* was measured compared to the ozone/granular activated carbon. It worth mentioning that residual concentrations of nonylphenol and nonylphenol ethoxylate in all analyzed samples from municipal wastewater treatment plants complied with the limits of the environmental quality standards (Directive 2008/105/EC).

Besides activated carbon, Mn and Fe modified zeolites have been tested in the oxidative degradation of alkylphenols in industrial wastewater (Urminska et al. 2018). As can be seen from the data presented in Fig. 4.12, both materials improved the ozonation efficiency in terms of target pollutants removal and dissolved organic carbon (DOC) and chemical oxygen demand (COD) abatement. However, the performance of the oxidation process with these two modified zeolites was lower than

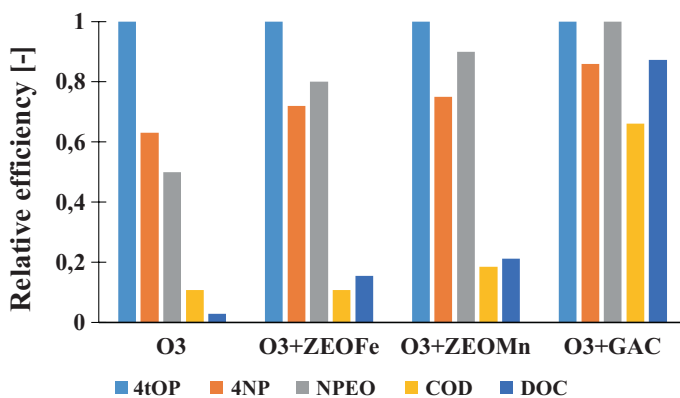


Fig. 4.12 Efficiencies of several applied advanced oxidation processes (*O3* ozone, *ZEO* zeolite, *ZEOFe* Fe-modified zeolite, *ZEOMn* Mn-modified zeolite, *GAC* granular activated carbon, *4tOP* 4-*tert*-octylphenol, *4NP* 4-nonylphenol, *NPEO* nonylphenol polyethoxylates, *COD* chemical oxygen demand, *DOC* dissolved organic carbon)

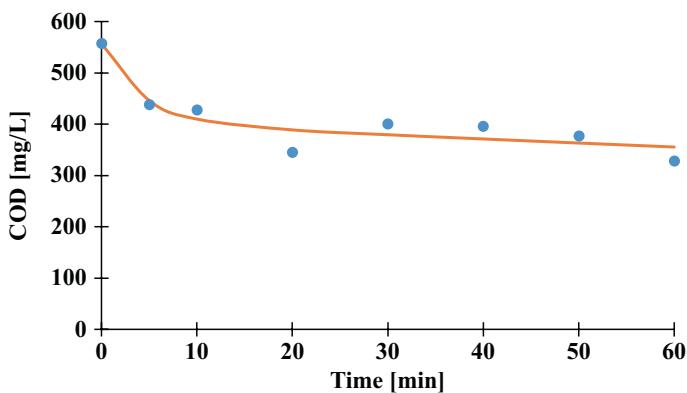


Fig. 4.13 Removal of chemical oxygen demand in raw industrial wastewater by ozone/granular activated carbon process

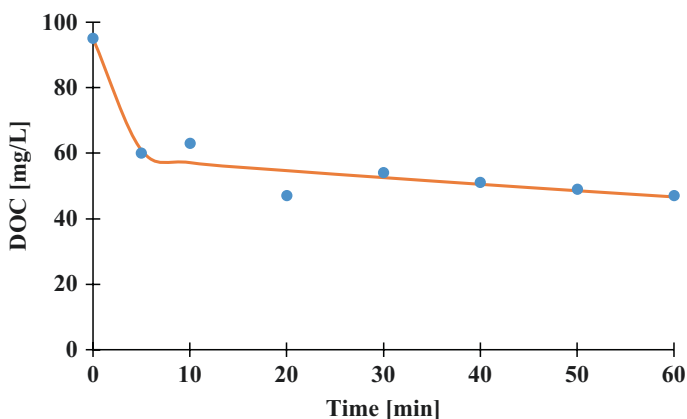


Fig. 4.14 Removal of dissolved organic carbon in raw industrial wastewater by ozone/granular activated carbon process

that of activated carbon assisted ozonation. For better comparison of the activity and selectivity of the proposed materials in alkylphenols removal, an assessment of the adsorption and oxidation contributions to the overall process must be done.

The highest chemical oxygen demand decrease and removal of dissolved organic carbon were observed during the first 5–10 min of the ozone/granular activated carbon process (Figs. 4.13 and 4.14). A higher proportion of readily oxidizable organic matter (0.73) was calculated for chemical oxygen demand compared to 0.62 for dissolved organic carbon. These results demonstrated that ozonation in combination with activated carbons is a feasible method for oxidation of alkylphenols, and also effective for chemical oxygen demand and total organic carbon reduction.

The survey of literature shows that the catalytic mechanism of activated carbon ozonation is not yet clear, but most of the results suggest that the role played by the

carbon is essentially to promote the decomposition of ozone with a subsequent increase in the production of radicals. Consequently, activated carbon would behave as an initiator of the radical-type chain reaction that transforms ozone into hydroxyl radicals. Ozonation on other materials such as supported metals has been less studied for the treatment of real industrial or municipal wastewaters but is a research topic in full development.

So far, only ozone technologies coupled with carbon adsorption and/or filtration steps have been widely used in drinking water treatment plants, e.g. in France, to treat residual organic pollution and pathogens, in order to meet regulatory requirements. This is also a growing market for wastewater treatment, particularly in Switzerland and Germany, e.g. to treat pharmaceuticals, hormones and industrial products (alkylphenols). Indeed, ozone/carbon or ozone/sand coupling is both technologically simple to implement on an existing treatment plant, effective in reducing the pollutant load and pathogens, and economically viable (relatively low operating and maintenance costs). Nevertheless, other so-called advanced oxidation methods (sonochemical methods, photolysis, photocatalysis, electrochemistry, Fenton process) or membrane filtration (the price of membranes has decreased significantly, as have the maintenance costs of this technology) are under development and could compete with the ozone/activated carbon or ozone/sand coupling. In all cases, pilot experiments are needed to demonstrate not only the chemical efficiency of the integrated processes but also the economic viability.

4.5.2 Electrochemical Degradation of Alkylphenols

A viable alternative for the degradation of alkylphenols or their polyethoxylates in wastewater and other environmental samples are electrochemical techniques. These can be broadly divided into classical, e.g. electrocoagulation, electrofiltration, and also electrooxidation. The latter, however, is nowadays more often classified among electrochemical advanced oxidation processes, mainly because of the use of modern electrodes. Other modern electrochemical approaches are electro-Fenton, photo-electrooxidation, and combination of electrodegradation with ozonation and other chemical oxidants. In the following overview, the research in this field is presented, mainly for the last 10 years. The detailed parameters of the electrochemical treatments are given in Table 4.7, while general descriptions and comparison of treatments are given below.

As one of the classical electrochemical treatment options, electrocoagulation is nowadays less often used for the removal of emerging contaminants. Nevertheless, it was applied to remove nonylphenol polyethoxylate (9 ethoxylate units) from synthetic solutions and hospital wastewater (Henriques et al. 2012). The electrochemical cell consisted of two aluminum electrodes with a surface of 2400 mm². NaCl was added to the solution as a supporting electrolyte. The removal of the pollutant was performed at 1.5 A and 60 °C and was monitored by high-performance liquid chromatography with fluorescence detection, while the transformation products

Table 4.7 Review of electrochemical treatments of alkylphenols and alkylphenol polyethoxylates (BDD: boron-doped diamond; COD chemical oxygen demand, DT duration/time of experiment, *dw* dry weight, *NPnEOs* nonylphenol ethoxylate, *NP* nonylphenol, *OP* octylphenol, *SCE* saturated calomel electrode, *SS* stainless steel, *TOC* total organic carbon, *WW* wastewater, *T* temperature, *RT* room temperature)

Sample characteristic	Process	Electrochemical reactor		Electrodes/Operational parameters	Degradation efficiency	Reference
		Configuration	V (L)			
40 mg/L NP9EO (9 ethoxylate units) in 2.8 g/L NaCl aq. sol. and real sample from hospital WW	Electrocoagulation	Undivided cell Batch process	0.6	Galvanostatic mode; cathode: Al; anode: Al; <i>T</i> = 60 °C; electric current: 1.5 A; DT: 30 min	NP9EO in aqueous solution: 95% at pH 5.0 NP9EOs in sample: 89%	Henriques et al. (2012)
21 µg/L NP in WW from municipal WW treatment plant	Electrocoagulation	Undivided cell Batch recirculation process	0.4875	Galvanostatic mode; cathode: Al; anode: Al; electric current: 9 to 15.5 A; electric potential: 85 to 98 V	NP: 98% at hydraulic retention time: 2 min/L; DT: 20 min	Cook et al. (2016)
500 mg/L NPnEO in 0.1 M NH ₄ OH / 0.05 M HCl solution	Electrochemical oxidation	Undivided cell Batch recirculation process	NA	Galvanostatic mode; cathode: SS; anode: BDD; current density: 20, 30, and 40 mA/cm ² ; flow rate: 12.6 L/min; temperature: 20 ± 2 °C; pH: 9.25	TOC: 90%; COD: ≈ 88% within 8 h at 40 mA/cm ²	Armijos-Alcocer et al. (2017)
50 mg/L NP10EO in 0.035 M Na ₂ SO ₄ solution and NP10EO in real WW sample	Electrochemical oxidation	Undivided cell Batch process	1	Galvanostatic mode; cathode: BDD; Cu and Fe; anode: BDD; current density: 3, 6 and 10 mA/cm ²	NP10EO in aqueous solution: COD: 92.2%, TOC: 45.6%; at pH 2.0 and 3 mA/cm ² , BDD - cu electrode arrang.; DT: 240 min NP10EO in WW sample: COD: 44.1%, TOC: 26.5%; at pH 4.5 and 6 mA/cm ² , BDD electrode arrangement; DT: 780 min	Vences-Benitez et al. (2017)

100 mg/L NPnEO in 0.5 g/L Na ₂ SO ₄ or NaCl solution 115 mg/L NP10EO in real WW	Electrochemical oxidation	Undivided cell Continuous process	2.5	Galvanostatic mode; cathode: SS; anode: BDD; flow rate: 2.5 L/min; current density: 62.5, 125, 187.5, 250, and 312.5 A/m ² ; pH: 3.5, 5.0, 6.5, 8.0, and 9.5; DT: 30, 45, 60, 75, 90, 135, 180, and 225 min.	NPnEO in 0.5 g/L NaCl solution: 85.3%; COD: 92.5%; TOC: 94.2%; at pH 8.0 and 250 A/m ² ; DT: 45 min NP10EO in real WW sample using NaCl as supporting electrolyte: 90.8%; COD: 93.0%; TOC: 95.0%; at pH 8.0 and 250 A/m ² ; DT: 45 min	Sivri et al. (2020)
50 mg/L NP in 0.05 M H ₂ SO ₄	Coupling of electrochemical oxidation and oxidation by H ₂ O ₂	Undivided cell Batch and batch recirculation processes	4	Galvanostatic mode; cathode: SS; anode: BDD; pH: 3.0; flow rate: 7, 14, and 22 L/min; concentration of H ₂ O ₂ : 0.5, 1.0 and 1.5 mL/L; current density: 30 mA/cm ²	NP: 97.6%; COD: 98%; TOC: 98%; at flow rate 7 L/min and 1.0 mL/L H ₂ O ₂ ; DT: 120 min	Rodriguez-Pena et al. (2019)
500 mg/L NPnEO in 0.2 M H ₂ SO ₄	Mediated electrochemical oxidation	Undivided cell Batch process	NA	Potentiostatic mode; working electrode: carbon paste electrode (home made); counter electrode: Pt; reference electrode: Ag/AgCl; potential: 6 V; mediator (Ce(III)) concentration: 0.05 to 0.02 M	NPnEO: 84.96% at 0.015 M Ce(III) NPnEO: 87.95% in the absence of Ce(III) ions; DT: 90 min	Setyanto et al. (2018)

(continued)

Table 4.7 (continued)

Sample characteristic	Process	Electrochemical reactor		Electrodes/Operational parameters	Degradation efficiency	Reference
		Configuration	V (L)			
260–2400 µg/L NPnEO in laundry WW	Electrochemical oxidation and electrocoagulation	Undivided cell Batch and batch recirculation processes	0.5 and 2.45	Galvanostatic mode; RT; electrocoagulation: graphite or SS cathode; Fe or Al anode; reactor configuration: current density 20, 40, and 80 mA/cm ² ; pH: 6, 8, and 9–10; DT: 15 to 120 min; electrochemical oxidation: graphite, vitreous carbon or Ti/Pt cathode; BDD, Ti/Pt, Ti/IrO ₂ anode; current intensity: 4, 6, 8, 10, and 12 A; pH: 6, 8, and 9–10; flow rate: 0.3 to 0.4 L/min; DT: 15 to 120 min	NPnEO: ≈ 80%; COD: ≈ 75% by electrocoagulation of ultrafiltration concentrate at 40 mA/cm ² and bipolar configuration for 60 min (anode: Fe; cathode: graphite) NPnEO: ≈ 90%; COD: 99% by electrooxidation of ultrafiltration filtrate (3 g/L Na ₂ SO ₄ solution) at 12 A for 120 min (anode: BDD; cathode: graphite)	Khosravanipour Mostafazadeh et al. (2019)
4.5 µmol NP in 0.1 M Na ₂ SO ₄	Electrochemical oxidation	Undivided cell Batch process	0.05	Potentiostatic mode; working electrode: molecular imprinted high-index facet SnO ₂ (MI-SnO ₂ _{HIP}) electrode; counter electrode: Pt; reference electrode: SCE; scan rate: 100 mV/s; T = 25 °C	NP: 95% at electrode voltage 1.8 V; DT: 480 min	Niu et al. (2020)
3975 ng/g dw of NP in sewage sludge which contains more than 98% of water and less than 2% of solids	Electrochemical oxidation	Undivided cell Batch process	0.6	Galvanostatic mode; cathode: BDD; anode: BDD; current density: 10, 20, and 40 mA/cm ² ; pH: 3.0, 5.0, and 7.0	NP: 89%; total solids: 14%; COD: 27%; at pH 3.0 and 40 mA/cm ² under stirring conditions; DT: 60 min	Barrios et al. (2015)

1583 ng/L NP (including isomers) from municipal sludge which contains more than 99% of water	Electrochemical oxidation	Undivided cell Batch recirculation process	1	Galvanostatic mode; cathode: BDD; anode: BDD; flow rate: 2.8 L/min; $T = 25\text{ }^{\circ}\text{C}$	NP: 69%; at current density 28.5 mA/cm ² ; DT: 180 min	Barrios et al. (2016)
937 ± 46 ng/g dw of NP in wastewater sludge	Coupling of electrochemical oxidation and ozonation	Undivided cell Batch process	0.9	Galvanostatic mode; cathode: BDD; anode: BDD; current density: 5, 10, and 20 mA/cm ² ; pH: 3.0, 5.0, and 7.5; ozone: 5.2 g/L	NP: 68%; COD: 62% at pH 7.5 and current density of 20 mA/cm ² ; DT: 60 min	de Leon-Condés et al. (2017)
50 mg/L NP in 0.05 M H ₂ SO ₄	Coupling of electrochemical oxidation and ozonation	Undivided cell Batch and batch recirculation processes	0.25	Galvanostatic mode; cathode: SS; anode: BDD; current density: 30 mA/cm ² ; pH: 7.0; flow rate: 12.6 L/min; concentration of O ₃ : 5 ± 0.5 mg/L	COD: ≈ 91%; TOC: ≈ 91%; DT: 120 min (ozone 30 min, and electrochemical 90 min)	Barrera-Díaz et al. (2018)
alkylphenols in landfill leachate	Electro-Fenton and electrochemical oxidation	Undivided cell Batch process	0.25	Galvanostatic mode; cathode: carbon felt (14x5x0.5 cm); anode: BDD (4x6 cm); $T = 23 \pm 2\text{ }^{\circ}\text{C}$; current intensity: 500 or 1000 mA	Electrochemical oxidation at pH 8.05; 4-NP monoethoxylate: 100%; 4-NP diethoxylate: 85%; 4-NP: 99.5%; 4-(<i>tert</i> -octyl)phenol: 99.6% Electro-Fenton at pH 3.0: 4-NP monoethoxylate: 100%; 4-NP diethoxylate: 96.1%; 4-NP: 99.7%; 4-(<i>tert</i> -octyl)phenol: 99.9%	Oturán et al. (2015)

(continued)

Table 4.7 (continued)

Sample characteristic	Process	Electrochemical reactor		Electrodes/Operational parameters	Degradation efficiency	Reference
		Configuration	V (L)			
51 mg/L NPnEO in 0.25 mg/L Na ₂ SO ₄	Photo-assisted electrochemical oxidation	Undivided cell Batch recirculation process	3	Galvanostatic mode; cathode: Ti/TiO ₂ ; anode: DSA (Ti/Ru _{30%} Ti _{70%} O ₂); flow rate: 1 L/min; light source: high-pressure commercial mercury vapor lamp, irradiation intensity of 125 and 250 W; current density: 5.0 and 10.0 mA/cm ² ; initial toxicity of sample (CL(I ₅₀ ;48 h) = 6.25%	TOC: 83%; toxicity (CL(I ₅₀ ;48 h) = 70.71%; at 10 mA/cm ² , pH 5.63 and 250 W; DT: 240 min	da Silva et al. (2015a)
51 mg/L NPnEO in 0.25 mg/L Na ₂ SO ₄	Electrochemical oxidation and photo-assisted electrochemical oxidation	Undivided cell Batch recirculation process	3	Galvanostatic mode; cathode: Ti/TiO ₂ ; anode: DSA (Ti/Ru _{30%} Ti _{70%} O ₂); flow rate: 1 L/min; light source: high-pressure commercial mercury vapor lamp, irradiation intensity of 125 and 250 W; current density: 5.0 and 10.0 mA/cm ²	TOC: 82.7%; at 10 mA/cm ² , pH 5.63 and 250 W; DT: 240 min	da Silva et al. (2015b)
1 mg/L NP	Coupling of electroresorption and photo-electrocatalysis	Undivided cell Batch process	NA	Potentiostatic mode; working electrode: composite Bi ₂ WO ₆ /carbon aerogel electrode; counter electrode: NA; reference electrode: NA; potential of electroresorption: 0.6 V; light source: simulated sunlight with irradiation intensity of 500 mW/cm ² ; temperature: 25 °C; pH: 12	NP: 99.36%; TOC: 66.1%; DT: 480 min	Fan et al. (2018)

10 mg/L NP, OP, and heptylphenol in 0.1 M Na ₂ SO ₄ solution	Coupling of electroosorption and photo-electrocatalysis	Undivided cell Batch process	0.1	Potentiostatic mode; working electrode: modified-TiO ₂ electrode; counter electrode: Pt; reference electrode: SCE; potential of electroosorption: 0.6 V; light source: Xe lamp, irradi., intensity of 300 mW/cm ² ; due to poor solubility of alkyl phenol, 10 vol% acetonitrile was added to facilitate the dissolution; T: 25 ± 2 °C	NP: 93.9%; OP: 77.9%; heptylphenol: 82.7%; DT: 300 min	Fan et al. (2019)
5 mg/L 4-NP	Photocatalytic or photoelectrocatalytic degradation	Undivided cell Batch process		Galvanostatic mode; cathode: Pt foil; anode: WO ₃ /TiO ₂ and TiO ₂ nanotube array; light source: Xe lamp, irradi. Intensity of 36.5 mW/cm ² ; RT	NP: 92.3% at photoelectrocatalytic process with WO ₃ /TiO ₂ photoelectrode; DT: 120 min	Xin et al. (2017)
100 µg/L 4- <i>n</i> -NP in 1 mM Na ₂ SO ₄ solution	Electroosorption	Undivided cell Batch process	0.02	Potentiostatic mode; working electrode: multi-walled carbon nanotube; counter electrode: Pt; reference electrode: SCE; potential of electroosorption: -0.6, -0.3, 0.3, and 0.6 V; T = 25 °C; pH: Nearly neutral	4- <i>n</i> -NP: 98.6% at -0.6 V; DT: 300 min	Li et al. (2014b)
150 mg/L NP for carbon nanotube saturation	Electrokinetic process (coupling of electromigration and electrooxidation)	Divided cell Batch process	NA	Galvanostatic mode; cathode: SS; anode: carbon, Ti, and three binary metallic electrodes (MnO ₂ /Ti, RuO ₂ /Ti, PbO ₂ /Ti); potential gradient: 2 V/cm; DT: 480 min	NP: 69% at RuO ₂ /Ti anode in 0.1 M NaCl processing fluid	Yuan et al. (2011)

(continued)

Table 4.7 (continued)

Sample characteristic	Process	Electrochemical reactor		Electrodes/Operational parameters	Degradation efficiency	Reference
		Configuration	V (L)			
150 mg/L NP for carbon nanotube saturation	Electrokinetic process (coupling of electromigration and electrooxidation)	Divided cell Batch process	NA	Galvanostatic mode; cathode: SS; anode: carbon and three binary metallic electrodes (PbO ₂ /Ti, PbO ₂ -co/Ti, and PbO ₂ -SnO ₂ + Sb ₂ O ₃ /Ti); potential gradient: 2 V/cm; DT: 480 min	NP: 80% at PbO ₂ -co/Ti anode in 0.1 M NaCl processing fluid	Yuan et al. (2012)
150 mg/L NP for carbon nanotube saturation	Electrochemical oxidation	Divided cell Batch process	NA	Galvanostatic mode; cathode: SS; anode: carbon, Ti and RuO ₂ /Ti; potential gradient: 2 V/cm; DT: 480 min	NP: 69% at RuO ₂ /Ti anode in 0.1 M NaCl processing fluid	Dai et al. (2017)
NP and OP in soil	Electrokinetic remediation	Divided cell Batch process	NA	Galvanostatic; cathode: Ti/Pt; anode: Ti/Pt; current intensity: 0, 10, and 20 mA	NP: 54%; OP: 74%; current intensity: 20 mA; DT: 54 h	Guedes et al. (2014)
NP in soil	Electrokinetic remediation	Divided cell Batch process	NA	Galvanostatic mode; cathode: NA; anode: NA; potential gradient: 1 V/cm; DT: 5 days	NP: 69% in 30% methanol processing fluid	Huang et al. (2015)

were identified by liquid chromatography-mass spectrometry. Moreover, chemical oxygen demand and biodegradability (by manometric respirometry test) were measured. The removal followed a pseudo-first-order kinetics. After 30 min of treatment, 95% of the pollutant was removed from synthetic and 89% from hospital wastewater, although the chemical oxygen demand decreased in the latter only by 26%. Liquid chromatographic-mass spectrometric analysis revealed the formation of degradation products with shorter ethoxylate chain (1–2 units), alkylphenoxy ethoxyacetic acid, and alkylphenoxy acetic acid. The biodegradability test initially performed better in the treated solution, but after 28 days reached the same level as in the untreated solution, i.e. 32–36%. Therefore, Henriques et al. (2012) concluded that both treated and untreated samples are not readily biodegradable, probably because only partial degradation into transformation products occurred.

A more recent study on electrocoagulation was published by Cook et al. (2016). They applied an electrocoagulation approach using aluminum blades as electrodes for the removal of six endocrine-disrupting (xenoestrogenic) chemicals from spiked influent wastewater and tertiary-treated effluent from a communal wastewater treatment plant. The reaction cell consisted of nine aluminum blades with a total volume of 221.2 cm³ with appropriate connections to obtain two anodes and one cathode. At the anode, aluminum (III) ions were generated, while hydroxide ions were produced at the cathode. Precipitated Al(OH)₃ adsorbed organic pollutants present in wastewater which was percolated through the cell by the aid of a peristaltic pump. Several parameters were optimized: voltage range, electric current range, arrangement of electrodes, retention time of wastewater in the cell, and cleaning procedure for electrodes. The efficacy of the treatment was monitored by gas chromatographic-mass spectrometric analysis preceded by solid phase extraction and derivatization to trimethylsilyl derivatives. After 20 min of treatment at retention time of wastewater 2 min/L, the removal of nonylphenol was 81% in influent wastewater and as high as 98% in tertiary-treated effluent wastewater. In fact, nonylphenol showed the highest removal ratio of all the studied compounds, which included bisphenol A and estradiol analogues. The study demonstrated high removal efficiency for nonylphenol. However, there was no attempt to elucidate the mechanism of its removal or possible transformation products.

Advanced electrochemical oxidation is one of the most frequently applied electrochemical processes for removing pollutants from wastewater. Electrooxidation of nonylphenol ethoxylate was studied by Armijos-Alcocer et al. (2017). They employed a DiaClean® electrochemical cell which is characterized by superior performance in terms of mass transfer, current distribution, and hydrodynamics. The cell was equipped with boron-doped diamond electrode with the surface area of 70 cm² as anode and a stainless steel cathode of the same area, and was operated in a galvanostatic mode. Nonylphenol ethoxylate was added in an initial concentration of 500 mg/L and the solution was circulating in the cell by the aid of a peristaltic pump. The tested electrolyte was either an acetate buffer (0.5 M, pH 4.0) or an ammonia buffer (0.1 M NH₃ + 0.05 M HCl, pH 9.25). With the former, cyclic voltammetry showed that a cathodic reduction occurs as well, causing a regeneration of the pollutant. In alkaline media, the oxidation was irreversible, but it was

necessary to apply anodic potential above 1.0 V. It was concluded that both direct and indirect oxidation by hydroxyl radicals occurred. Authors also studied the effect of current density and electrolyte flow and determined the optimal conditions to be 40 mA/cm² and 12.6 L/min, respectively. The effectiveness of the treatment was monitored by measuring total organic carbon, chemical oxygen demand and absorbance of the solution at 200–500 nm. From the changes in UV spectra during the treatment, authors concluded that quinone and hydroquinone oxidation by-products were formed and then further degraded. Under optimal conditions, total organic carbon decreased by 90% after 8 h of treatment. Finally, Armijos-Alcocer et al. (2017) provided the operational cost analysis and concluded that electrochemical oxidation would be a feasible approach to remove nonylphenol ethoxylates from wastewater.

Electrooxidation of nonylphenol decaethoxylate was studied by Vences-Benitez et al. (2017) as well, both in aqueous solution and in textile industry wastewater. Three different electrode configurations were tested: boron-doped diamond anode combined with copper, iron, or boron-doped diamond cathode, and the supporting electrolyte was Na₂SO₄. Besides, the current density and pH of the solution were optimized as well. Total organic carbon, chemical and biochemical oxygen demand were monitored. Additionally, UV/Vis and IR spectra were taken before and after the treatment. Hydrogen peroxide concentration was also measured during the process. Cu and Fe cathodes were chosen because a small amount of the material was dissolved in an electrochemical system, resulting in a catalytic production of H₂O₂. In aqueous solutions, total organic carbon reduction (as a measure of mineralization) after 4 h was 39.7% with boron-doped diamond cathode, 45.6% with Cu cathode, and 31.8% with Fe cathode. Optimal current density was either 3 or 6 mA/cm², while pH differed between the systems used. For textile wastewater, total organic carbon decrease was 26.5% and 37% for boron doped diamond and Cu cathode, respectively, while the system with Fe cathode was less efficient because the dissolved iron reacted with hydroxide and phosphate ions. However, an interesting finding was that the biodegradability of the treated wastewater was decreased in all three systems, as evaluated from the biochemical to chemical oxygen demand ratio. Finally, Vences-Benitez et al. (2017) estimated the consumption and cost of the energy for the optimal treatment system.

Parameters of the electrooxidation process on boron-doped diamond anode were studied for the removal of nonylphenol ethoxylate from synthetic and real wastewater (Sivri et al. 2020). The cathode was made of stainless steel. Authors studied the effect of the supporting electrolyte (Na₂SO₄ or NaCl), initial pH, current density, and electrolysis time by response surface methodology. They monitored total organic carbon, chemical oxygen demand and concentration of the pollutant, the latter by ready-to-use-kit. The optimal treatment conditions were found to be initial pH 8, current density 250 A/m², and treatment time 45 min. In a NaCl electrolyte, the process was more efficient and fitted well to the zero-order kinetic model compared to the first-order model for Na₂SO₄. However, Na₂SO₄ was a better choice for real wastewater, presumably because this sample already contained a significant concentration of chloride ions. In synthetic wastewater, 85.3% of nonylphenol

ethoxylate was removed under optimal conditions, while the other two monitored parameters diminished by 92–94%. Similar removal percentages were achieved in real spiked wastewater. Sivri et al. (2020) concluded that NaCl was a better choice for the supporting electrolyte because of the lower cost of treatment. However, no transformation products were monitored in this study.

Mediated electrochemical oxidation combines electrooxidation with the addition of a chemical oxidant. Rodriguez-Pena et al. (2019) applied electrooxidation on boron-doped diamond anode either alone or combined with oxidation by H_2O_2 for the removal of nonylphenol from simulated wastewater. A DiaClean® reactor was used with boron-doped diamond electrode on silicon as anode/working electrode and a stainless steel cathode. The electrolyte was H_2SO_4 . The reactor was operating in a recirculation mode by means of a peristaltic pump. The process was followed by total organic carbon, chemical oxygen demand, UV/Vis spectrometry (200–600 nm), and consumption of H_2O_2 . The dose of hydrogen peroxide was optimized to allow for the maximal production of hydroxyl radicals and avoiding the production of less reactive hydroperoxyl radicals. Under optimal conditions, i.e. pH 3, current density 30 mA/cm², flow rate 7 L/min, 2 h of treatment and peroxide addition 1.0 mL/L, nonylphenol removal was 97.6% as determined by chemical oxygen demand and total organic carbon measurements. To show the applicability of their approach for the treatment of wastewater, Rodriguez-Pena et al. (2019) calculated the operational costs as well. However, it should be noted that the process was tested only on synthetic solutions with no interfering substances.

Another example of mediated electrochemical oxidation is given in a paper by Setiyanto et al. (2018). They studied electrochemical oxidation with and without addition of an oxidant, cerium(IV) ions, for the removal of nonylphenol ethoxylate. The optimized parameters were the potential difference, electrolyte concentration, concentration of pollutant, concentration of Ce(III) ions, and oxidation time. Ce(III) ions were oxidized to Ce(IV), which in turn oxidized the nonylphenol ethoxylate. The maximum removal was obtained with 0.015 M Ce(III) in the electrolyte 0.2 M H_2SO_4 , and the potential 6 V. With treatment time 1.5 h, the removal was 80–90%, but it was even slightly higher in the absence of Ce(III) ions. Setiyanto et al. (2018) offered no explanation for this finding. The information on the measurement method for the concentration of the pollutant is missing as well.

The most interesting studies are those that show the effectiveness of a certain treatment approach under realistic conditions. Raw laundry wastewater was treated with a sequential system (Khosravanipour Mostafazadeh et al. 2019), beginning with ultrafiltration and continuing with one of the following: adsorption processes on granular activated carbon or polymeric resin, nanofiltration, or electrooxidation. Additionally, the concentrate after ultra- or nanofiltration was treated by electrocoagulation and electrooxidation. Authors monitored total suspended solids, turbidity, chemical oxygen demand, and concentration of nonylphenol ethoxylates with different chain lengths (by solid-phase extraction and liquid chromatography-tandem mass spectrometry). For electrooxidation, a two electrode system was applied with grid anode (boron-doped diamond, Ti/Pt, and Ti/IrO₂) and cathode (graphite, vitreous carbon, and stainless steel). For electrocoagulation, an iron or aluminum anode

was used, and a stainless steel or graphite cathode. Na_2SO_4 was used as the electrolyte in all cases. The most efficient processes for nonylphenol ethoxylates removal were adsorption on both types of sorbents, nanofiltration, and electrooxidation of the nanofiltrate, as well as of the concentrate after nanofiltration. The boron-doped diamond electrode showed the highest percentage of removal. Electrocoagulation was less efficient, especially for longer-chained nonylphenol ethoxylates, presumably because of decreased adsorption on flocs due to increased hydrophobicity. Thus, the most efficient process to apply for regeneration of laundry wastewater was nanofiltration, which reduced all monitored parameters by 80%. The concentrate that contained a high concentration of nonylphenol ethoxylates could be successfully treated by electrooxidation.

Another interesting study was performed by Niu et al. (2020). They designed a novel molecular imprinted high-index facet SnO_2 (MI- SnO_2 ,_{HIF}) electrode and applied it for specific removal of nonylphenol from tannery wastewater before the biological treatment. A three-electrode system was used with the mentioned working electrode, a Pt counter electrode, a saturated calomel reference electrode, and with Na_2SO_4 as a supporting electrolyte. In addition to MI- SnO_2 ,_{HIF}, three other novel electrodes, namely NI- SnO_2 ,_{HIF} (non-imprinted high-index facet SnO_2), MI- SnO_2 ,_{SG} (molecular imprinted sol-gel SnO_2) and NI- SnO_2 ,_{SG} (non-imprinted sol-gel SnO_2) were tested. The purpose was to preferentially remove toxic and non-biodegradable chemicals from the majority of the biodegradable substances and thus improve biodegradability and decrease the estrogenic potential of wastewater. After 8 h of treatment at an electrode voltage of 1.8 V with the MI- SnO_2 ,_{HIF} electrode, 95% of nonylphenol was removed, while the other two electrodes were less efficient. The predominant mechanisms were adsorption and subsequent oxidation at the electrode. The oxidation products were identified by liquid chromatography-tandem mass spectrometry. Three degradation pathways were also proposed, leading to the mineralization of the pollutant. Additionally, the ratio of biological oxygen demand to chemical oxygen demand increased from 0.186 to 0.412, showing increased biodegradability. The estrogenicity of wastewater was determined by an enzyme-linked immunosorbent assay and had fallen to zero after 5 h of treatment with the chosen electrode. This approach to treat wastewater by preferential electrooxidation before biological treatment has shown undisputable advantages over the more common reverse approach (Niu et al. 2020).

Wastewater sludge is a by-product of wastewater treatment by biological degradation. It can contain significant amounts of more recalcitrant pollutants. Barrios et al. (2015) tested the electrooxidation of sludge from industrial wastewater on boron-doped diamond electrode. The same type of electrode was used as a cathode as well. Authors studied the effect of pH and current density on the removal of selected pollutants, including nonylphenol. The efficiency of the treatment was monitored by measuring soluble chemical oxygen demand, UV/Vis spectra (200–900 nm) and by gas chromatography-mass spectrometry preceded by accelerated solvent extraction in combination with solid phase extraction with derivatization. Under optimal conditions of pH 3 and current density 40 mA/cm², 89% of nonylphenol was removed in 1 h. However, some difficulties were encountered

because the gas generation caused phase separation, i.e. flotation of solids, but these were overcome by improved mixing (Barrios et al. 2015).

The same research group further studied the electrooxidation of sludge in a total recirculation mode at 2.8 L/min in a Diacell® reactor with boron-doped diamond electrodes (Barrios et al. 2016). The focus of the research was on the reduction of organic matter in the sludge, measured as volatile solids and chemical oxygen demand. Authors also followed the removal of specific pollutants, among them nonylphenol isomers. Accelerated solvent extraction was performed, followed by solid-phase extraction, derivatization and gas chromatographic-mass spectrometric analysis. Other pollutants of interest were bisphenol A and triclosan. After 3 h of treatment, the achieved removal of nonylphenol isomers was 69% and it was the highest compared to other pollutants.

A coupled ozonation-electrooxidation treatment was employed for the treatment of wastewater sludge by the same research group (de Leon-Condes et al. 2017) for the removal of nonylphenol, bisphenol A, and triclosan. They optimized each process separately and then combined them to obtain the one most efficient at pollutant removal. For the electrooxidation, a batch electrochemical reactor with two boron-doped diamond anodes was used. The optimized parameters were the current density and pH of solution. In the combined process, ozone was generated and bubbled into solution. To evaluate the efficiency of pollutant degradation, soluble chemical oxygen demand was measured and UV/Vis spectra recorded. Additionally, accelerated solvent extraction of the sludge was performed, followed by gas chromatographic-mass spectrometric analysis. Although the best conditions for both processes were somewhat contradictory, the final conditions selected for the combined process were such as to achieve the best oxidation power, i.e. pH 7.5 and current density 20 mA/cm². With these, the soluble chemical oxygen demand was decreased by 62% and nonylphenol removal was 68%. No degradation products were monitored, however (de Leon-Condes et al. 2017).

Electrooxidation can be combined with other processes as well. A combination of ozone treatment and electrochemical oxidation was studied by Barrera-Díaz et al. (2018) as a means to remove nonylphenol from wastewater and was compared to electrochemical oxidation alone or ozone treatment alone or other advanced oxidation processes. To monitor the removal of the pollutant, chemical oxygen demand, total organic carbon, and absorbance spectra in the 200–600 nm range were measured. Electrochemical oxidation was performed in a batch mode with boron-doped diamond anode and stainless steel cathode, both with a surface area of 25 cm², or in a continuous mode (DiaClean® cell, same electrodes as in batch mode, but with area 70 cm² and flow rate 12.6 L/min). The solution was composed of 0.05 M or 0.1 M H₂SO₄ and 50 mg/L of nonylphenol. The pH was adjusted to 3, 5, and 7 by addition of NaOH solution. Effect of solution pH and current density was studied and the optimal conditions were found to be 3 and 30 mA/cm², respectively. However, ozone treatment was more effective at pH 7 due to formation of hydroxyl radicals which are stronger oxidants than ozone. While after 1 h of combined treatment, 70% of the pollutant was removed, the same time of treatment with ozone alone removed only 30% of pollutant, and electrochemical treatment alone achieved

the same removal success after 2 h. Barrera-Díaz et al. (2018) calculated the operational costs of the combined treatment as well and compared it to the data for UV/ozone treatment from the literature. They concluded that due to lower cost, the proposed system was an attractive alternative for the treatment of persistent pollutants in wastewater.

Among the novel electrochemical advanced oxidation processes, electro-Fenton is quite popular for degradation of different pollutants in wastewater. However, only one paper was found for the treatment of alkylphenols and their ethoxylates. Oturan et al. (2015) tested the electro-Fenton process and electrooxidation for the removal of 55 different pollutants with low degradability, among them 7 alkylphenols and their ethoxylates, from mature landfill leachates (>10 years old). Electro-Fenton was performed using a Pt or a boron-doped diamond anode and a carbon felt cathode. Na_2SO_4 and 0.2 mM Fe^{2+} were added to the landfill leachate that was saturated with O_2 , with the pH set to 3. At a constant current of 500 or 1000 mA, H_2O_2 was produced in situ from the dissolved oxygen. The electrooxidation process was conducted with a boron-doped diamond anode and a carbon felt cathode in a landfill leachate with or without added Na_2SO_4 and without pH adjustment. The same currents as in electro-Fenton were applied. The overall performance of both processes for the removal of contaminants was followed by dissolved total organic carbon measurement. Specific analyses were also performed for each group of pollutants. For alkylphenols and their ethoxylates, solid-phase microextraction in combination with gas chromatography-mass spectrometry or solid-phase extraction followed by ultrahigh-performance liquid chromatography-tandem mass spectrometry was applied. An electro-Fenton on a boron-doped diamond electrode removed 87–93% of total organic carbon in 18 h of operation, compared to a Pt electrode that removed 71–78%. The reason was most probably the better availability of physisorbed hydroxyl radicals on the boron-doped diamond electrode, while they were chemisorbed on the Pt electrode. Increasing the current from 500 mA to 1000 mA increased the removal of pollutants, but significantly less than would be expected because the parasitic reactions on the electrode were increased as well. The same was true for electrooxidation on the boron-doped diamond anode: by increasing the current, the removal was enhanced by only around 6%, showing that the efficiency of the current was higher at lower current density. Overall, both electrochemical processes were very efficient for the removal of the specific pollutants. For alkylphenols and their ethoxylates, the removal was 85–100% by electrooxidation and 96–100% by electro-Fenton. Therefore, both processes can be used to successfully treat complex mature landfill leachates containing several recalcitrant pollutants (Oturan et al. 2015).

Photoelectrooxidation is a combined electrochemical and photolytic treatment yielding good results with different emerging contaminants. da Silva et al. (2015a) applied it for the treatment of nonylphenol ethoxylate. The electrochemical cell contained a concentric dimensionally stable $\text{Ti}/\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ anode and a Ti/TiO_2 cathode around the high-pressure commercial mercury vapor lamp (principal emission band at 254 nm). Authors optimized several parameters: lamps of different voltage, current density, and treatment time. The removal of the pollutant was

monitored by UV/Vis spectrometry, total organic carbon measurement, gas chromatography-mass spectrometry, and ecotoxicity assay. The maximal removal in a Na_2SO_4 solution (supporting electrolyte) was obtained with a 250 W lamp, current density 10 mA/cm^2 , and 4 h of treatment. Under these conditions, 83% of the pollutant was mineralized as evidenced by total organic carbon measurement and reduced toxicity. With the weaker lamp (125 W), what formed was mainly nonylphenol which is even more problematic than the parent compound. Based on the gas chromatographic-mass spectrometric analysis, authors were able to propose the degradation pathway with the intermediates alkylphenol and alkyl-alcohol, further mineralized to CO_2 and water (da Silva et al. 2015a).

The same research group published another paper where they compared direct photolysis, heterogeneous photocatalysis, electrochemical oxidation, and photo-assisted electrochemical oxidation for the removal of nonylphenol ethoxylate from synthetic wastewater, containing the commercial degreasing product ULTRANEX NP40® and Na_2SO_4 as a supporting electrolyte (da Silva et al. 2015b). In both electrochemical processes, the same electrodes were used: a dimensionally stable Ti/ $\text{Ru}_{0.3}\text{Ti}_{0.7}\text{O}_2$ anode and a Ti/ TiO_2 cathode. All treatments were performed for 4 h and the removal was assessed by UV/Vis spectrometry, total organic carbon measurement, gas chromatography-mass spectrometry, and phytotoxicity assay (*Lactuca sativa* and *Allium cepa* seeds as test organisms). The highest removal and mineralization up to 83% was achieved with the photo-assisted electrochemical oxidation system described in their previous paper (da Silva et al. 2015a). Phytotoxicity assays didn't show any change in toxicity compared to non-treated samples, except for samples treated by photo-assisted electrochemical oxidation with a lamp of lower intensity (125 W), where nonylphenol was produced as a stable intermediate and the toxicity to *Lactuca* was actually increased. The optimal process was also economically feasible as shown by the cost analysis (da Silva et al. 2015b).

Among the novel electrochemical advanced oxidation processes, photoelectrocatalysis is a combination of photolytic degradation and electrochemical catalysis. Fan et al. (2018) applied photoelectrocatalysis and electrosorption to degrade trace concentrations of nonylphenol. They synthesized three types of electrodes: carbon aerogel, Bi_2WO_6 on carbon aerogel, and Bi_2WO_6 on F-doped SnO_2 . These electrodes were used as working electrodes in a three-electrode cell containing Na_2SO_4 as a supporting electrolyte. Nonylphenol concentration in a solution or on an electrode was monitored by solvent extraction, followed by high-performance liquid chromatography with UV detection. Firstly, electrosorption parameters were studied. The key parameters were found to be the potential of the working electrode and the pH of solution, due to the weakly acidic nature of nonylphenol ($\text{p}K_a$ 10.7). Best adsorption was achieved at potentials around $+0.6 \text{ V}$ (vs. saturated calomel electrode) and alkaline $\text{pH} > 12$. Adsorption fitted well to the pseudo-first-order kinetics model for $\text{Bi}_2\text{WO}_6/\text{F-doped SnO}_2$, and to the pseudo-second-order model for carbon aerogel and $\text{Bi}_2\text{WO}_6/\text{carbon aerogel}$. Maximal adsorption capacity of the latter electrode under optimal conditions was $920 \mu\text{g/L}$ while the other two electrodes performed less well. Next, photocatalytic and photoelectrocatalytic processes under simulated sunlight were compared for nonylphenol degradation. Bi_2WO_6 material

absorbs visible light at 426 nm, but carbon aerogel presence decreases the absorption. Nevertheless, photoelectrocatalysis on the Bi_2WO_6 /carbon aerogel electrode was the most efficient and was further applied on real wastewater mixed with a nonylphenol solution. Despite the competition for adsorption by matrix components, the electrode retained good performance and reduced the concentration of nonylphenol from 1 mg/L to 6.4 $\mu\text{g/L}$ after 8 h of photoelectrocatalysis. Total organic carbon was reduced by 66.1%. Moreover, the electrode showed good self-cleaning properties (Fan et al. 2018).

The same research group synthesized two other novel electrodes, namely a $\{0\ 0\ 1\}$ - TiO_2 electrode and the same electrode decorated with hydrophobic perfluoroalkyl groups – a D- $\{0\ 0\ 1\}$ - TiO_2 electrode (Fan et al. 2019). Both were used in a three-electrode system as working electrodes with a Pt counter electrode, a saturated calomel reference electrode, and Na_2SO_4 as a supporting electrolyte. The working electrode was irradiated by a xenon lamp (300 mW/cm^2). The experiments were performed in alkyl phenol (octyl, nonyl, and heptyl) solutions, the removal of which was monitored by high-performance liquid chromatography with UV detection. The optimal potential of the working electrode was +0.6 V. Fan et al. (2019) tested static adsorption of pollutants on the electrode for 2 h, and in a separate experiment, photoelectrocatalytic degradation for 5 h. The perfluoroalkyl-decorated electrode showed approximately twice higher adsorption due to matching polarity with the pollutants, which was confirmed by infrared spectroscopy. Similarly, the developed photocatalytic current upon irradiation was up to twice higher compared to a bare electrode. These results showed the possibility of selective degradation of specific pollutants in the wastewater treatment.

Similarly, Xin et al. (2017) prepared WO_3/TiO_2 and TiO_2 nanotube array photoelectrodes and applied them for either photocatalytic or photoelectrocatalytic degradation of 4-nonylphenol. The experiments were performed in an electrochemical cell with one of the prepared electrodes as the anode and a Pt foil cathode. The anode was irradiated with a xenon lamp (400–650 nm). The removal of the pollutant was monitored by high-performance liquid chromatographic analysis. Besides, the hydroxyl radical concentration was determined by means of formation of a fluorescent product. In addition to the type of electrode, the effect of pH and the presence of inorganic anions (SO_4^{2-} , Cl^- , HCO_3^- , and NO_3^-) was studied. After 2 h of photoelectrocatalytic process, the degradation of nonylphenol was 80.1% and 92.3% with a TiO_2 or a WO_3/TiO_2 photoelectrode, respectively, and was higher for both electrodes than with photocatalysis or electrocatalysis alone. The WO_3/TiO_2 photoelectrode had a better performance because of lower band gap of WO_3 , leading to a higher production of hydroxyl radicals. The effect of pH was twofold: firstly, acidic or alkaline pH promoted the formation of hydroxyl radical better than in the neutral solution, but on the other hand, the actual degradation of the pollutant was the highest at neutral pH. The authors explained this behavior by decreased adsorption of the pollutant on the electrode at alkaline pH due to coulombic repulsion, while at the acidic pH, excess oxonium ions hindered the degradation. Finally, the effect of commonly present anions (SO_4^{2-} , Cl^- , HCO_3^- , and NO_3^-) was studied. All four anions inhibited the degradation of nonylphenol to various degrees. The inhibition was

more pronounced on the TiO_2 photoelectrode, except for NO_3^- , which showed a greater negative effect on the WO_3/TiO_2 photoelectrode. Xin et al. (2017) identified different reasons for the inhibitory effect of anions, among them hydroxyl radical scavenging, adsorption on the photoelectrode, formation of new radical species with lower activity, etc. In spite of promising results, these findings limit the use of fabricated electrodes in real wastewater.

Electrochemical approaches can be combined also with other established treatment options for the removal of pollutants from wastewater. The adsorption of nonylphenol on multi-walled carbon nanotubes was studied in a Na_2SO_4 electrolyte without applying electricity, with electrochemical assistance under open circuit conditions, and at different polarization potentials (Li et al. 2014b). For the latter, a three-electrode system consisting of a carbon nanotubes working electrode, a Pt counter electrode, and a saturated calomel reference electrode was used to apply working electrode potentials of 0.6 V, 0.3 V, -0.3 V, and -0.6 V. The concentration of the pollutant was determined by high-performance liquid chromatography with fluorescence detection. The best results were achieved at a potential of -0.6 V with 7.9-fold increase in adsorption rate and 1.7-fold increase in adsorption capacity compared to adsorption without electrochemical assistance. Adsorption kinetics were fitted to several different models, while the isotherms were fitted to the Langmuir and Freundlich models. The former showed better correlation and fit with the experimental data (Li et al. 2014b).

Nonylphenol can be removed from the wastewater by a wide variety of approaches as evidenced in this chapter. One of the possible removal methods is adsorption on carbon nanotubes. The electrokinetic regeneration of carbon nanotubes saturated with nonylphenol was studied by Yuan et al. (2011). Carbon nanotube layers and Ottawa sand layers were placed in the middle compartment between the anode and cathode compartments. Different electrodes, commercial or made by authors, were tested as anodes: carbon, titanium, and three binary metallic electrodes (MnO_2/Ti , RuO_2/Ti , and PbO_2/Ti). The cathode was made of stainless steel. Different processing fluids were tested as well: de-ionized water, citric acid, NaOH, and NaCl. The treatment proceeded at 2 V/cm for 8 h. The concentration of nonylphenol in different compartments was determined (by high-performance liquid chromatography), as well as pH, electric current, and electroosmotic flow. The degradation of nonylphenol was the most efficient (38.4–69.0% by different electrodes) in NaCl, presumably because of the formation of hydroxyl radicals and hypochlorite ions compared to other fluids where only hydroxyl radicals were formed. Of the tested electrodes, the RuO_2/Ti electrode was the most efficient for nonylphenol removal (69.0%). The principal mechanism was the electromigration of the pollutant into the anode compartment and its subsequent electrooxidation (Yuan et al. 2011). The same research group published very similar study on electrokinetic regeneration of carbon nanotubes saturated with nonylphenol (Yuan et al. 2012). The design of the experiment was very similar as in their previous paper (Yuan et al. 2011), except for some new binary metallic oxide electrodes. Namely, they tested the following anodes: carbon, PbO_2/Ti , $\text{PbO}_2\text{-Co}/\text{Ti}$, and $\text{PbO}_2\text{-SnO}_2 + \text{Sb}_2\text{O}_3/\text{Ti}$. The same

electrokinetic set-up and the same processing fluids were used as in their previous experiment. They achieved the highest removal of nonylphenol in a system with NaCl processing fluid and a PbO₂-Co/Ti electrode, namely 71.4–80.0%, which was better than with electrodes studied in their previous paper (Yuan et al. 2011).

Coming from the same research group, Dai et al. (2017) studied the possibility of regeneration of carbon nanotubes with adsorbed nonylphenol by electrochemical oxidation. The electrochemical cell consisted of an anode (different materials listed below) and a stainless steel cathode, while the carbon nanotubes with adsorbed nonylphenol were placed between the electrodes, with their migration restricted by filters. Different parameters were optimized. Three anode materials were tested: carbon, titanium, and RuO₂/Ti. Different electrolytes were studied as well: citric acid, NaOH, and NaCl. Voltage and time of treatment were also studied. The concentration of nonylphenol in the cell was monitored by high-performance liquid chromatography with UV detection. The best removal efficiency was achieved in NaCl on a homemade RuO₂/Ti electrode, namely 69%. The main degradation mechanisms were established to be electroosmotic migration, followed by anodic oxidation. The species responsible for degradation were found to be hydroxyl radical and hypochlorite ion in NaCl solution, while in the other two electrolytes, only the former were active. Nonylphenol was mineralized to CO₂ and water. Regenerated carbon nanotubes maintained 96.2% of their initial adsorption capacity. Dai et al. (2017) also provided a cost estimation by taking into account the electrode cost, as well as power and electrolyte consumption. They concluded that the estimated cost was lower than that of the comparable approaches in the literature.

Electrochemical treatment options are applied to other samples besides wastewater and similar but even more complex landfill leachate. A similar approach as for the regeneration of carbon nanotubes can be applied for direct removal of pollutants from contaminated soil. It is called electrokinetic treatment and removes pollutants by applying low direct current, causing their electroosmosis, electromigration, and electrophoresis. Guedes et al. (2014) applied electrokinetic treatment to remove six emerging contaminants, among them nonylphenol and octylphenol, from three types of soil. The concentration of target compounds was determined by high-performance liquid chromatography with diode-array detection preceded by solvent extraction. Experiments were performed in an electrochemical cell with two electrode compartments with platinized titanium electrodes. Soil saturated with deionized water was placed between them and separated by cellulose filters. The electrolyte was a NaNO₃ solution, which was percolated through compartments by a peristaltic pump. Under galvanostatic conditions, hydroxyl radicals were produced, capable of degrading pollutants. Authors studied the effect of applied current, electroosmotic flow and permeability of different soils, as well as the volume and pH in the anode and cathode compartments. The final percentage of remaining pollutants was statistically similar for different treatments and ranged between 17–50% or 27–48% for two different soils. Octylphenol was better degraded than nonylphenol, probably because of lower water solubility and lower mobility of the latter. Pollutants reaching the electrodes were presumably degraded, but the transformation products were not studied (Guedes et al. 2014).

In a study by Hung et al. (2010), nonylphenol was removed from soil by an electrokinetic process. The effect of the following parameters was studied: processing fluid (de-ionized water, citric acid, NaOH, and methanol) and current density. The concentration of the pollutant was monitored in the soil and both electrode compartments, using high-performance liquid chromatography with UV detection. The best removal was achieved in methanol, i.e. 53–69% after 5 days at 1 V/cm. Most of the pollutant (88.8–94.2%) was found in the cathode compartment after the treatment, leading to the conclusion that the predominant process of nonylphenol removal from the soil was electroosmosis rather than electromigration.

To summarize, electrochemical advanced oxidation processes are a viable option for the removal of alkylphenols and their ethoxylates from wastewater, landfill leachate, and even solid environmental samples such as the soil. Electrooxidation alone or in combination with chemical or photolytic treatment is the most popular approach, which is effective, fast, and cost-efficient. The main shortcoming of the reviewed studies, however, is the lack of thorough analysis of the transformation products. Only too frequently it is simply assumed that the pollutants are mineralized during treatment, based on total organic carbon measurements.

4.5.3 Photocatalyst Nanoparticles for Degradation of Alkylphenol Polyethoxylates

Among the advanced oxidation processes used in water and wastewater treatment, photocatalysis, as a green chemical pathway, plays an important role as it is capable of degrading and mineralizing contaminants such as dyes, phenols and pesticides into harmless products under mild conditions (Ike et al. 2002; Oh 2004; Wang et al. 2009; De la Fuente et al. 2010; Ameta et al. 2012; Rammohan and Nadagouda 2013; Umar and Aziz 2013; Pirilä et al. 2015; Liang et al. 2020). This process involves chemical reactions that take place in the presence of light and a photocatalyst. A photocatalyst such as titanium dioxide is a semiconductor, which increases the rate of reaction by its presence. Titanium dioxide (TiO_2) has been widely used not only in environmental chemistry but also in energy domain and other applications such as sanitation and anti-fog coatings because of its high photoactivity, high stability, low cost, non-toxicity (safety to the environment and humans). TiO_2 -based photocatalysis is known to be one of the most promising avenues for water purification and wastewater treatment. However, the cost of using UV radiation (titania is activated in the UV range due to its wide band gap energy) still prevents its widespread application. Work is therefore proposed to reduce the energy bandgap of titanium dioxide, so as to promote visible activation.

Over the past two decades, numerous studies demonstrated that heterostructured photocatalysts have shown higher photocatalytic activity, compared to individual photocatalysts, in mineralizing harmful organic substances in water (Hojamberdiev et al. 2012; Ibhaddon and Fitzpatrick 2013; Wang et al. 2013; Dong et al. 2015; Liang

et al. 2020). In particular, heterostructured photocatalysts based on titanium dioxide, such as $\text{ZrO}_2/\text{TiO}_2$, ZnO/TiO_2 , CdS/TiO_2 , etc. have attracted a great deal of interest due to their higher charge separation efficiency and their UV-visible light photocatalytic activity (Xu et al. 2006; Chen et al. 2008; Gao et al. 2009). The applications of this research concern not only the environmental field but also photoelectrochemical processes and clean energy production (Tsuji et al. 2004; Kim et al. 2005a; Hasegawa et al. 2013).

The adsorption of anionic, cationic and non-ionic surfactants on fly ash carbon (used as an additive in concrete mix to remove surfactants) has been found to be affected by oxidation of the carbon surface (McKay 1996). This study showed that oxidation of the carbon surface in air or by ozone suppresses surfactant adsorption, suggesting that surfactant adsorption occurs primarily on the non-polar surface of the carbon, where adsorption is driven by hydrophobic interaction (i.e. the hydrocarbon chain of the surfactant molecule interacts with the carbon surface). In the analysis of the adsorption of a commercial non-ionic surfactant (Triton™ X-100) from an aqueous solution by carbons, González-Carcía et al. (2001) observed that at very low coverage, the adsorption was highly exothermic, corresponding to adsorption in the narrowest pores. The authors suggested that after this initial phase, the exothermic adsorption of the surfactant continued, but at less energetic adsorption sites, and that a second interaction begins to occur: the lateral interaction between the hydrocarbon chains of the already adsorbed molecules. This interaction was considered endothermic for the carbons with the lowest amount of porous structure, i.e. the carbon blacks studied. As the coverage increases this endothermic effect became more dominant and an endothermic plateau was observed in the differential enthalpy at coverage of greater than 0.6 (González-Carcía et al. 2001; Loureiro and Kartel 2006). As with the study of adsorbents, the photocatalytic degradation of phenol has received more attention than many chemical species. The reasons for using the phenol molecule are much the same for the study of adsorbents and photocatalysts. Phenol molecules have a good water solubility, are easily detectable by a number of different techniques (UV absorption, high performance liquid chromatography, etc.) and phenol is the parent structure for a number of common organic pollutants, such as chlorophenols, bisphenol A, cresols, nitrophenols, and alkylphenols (Mao et al. 1993).

Serpone's group has studied the photocatalytic degradation of ionic and non-ionic surfactants such as sodium dodecylbenzenesulfonate and benzyldodecyldimethyl-ammonium chloride (Serpone and Pellizetti 1989; Hidaka et al. 1990; Pelizzetti et al. 1992; Zhao et al. 1993; Serpone et al. 1994). Their work indicated that there was a relationship between the initial rate of photo-oxidation and the structure of the surfactant (Serpone et al. 1994). Degradation of non-ionic surfactants was also somewhat slower than that of cationic and anionic surfactant. In summary, all the major surfactant types (anionic, cationic and non-ionic) had at least one example member that showed complete photocatalytic conversion or even complete mineralization. Degradation of long hydrocarbon chains within surfactant molecules appeared to occur only slowly, if at all. However, it is important to note

that the degradation of the initial surfactant was found to rapidly destroy the surface activity.

Photocatalytic degradation of nonylphenol ethoxylates such as nonylphenol pentaethoxylate using titanium dioxide as the photocatalyst has received some attention in the past (Pelizzetti et al. 1989; Zhao et al. 1993; Sherrard et al. 1996). Oxidation of the ethoxylate chain has been attributed generally as a primary degradation pathway for nonylphenol ethoxylates. Serpone and co-workers proposed a model in which oxidation of the aromatic ring and ethoxylate chains were competitive (Serpone et al. 1994). The degradation pathways are initiated by the attack of hydroxyl radicals on the ethoxylate chain and the benzene ring with preferential attack on the longer ethoxylate chains. This was demonstrated by the comparative photodegradation of nonylphenol ethoxylates with different initial ethoxylate chain lengths (Hidaka et al. 1990). Further oxidation also involves the aliphatic chain, resulting in intermediate products as ethylene glycols and various acidic compounds, and finally a near quantitative conversion to CO_2 (Serpone et al. 1994). Sherrard et al. (1996) observed that the degradation of nonylphenol pentaethoxylate occurred preferentially with cleavage of the ethoxylate chain producing short-chain alkylphenol ethoxylates of low solubility. After an initial induction period, cleavage of aromatic rings became an increasingly important route of decomposition. Short-chain nonylphenol pentaethoxylates have also been observed to be persistent and adhere to the surface of titanium dioxide, i.e. they are not observed in free solution, but are observed when extracted from the surface of titanium dioxide using an organic solvent. In all the studies mentioned, complete removal of the non-ionic surfactant is observed with an adequate irradiation time.

To prepare and characterize titanium dioxide -based nanocomposites for use in removing phenol and alkylphenol ethoxylates from wastewater, TiO_2/C and $\text{TiO}_2/\text{SiO}_2$ nanocomposites have been prepared and a wide range of characterization techniques have been used to define the physical and chemical properties of these composites. Nanostructured composites were evaluated for the adsorption and photocatalytic decomposition of phenolic endocrine disruptors. Two methods were used for the preparation of titania-coated carbon particles, TiO_2/C . The first used sol-gel chemistry by hydrolysis of titanium isopropoxide for coating spherical activated carbon particles (Brinker and Scherer 1990). The second involved the hydrolysis of the titanium isopropoxide to take place after the carbon has been in contact with the reagent solution. The first method of contacting the carbon spheres with a pre-formed TiO_x gel is capable of giving a high TiO_2 charge on the outer surface of the spheres, while the second method gives a lower charge, which can result in a more uniform and also more stable coating for application in the field of water treatment.

Polyethylene glycols are synthetic polyethers with multifunctional properties, available in a range of molecular weights, used as non-ionic surfactants, e.g. in the formulation of cosmetic and medical products. Sermon et al. (2012) investigated the use low-molecular weight polyethylene glycol (PEG 400) as a template for the synthesis of the nanostructured silica-titania matrix. The synthesis of mesoporous silica and titanium oxide was carried out using tetraethoxysilane and titanium alkoxide

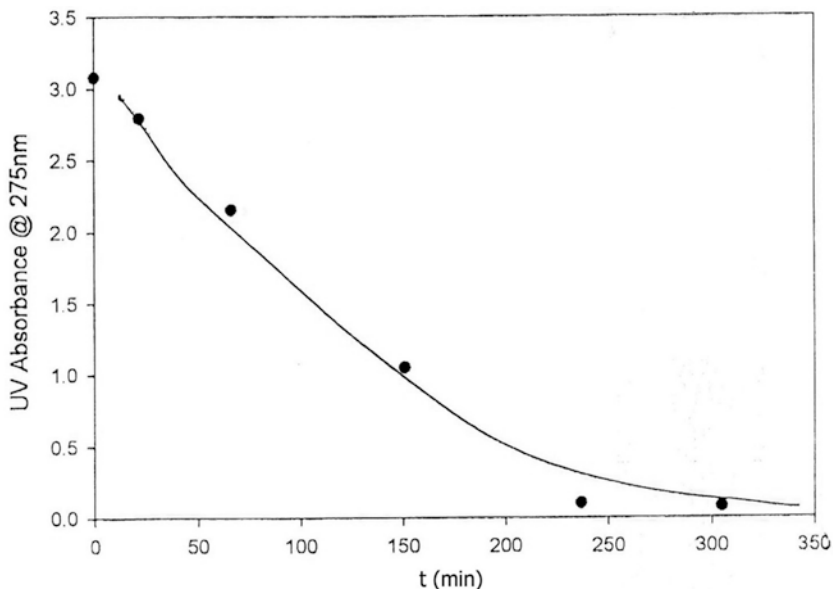


Fig. 4.15 Photodegradation of a 1000 ppm aqueous solution of nonylphenol ethoxylate by TiO_2 at pH 7

precursors, NH_4OH and HCl as catalysts in the presence of PEG 400 as the template or structure-directing compound. The removal of the templates by solvent extraction and calcination has resulted in mesoporous silica-titania materials.

The photocatalytic degradation of two commercial alkylphenol ethoxylates, IGEPAL® CO-520 (a nonylphenol ethoxylate with 5 moles of ethoxylates) and Triton™ X-100 (an octylphenol ethoxylate with 9.5 ethylene oxide units) using PEG-templated TiO_2 and $\text{SiO}_2\text{-TiO}_2$ has been studied in detail (Musaev et al. 2019). The results showed that photodegradation initially occurs by cleavage of the ethoxylate chain and shorter-chain alkylphenol ethoxylates result. Agglomeration of suspended SiO_2 and TiO_2 nanoparticles and their sedimentation was also observed during photodegradation of surfactants. The photocatalytic performance of the combined carbon and titania system follows the same trend as the titania system alone, since the pH is modified. As the pH increases, the photocatalyst performance also increases. It has been found that the performance varies by a factor of 8 in the pH range studied. Therefore, to get the most out of these photocatalyst systems, the pH of solution must be carefully monitored and controlled. The effect of pH on the photocatalytic performance of the TiO_2/C composites is the same for TiO_2 alone. As with the photodegradation of phenol, the photodegradation of nonylphenol ethoxylates was investigated initially using only the Hg discharge lamp first (Fig. 4.15). The analysis of the results suggests that a by-product/intermediate is formed in the early stages of the reaction and is then degraded by photocatalysis. Following the photocatalytic reaction, the titanium dioxide aggregated and adhered to the walls of the photoreactor. To determine the reason for this aggregation, the titanium dioxide was removed from the reactor and dried overnight at 348 K. The resulting gray paste was

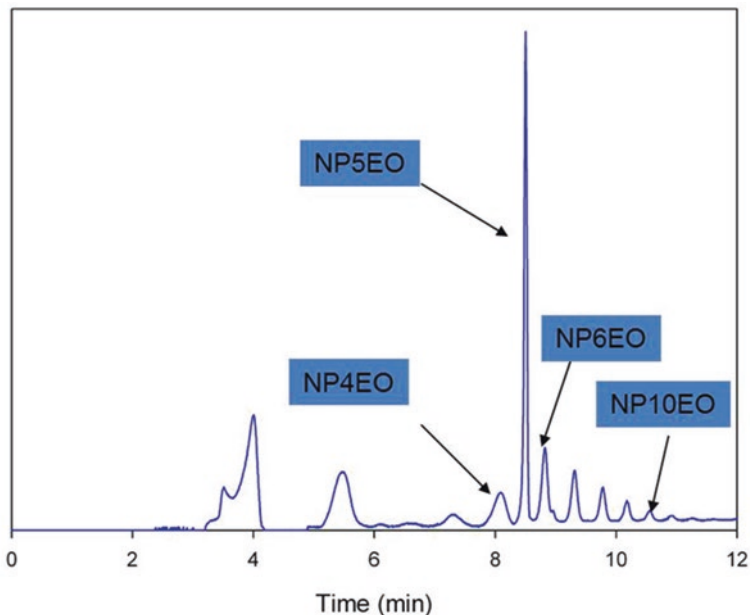


Fig. 4.16 High performance liquid chromatogram of a nonylphenol pentaethoxylate (NP5EO) solution with UV-irradiated PEG-templated $\text{SiO}_2\text{-TiO}_2$ (time = 90 min, NP4EO nonylphenol tetraethoxylate, NP6EO nonylphenol hexaethoxylate, NP10EO nonylphenol decaethoxylate)

placed in a vial and hexane (or methylene chloride) was added in two steps for the extraction of adsorbed compounds. The extract was analyzed by high performance liquid chromatography (Fig. 4.16). The results showed that several products of photocatalytic degradation have formed and remained adsorbed on the titanium dioxide surface. Nonylphenol and nonylphenol monoethoxylate which are found in very low concentrations in the aqueous solution are found in great abundance on the surface of TiO_2 . The analysis of the first elution peaks in the chromatogram shows the products of the cleavage of the aromatic ring. These products could not be determined in free solution so, like short-chain, they must be strongly bound to the surface of the titanium dioxide particles.

The main conclusion of this work was that the incorporation of a polymer matrix into the inorganic network, with subsequent formation of a nanoporous structure, increases the efficiency of sol-gel materials during adsorption/photocatalytic purification and separation of various organic pollutants. The composite structure shows molecular selective photocatalysis while the photocatalytic activity of titanium dioxide is non-selective. Although the photocatalytic approach can be applied to remove alkylphenol ethoxylates, many questions remain unanswered. The sedimentation of titanium dioxide particles is a major problem for the application of photocatalysis in the removal of alkylphenol ethoxylates. The use of a stationary support could overcome this problem and ensure that titanium dioxide activity remains high even after prolonged use in the photodegradation of these surfactants. Another possibility for further study arises from the large number of molecules present in the commercial

nonylphenol pentaethoxylate and all the intermediates formed during photodegradation. The use of a nonylphenol pentaethoxylate with only one ethoxylate chain length would make it possible to identify the photodegradation intermediates and to more accurately measure the concentration of the nonylphenol pentaethoxylate used.

4.5.4 Zero-Valent Iron-Activated Persulfate Oxidation of Alkylphenol Polyethoxylates

Zero-valent iron, Fe(0), was originally developed to mitigate chlorinated hydrocarbon industrial solvents disposed in soil and many other toxic species including arsenic in the environment (Lackovic et al. 2000; Balarama Krishna et al. 2001; Farrell et al. 2001; Manning et al. 2002; Kim et al. 2003; Lien and Wilkin 2005). In recent years, significant improvements were made with iron-based technologies and the use of zero-valent iron for the treatment of a variety of other organic contaminants and heavy metals in surface water, groundwater and wastewater has received considerable attention and encouraging results have been reported (Bokare and Choi 2014; Han et al. 2016; Minella et al. 2019). The major contaminant groups that have been treated by zero-valent iron materials are industrial dyes, pharmaceuticals, personal care products, explosives, pesticides, heavy metals, surfactants, arsenic and hexavalent chromium.

Among the advanced oxidation processes, in particular Fenton, Fenton-like and photo-Fenton processes have gained more attention due to their superior reaction kinetics and treatment efficiencies (Safarzadeh-Amiri et al. 1996; Nadtochenko and Kiwi 1998; Arslan-Alaton and Teksoy 2007). Since iron-based advanced oxidation processes are technically and economically attractive compared to other treatment methods, extensive research on treatment applications, reaction pathways and critical process parameters has already been published. However, their common, major drawback is the requirement of a strictly acidic pH (typically between 2 and 5) to enhance iron solubility, and the problem of a solid waste management after treatment (pH re-adjustment) as a consequence of Fe(OH)₃ sludge formation. To overcome these limitations, heterogeneous Fenton-like treatment systems including iron oxides/oxyhydroxides, supported iron salts and more recently zero-valent iron-mediated treatment systems have been explored for water and wastewater treatment (Li et al. 2014a; Zhou and Jiang 2015).

An abundant literature (Mueller et al. 2012; Kharisov et al. 2012; Crane and Scott 2012; Fu et al. 2014) in the treatment applications of zero-valent iron and oxidants (mainly peroxides such as hydrogen peroxide) activated by zero-valent iron has recently appeared. In fact, zero-valent iron offers several advantages since it is a very reactive material with a reduction potential of -0.44 V vs. standard hydrogen electrode, relatively non-toxic, abundant, inexpensive, easy to produce and handle (Grieger et al. 2010; Greenlee et al. 2012). The reaction mechanism has

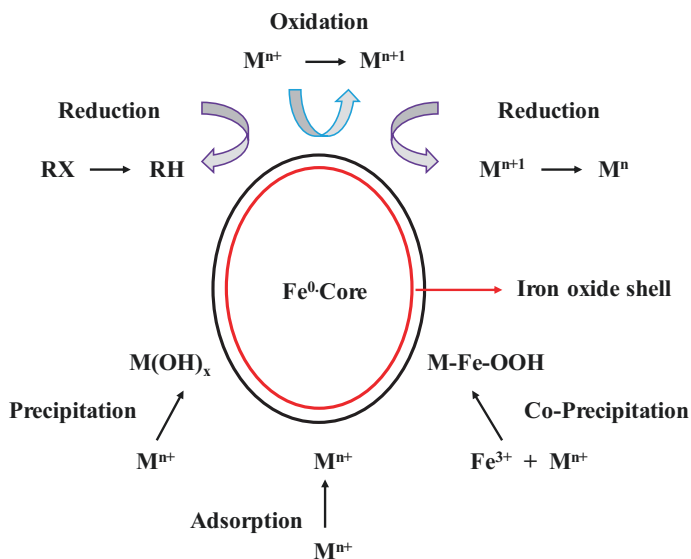
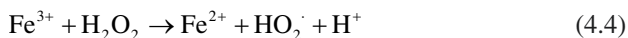
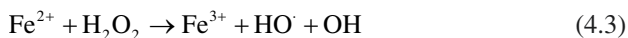
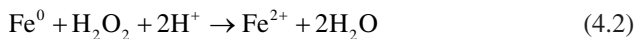
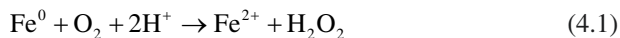


Fig. 4.17 Schematic illustration of zero-valent iron surface reactions

been postulated as follows (Bremner et al. 2006; Bergendahl and Thies 2004; Fu et al. 2014; Zhao et al. 2010):

- (i). When zero-valent iron undergoes surface oxidation (corrosion), two electrons are transferred from zero-valent iron to dissolved oxygen to produce hydrogen peroxide;
- (ii). Then, Fe^{2+} ions released from the zero-valent iron surface to the reaction bulk react with the *in-situ* formed hydrogen peroxide and produce HO^\bullet and HO_2^\bullet by Fenton and Fenton-like reactions, respectively;
- (iii). The Fenton and Fenton-like reactions can be enhanced by direct (external) hydrogen peroxide addition to the reaction solution.

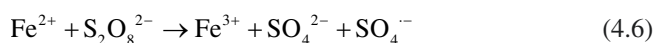
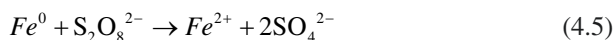
The above-listed basic reactions of the zero-valent iron/ H^+ / O_2 treatment system are given in Eqs. 4.1, 4.2, 4.3 and 4.4 (Bergendahl and Thies 2004; Fu et al. 2014). Figure 4.17 shows a schematic illustration of zero-valent iron surface reactions.



Zero-valent iron has also been used on supported materials such as carbon, resin, bentonite, kaolinite and zeolites (Diao and Yao 2009; Zhao et al. 2010; Kusic et al.

2011; Wang et al. 2011; O'Carroll et al. 2013; Trujillo-Reyes et al. 2014; Salam et al. 2015; Mao et al. 2019). In this way oxidation, reduction and adsorption capacities could be improved and aggregation - corrosion problems could be hindered. Considering the potential applicability of zero-valent iron treatment technology, some full-scale examples are available including zero-valent iron-based permeable reactive barriers for the in-situ remediation of groundwater that has been designated as a standard treatment technology for contaminated groundwater in 2002 by the US EPA.

Peroxydisulfate ($S_2O_8^{2-}$) appears to be an alternative, interesting oxidant to the more classical hydrogen peroxide since it offers several advantages such as high aqueous solubility, high thermal stability, relatively low cost and environmentally acceptable end products such as sulfate (Zhao et al. 2010; Rodriguez et al. 2014). Sulfate is regulated by water associations and agencies but its toxicity limit is relatively high (>200 mg/L) rendering peroxydisulfate-based treatment processes very promising and ecotoxicologically safe as well. Peroxydisulfate treatment is generally associated with the production of sulfate ($SO_4^{\cdot-}$) radicals which are very strong and hence reactive oxidizing agents. $SO_4^{\cdot-}$ can be generated in different ways; from the activation of persulfate by short UV (UV-C) light, thermally, *via* power ultrasound and microwave radiation, as well as transition metals and metal oxides. Zero-valent iron activation with peroxydisulfate on the other hand is a relatively cost-effective, efficient and environmentally friendly method and thus has received considerable attention for the removal of emerging contaminants and pollutants (Kusic et al. 2011; Xiong et al. 2014; Nguyen and Oh 2019). Zero-valent iron activation not only serves as a slow-releasing source of Fe but also provides a heterogeneous medium for peroxydisulfate activation via direct electron transfer. The mechanism of zero-valent iron-mediated peroxydisulfate treatment involves direct electron transfer from the zero-valent iron or surface-bound Fe^{2+} to peroxydisulfate, continuing with a homogenous Fenton-like reaction (Eq. 4.6) that results in $SO_4^{\cdot-}$ production in the reaction bulk (Xu and Li 2010). These reactions are analogous to the hydrogen peroxide activation by zero-valent iron and are shown in Eqs. 4.5 and 4.6.



The environmental problem associated with alkylphenol polyethoxylates is the fact that their aerobic/anaerobic transformation products such as nonylphenol and octylphenol (Ying et al. 2002; Ying 2006) are usually much more biotoxic and estrogenic than the original surfactants (Routledge and Sumpter 1996). Alkylphenol polyethoxylates currently cannot be replaced by alternative surfactants due to technical and economic reasons (Arslan-Alaton and Olmez-Hanci 2012). Consequently, the discharge of nonionic surfactants into industrial and sewage treatment plants as well as the evolution of degradation products in aquatic and terrestrial ecosystems is expected to continue (Staples et al. 2001).

Oxidation and electrochemical processes have been proposed for their degradation. Studies related with zero-valent iron-mediated treatment of alkylphenol polyethoxylates are relatively rare. In a relatively recent study, 20 mg/L aqueous Triton™ X-45 which is a commercially important octylphenol polyethoxylate formulation, was subjected to peroxydisulfate oxidation activated with zero-valent iron nanoparticles (Temiz et al. 2016). Nano-sized zero-valent iron is one of iron-based nanomaterials with a diameter ranging from 10 to 100 nm. In the first part of this study, zero-valent iron activated peroxydisulfate oxidation of Triton™ was optimized on the basis of pH (pH = 3–9), zero-valent iron (0.5–5 g/L) and peroxydisulfate (0.5–5.0 mM) concentrations by following Triton™ degradation and dissolved organic carbon removal. Poor/inefficient treatment performance ($\leq 15\%$ Triton™ degradation; $\leq 10\%$ dissolved organic carbon removal) was evident for zero-valent iron treatment in the absence of peroxydisulfate, revealing that peroxydisulfate activation by zero-valent iron is important for effective oxidation of Triton™ and its degradation products. Optimum surfactant treatment conditions were determined as the following: pH = 5, 1 g/L zero-valent iron and 2.5 mM (0.48 g/L) peroxydisulfate. There was no need to carry out Triton™ treatment at pH = 3 since practically equal Triton™ degradation was obtained at pH = 5, which is an environmentally and technically more acceptable pH. The peroxydisulfate/zero-valent iron treatment system was even effective at pH 7, where 80% Triton™ and 30% dissolved organic carbon removal were achieved in 60 min. For selected treatment conditions, 20 mg/L aqueous Triton™ could be degraded in 60 min by $>90\%$ accompanied with dissolved organic carbon removal reaching 40%. In addition to Triton™ and dissolved organic carbon abatements, peroxydisulfate consumption and Fe release were also followed during treatment. From the experimental findings it was evident that peroxydisulfate consumption and Fe release followed a parallel trend to Triton™ degradation rates. Acute toxicity bioassays were also conducted to examine the ecotoxicological safety of zero-valent iron/peroxydisulfate treatment system. Acute toxicity profiles decreased significantly from an original inhibition value of 66% and 16% to 21% and practically non-toxic values ($< 10\%$) according to *Vibrio fischeri* and *Pseudokirchneriella subcapitata* bioassays, respectively. Apparently, the photobacterium *Vibrio fischeri* appeared to be more sensitive to the original Triton™ solution and its degradation products than the microalga *Pseudokirchneriella subcapitata*. In Table 4.8, Triton™ and dissolved organic carbon removal efficiencies obtained for zero-valent iron-mediated peroxydisulfate treatment are summarized for different initial pH values (Temiz et al. 2016). It is interesting to note that with

Table 4.8 Percent Triton™ and dissolved organic carbon removal obtained for zero-valent iron-mediated peroxydisulfate treatment at varying pH values in un-buffered aqueous solution (other experimental conditions: Triton™ concentration 20 mg/L; dissolved organic carbon 14 mg/L; zero-valent iron concentration 1 g/L; peroxydisulfate concentration 0.48 g/L; time 60 min)

Initial reaction pH	Triton™ removal (%)	Dissolved organic carbon removal (%)
3.0	90	30
5.0	90	35
7.0	80	20

zero-valent iron/peroxydisulfate treatment, acceptable and Fenton-comparable Triton™ and dissolved organic carbon removal efficiencies could be achieved even at a neutral pH value.

These results demonstrate that iron-based oxidative processes are efficient in terms of treatment performance. Nevertheless, much work is still needed to develop more compact, efficient, affordable, and ecotoxicologically safe processes for the destructive treatment of industrial pollutants.

4.5.5 Catalytic Ozonation of Alkylphenols

Catalytic ozonation, i.e. the combination of a solid catalyst with ozone, is a promising technology for application in water treatment because of its simplicity (oxidation in the ambient temperature and pressure) and efficiency. Catalytic ozonation shows great advantages in removing refractory organics in water. The technique can be used either in homogeneous phase (metal ions as catalyst present in the reaction system) or in heterogeneous phase (catalysts are metal oxide and metal or metal oxide on supports). Many works showed the potential of this process to degrade pharmaceuticals such as diclofenac in water (Castro et al. 2019). As already discussed, this method coupled with an activated carbon step is promising in water treatment.

However, there are few literatures on destruction of alkylphenols by catalytic ozonation process. Anandan et al. (2012) used Bi₂CuO₄ nanoparticles catalyst for catalytic ozonation of nonylphenol ethoxylate. This study showed significantly improved destruction of the pollutant as compared to non-catalytic ozonation. Restivo et al. (2013, 2016) showed that both non-catalytic and catalytic ozonation achieved similar degradation degree of nonylphenol while using carbon nanofibers as catalyst in a continuous process. Nonylphenol very quickly reacted with molecular ozone as its aromatic ring is very vulnerable to ozone attack. However, introduction of catalyst improved the extent of mineralization of the pollutant since reactive oxygen species like hydroxyl radicals are less selective. This less selective species is also found to mineralize lower molecular weight recalcitrant compounds such as oxalic acid (Wang et al. 2018). Though somewhat promising, this catalytic ozonation of alkylphenols is still a developing topic.

4.6 Conclusion

Although legislation concerning the use of alkylphenols and their polyethoxylated derivatives, classified as priority substances in terms of monitoring and action, has become increasingly strict in recent years, these molecules are found in the various environmental compartments, especially in the aquatic environment. This is a result of their wide use and their presence in the environment is entirely due to human

activity. Alkylphenols and alkylphenol polyethoxylates can end up directly in the environment through industrial effluent or transit through municipal wastewater treatment plants. Existing conventional water and wastewater treatment plants were not designed for these new contaminants. In this context, it is necessary to propose and develop various efficient technologies for the elimination of alkylphenols from water and wastewater that are efficient, economically viable, technologically simple, and without environmental impact. Over the past two decades, alkylphenols have indeed become a relevant research topic for scientists interested in water engineering issues related to their treatment. Using selected examples, this chapter summarizes recent trends in proposed advanced treatment methods for the removal of alkylphenols and alkylphenol polyethoxylates from wastewater. The techniques such as adsorption onto cyclodextrin polymers or molecularly imprinted polymer, biodegradation using algae-based technologies or catalytic ozonation, are still at the pilot test stage. Others, such as ozonation-activated carbon and advanced oxidation treatments, have already been proven at the industrial wastewater scale. Among these technologies cited in this chapter, advanced oxidation processes, in association with biodegradation and/or adsorption, seem to be the technique of the future, although their costs still prevent their widespread use. Indeed, these techniques could be part of the operating scheme of municipal wastewater treatment plants. They could be used either in primary treatment, as a complement to biological methods to help the degradation processes of refractory substances, or in tertiary treatment, as a complement to an adsorption step on activated carbon, to eliminate residual pollution. The latter option seems to be preferred as it can be useful in the context of a more generalized reuse of treated wastewater.

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