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Innovative technologies to remove alkylphenols from wastewater: a review

Grégorio Crini¹  · Cesare Cosentino² · Corina Bradu³ · Marc Fourmentin⁴ · Giangiacomo Torri² · Olim Ruzimuradov⁵ · Idil Arslan Alaton⁶ · Maria Concetta Tomei⁷ · Ján Derco⁸  · Mondher Barhoumi⁹ · Helena Prosen¹⁰ · Borislav N. Malinović¹¹ · Martin Vrabel⁸ · Mohammad Mahmudul Huq¹² · Jafar Soltan¹² · Eric Lichtfouse¹³  · Nadia Morin-Crini¹ 

Abstract

Alkylphenols and alkylphenol polyethoxylates are emerging hazardous contaminants due in particular to their endocrine-disrupting properties. These compounds originate from consumer products such as 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. Since classical wastewater treatments have not been designed to remove alkylphenols, these compounds end up polluting ecosystems. Here we review three advanced methods to remove alkylphenols and derivatives. First, innovative polymers, such as cyclodextrin polymers and molecularly imprinted polymers, allow to remove alkylphenols from effluents by adsorption. Second, biotechnologies such as microalgae, biodegradation in constructed wetlands and sequential anaerobic–aerobic digestion treatments. Third, advanced oxidation processes to degrade recalcitrant alkylphenols, e.g., ozone-carbon coupling, electrochemical degradation, photocatalysis, zero-valent iron-activated persulfate coupling, and catalytic ozonation.

Keywords Alkylphenols · Cyclodextrin polymers · Molecularly imprinted polymers · Biodegradation · Advanced oxidation processes

Introduction

Many substances have been recently classified as priority hazardous substances because of their adverse effects on human health (Luo et al. 2014; Ribeiro et al. 2015). Issues include toxicity, persistence, bioaccumulation, transfer in the food chain, and recalcitrance to conventional treatments. These issues induce new challenges in terms of monitoring, toxicity, and treatment (Luo et al. 2014). Alkylphenols and their derivatives, namely alkylphenol polyethoxylates, deserve particular attention (Sayed et al. 2018, 2019; Ahmadpanah et al. 2019; Bodzek 2019; Gupta and Nux 2019; Hung et al. 2019; Musaev et al. 2019; Salomon et al. 2019; Saravanan et al. 2019; Tomei et al. 2019; Xie et al. 2019; Zaytseva and Medvedeva 2019; Dan et al. 2020;

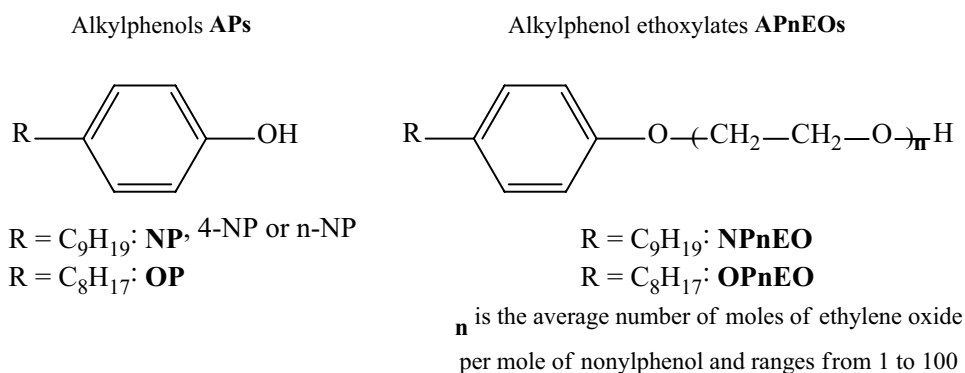
Janousek et al. 2020; Kaur et al. 2020; Olaniyan et al. 2020; Gautam and Chaube 2021).

Alkylphenols refer to nonylphenols and octylphenols (Fig. 1). Alkylphenols and alkylphenol polyethoxylates are used in 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. As a consequence, these compounds end up polluting ecosystems, notably water resources. In Europe, these compounds are highly regulated because some of them are endocrine disruptors. These compounds are difficult to remove from wastewater because they occur at trace levels, typically few nanograms per liter. They are also difficult to analyze in complex matrices (Priac et al. 2017).

Domestic effluents from wastewater treatment plants are the main source of alkylphenols in the environment because conventional municipal treatment plants were not designed to remove these contaminants (Qiang et al. 2013; Priac et al. 2017). Indeed, common biological treatments are unable

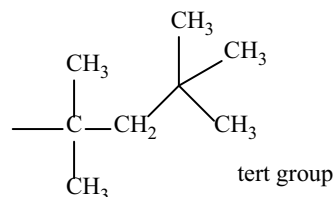
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Fig. 1 Molecular structure of alkylphenols (APs) and alkylphenol polyethoxylates abbreviated (APnEOs). NP: nonylphenol; OP: octylphenol; NPnEO: nonylphenol ethoxylates; OPnEO: octylphenol ethoxylates



- for NP: C_9H_{19} = linear and/or branched,
in ortho, meta or para position

- for OP: C_8H_{17} = tert group in para position



to remove most organic refractory pollutants, including alkylphenols (Shao et al. 2005; Qiang et al. 2013; Eggen et al. 2014; Priac et al. 2017). Industrial effluents are also a source of alkylphenol pollution, either by direct discharge or through wastewater treatment plants, into the aquatic environment. Even after intense purification, effluents from the surface treatment industry always contain many organic and inorganic substances (Charles et al. 2014, 2016).

The drinking water sector is also concerned by the presence of organic pollutants in surface or ground water. Faced with ever-changing regulations, all these water treatment industries must look for additional treatments capable of dealing with emerging contaminants and integrate these problems into their management. However, from a water engineering perspective, 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 with variable concentrations, variability of the pH of the effluents, important salinity) by conventional methods (e.g., adsorption using activated carbon, advanced oxidation, and membrane filtration) used in water and wastewater treatments. In addition, other disadvantages often cited are: investment costs, high energy requirements, high maintenance and operation costs, and rapid membrane clogging. 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.

To improve effluent quality, research has proposed to add a tertiary technology in wastewater treatment plants such as chemical treatments to remove pollutants that are refractory

to biological treatments (Vazquez-Duhalt et al. 2005; Soares et al. 2008; Basile et al. 2011; Garcia-Rodríguez et al. 2014; Ribeiro et al. 2015; Alvarino et al. 2016; Grandclement et al. 2017). Nonetheless, these tertiary treatments are actually rare in real plants due to their higher cost. Some industrial sites use adsorption on activated carbon coupled with an ozonation stage (Jones et al. 2007; Hollender et al. 2009; Cases et al. 2011).

This review presents proposed advanced technologies for alkylphenol removal including adsorption-based processes using innovative polymers, biotechnological methods, e.g., algae-based treatment and membrane bioreactor technology, and advanced oxidation methods such as catalytic oxidation. This article is an abridged version of the chapter published by Crini et al. (2021a) in the series Environmental Chemistry for a Sustainable World.

Innovative polymers

Adsorption using commercial-activated carbons is used as tertiary treatment to remove organic contaminants in general, and alkylphenols in particular, and also to reduce chemical oxygen demand and biochemical oxygen demand of wastewater. However, even though the high performance of activated carbons is widely recognized, this technology has drawbacks such as the high price of active carbons, the rapid saturation of reactors, and the need to regenerate the saturated carbon, which is also expensive, not very simple, and leads to a loss of adsorbent. Therefore, it is of interest to find new materials that can have the same performance as activated carbon without its drawbacks. Among the

materials proposed to remove alkylphenols are cyclodextrin polymers and molecularly imprinted polymers.

Adsorption of alkylphenols on cyclodextrin polymers

Cyclodextrins are natural oligosaccharides obtained by enzymatic degradation of starch. These molecules 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 (Crini 2014). Cyclodextrins also find many applications in our daily lives, from food to cosmetics, textiles, agrochemicals, chromatography, catalysis, in the packaging industry and in the veterinary field (Morin-Crini et al. 2021). In recent years, cyclodextrin polymers have been proposed as innovative materials for their ability to selectively complex contaminants substances present in complex effluents, such as dyes, aromatic compounds, chlorophenols, pesticides, and metals. These commercial polymers are also becoming very popular for the removal of trace emerging contaminants 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. 2). 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. 3).

Cyclodextrin polymers are suitable materials for several reasons. Their one-step synthesis in water in simple, easy to set up in a lab, requires only mild reactions conditions. Epichlorohydrin is not expensive and its mode of action is well understood. Epichlorohydrin 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,

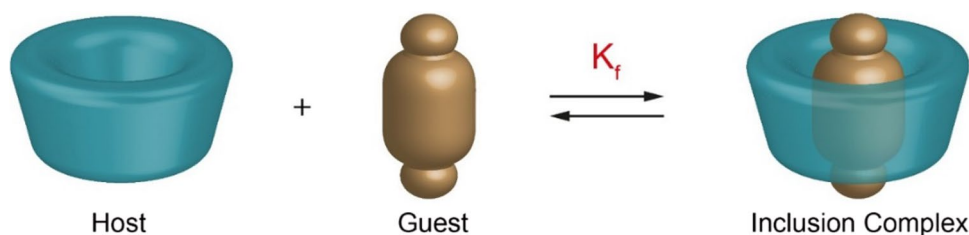
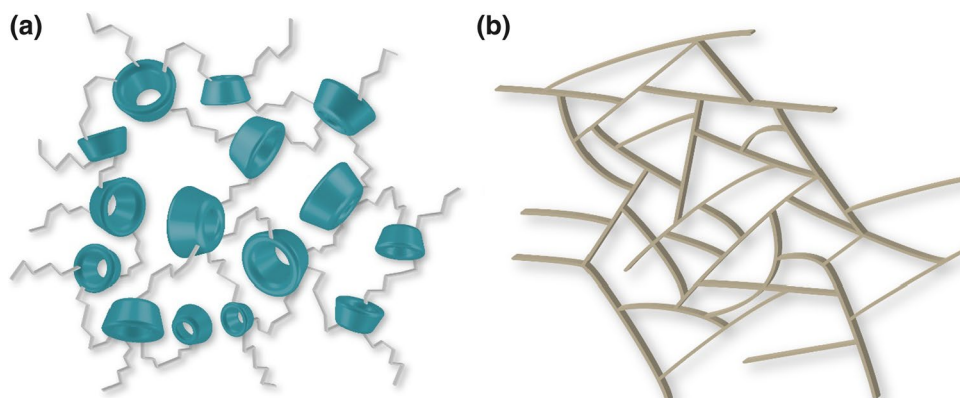


Fig. 2 Inclusion phenomena between a cyclodextrin molecule, the host, and a contaminant, the guest, to form inclusion complexes through host–guest interactions. Formation of an inclusion complex is

the result of an association/dissociation equilibrium between the free guest, the free host, and the complex, K_f being the constant of formation or stability constant

Fig. 3 Comparison of the structures of **a** a cross-linked epichlorohydrin cyclodextrin polymer and **b** a cross-linked epichlorohydrin dextran resin (Sephadex®). During the chemical synthesis to produce these structures, epichlorohydrin as high reactive cross-linking agent can form bonds with cyclodextrin molecules or dextran to form three-dimensional polymer network



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) and association complexes. Indeed, cyclodextrin molecules preserve their complexation properties in spite of the cross-linking reaction that locks the cyclodextrins into a polymer network (Morin-Crini and Crini 2013). 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. They 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: one gram of material was able to adsorb 85% of alkylphenol ethoxylate from a 150 mL solution containing 200 ppm of non-ionic 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 (Crini et al. 2021b).

Figure 5 compares the performance of five materials on the removal of several alkylphenols, present in synthetic solution at a concentration of 100 µg/L. Results show 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

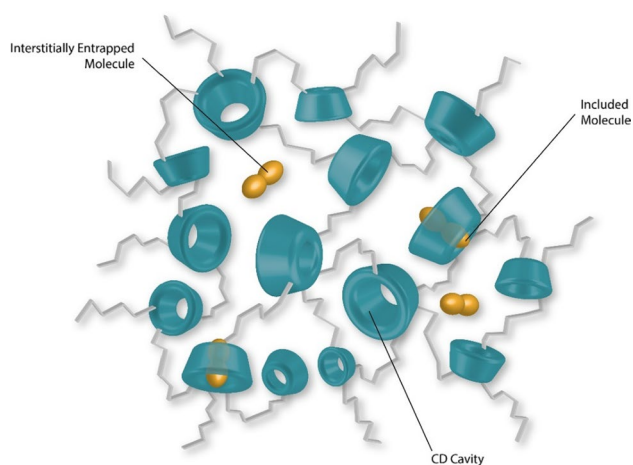


Fig. 4 Role of cyclodextrin cavities and the three-dimensional polymer network during the complexation of a pollutant by a cyclodextrin polymer. This illustration shows not only the role of cyclodextrin molecules in the adsorption mechanism but also the cooperation effect of the 3D polymer network to complex the pollutant

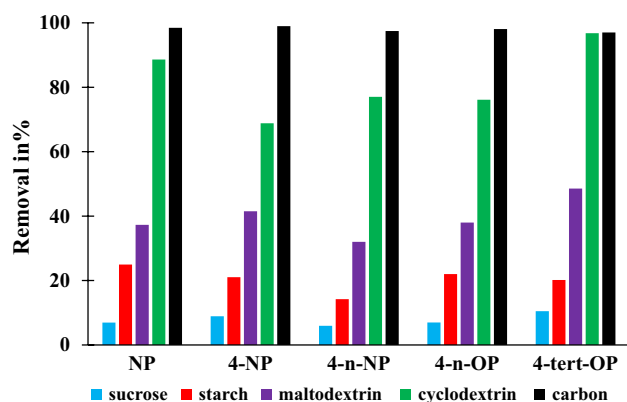


Fig. 5 Comparison of different materials for the removal of several alkylphenols. NP: nonylphenol mixture, CAS 25154–52-3. 4-NP: 4-nonylphenol mixture, CAS 84852–15-3. 4-n-NP: linear para-nonylphenol, CAS 104–40-5. 4-n-OP: linear para-octylphenol, CAS 1806–26-4. 4-tert-OP: para-octylphenol, CAS 140–66-9.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

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, less than 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. Noteworthy, even though maltodextrin do not have cavities for inclusion, maltodextrin adsorb alkylphenols, implying that the macromolecular structure should be taken into account in the adsorption mechanism.

Figure 6 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%.

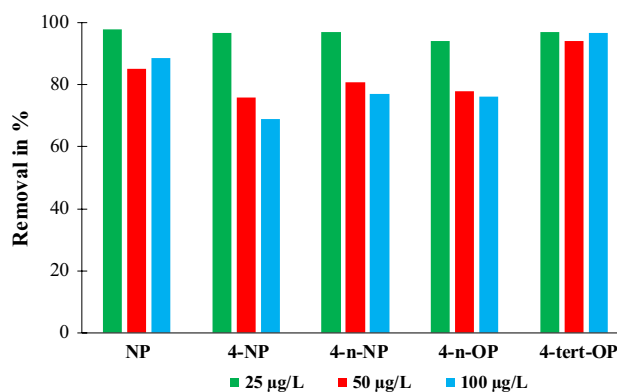


Fig. 6 Effect of initial alkylphenol concentration on the removal, expressed as abatement percentage, of five alkylphenols present in a mono-contaminated solution by a cyclodextrin polymer (NP: nonylphenol mixture, CAS 25154–52-3. 4-NP: 4-nonylphenol mixture, CAS 84852–15-3. 4-n-NP: linear para-nonylphenol,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

Figure 7 compares the removal of five alkylphenols in a mixture at three concentrations by a cyclodextrin polymer. 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. 1). 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 differences of adsorption observed for cyclodextrin polymer between alkylphenols when they were in a mixture. Figure 8 shows the effect of the presence of NaCl on the performance

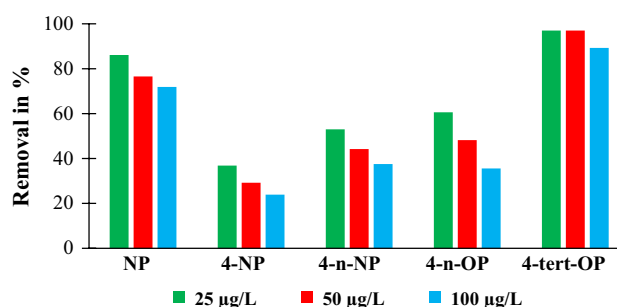


Fig. 7 Effect of initial alkylphenol concentration on the removal, expressed as abatement percentage, of five alkylphenols present in a mixture by a cyclodextrin polymer. NP: nonylphenol mixture, CAS 25154–52-3. 4-NP: 4-nonylphenol mixture, CAS 84852–15-3. 4-n-NP: linear para-nonylphenol, CAS 104–40-5. 4-n-OP: linear para-octylphenol, CAS number 1806–26-4. 4-tert-OP: para-octylphenol, CAS 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, $n = 2$

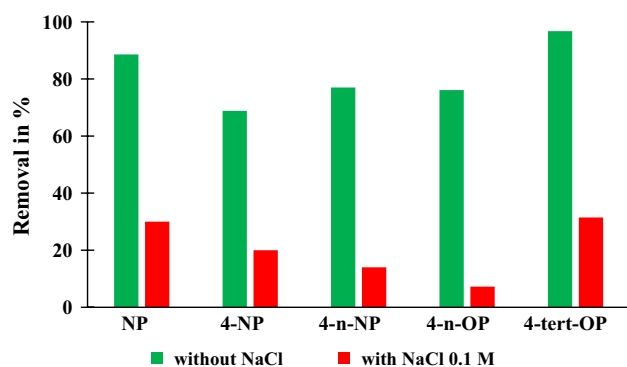


Fig. 8 Effect of NaCl on the removal, expressed as abatement percentage, of five alkylphenols present in solution by a cyclodextrin polymer. NP: nonylphenol mixture, CAS 25154–52-3. 4-NP: 4-nonylphenol mixture, CAS 84852–15-3. 4-n-NP: linear para-nonylphenol, CAS 104–40-5. 4-n-OP: linear para-octylphenol, CAS 1806–26-4. 4-tert-OP: para-octylphenol, CAS 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, $n = 1$

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.

With the exception of a few works (Charles et al. 2014, 2016), studies of real concrete cases are rare. Table 1 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, 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 (Table 1).

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.

Sequestration by molecularly imprinted polymers

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,

Table 1 Concentrations, in µg/L, of alkylphenols present in three industrial effluents before and after sorption on cyclodextrin polymer

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-n-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-n-OP	12.3	<1	32.1	1.32	5.99	0.99
4-tert-OP	7.9	<0.5	44.2	4.44	1.23	<0.5
4-tert-OP1EO	6.12	1.05	<0.1	<0.1	<0.1	<0.1
4-tert-OP2EO	<0.1	<0.1	<0.1	<0.1	0.99	<0.1

NP nonylphenol mixture, CAS 25154–52-3. 4-NP: 4-nonylphenol, CAS 84852–15-3. 4-n-NP: linear para-nonylphenol, CAS 104–40-5. 4-n-OP: linear para-octylphenol, CAS 1806–26-4. 4-tert-OP: para-octylphenol, CAS 140–66-9. Adsorbent dose 2 g/L, contact time 4 h.; agitation 250 rpm, T 25 °C, pH 6.5, $n = 1$

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 Örmeci 2012; Alvarez-Lorenzo and Concheiro 2013; Chen et al. 2015, 2016; Huang et al. 2015; Madikizela et al. 2018; Cantarella et al. 2017, 2019; Metwally et al. 2021; Parlapiano et al. 2021). 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 Örmeci 2012; Alvarez-Lorenzo and Concheiro 2013; Matějčíček 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 molecularly imprinted polymer 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 5 times. The polymers also showed high selectivity toward alkylphenols and real water samples gave satisfactory results.

Based on data from the literature, molecularly imprinted polymers have high adsorption capacities (Bagheri et al. 2021; Metwally et al. 2021; Parlapiano et al. 2021; Yusof et al. 2021). However, studies on these materials in the field of water treatment are at the laboratory stage and pilot studies need to be conducted.

Biotechnological processes

Microalgae-based technology

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; Do et al. 2022; Li et al. 2022; López-Sánchez et al. 2022; Morillas-España et al. 2022; Ricky and Shanthakumar 2022; Sousa et al. 2022; You et al. 2022). 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 (López-Sánchez et al. 2022; Morillas-España et al. 2022; You et al. 2022).

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). Other advantages can be found in the following references: Biris-Dorhoi et al. 2016, Hwang et al. 2016, Molazadeh et al. 2019, and 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. 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. However, 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.

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 removal of emerging substances such as alkylphenols is not yet systematically realized. There is also a need for research into degradation mechanisms (Do et al. 2022; Morillas-España et al. 2022; Sousa et al. 2022).

Alkylphenols remediation in constructed wetlands

Constructed wetlands in combination with the use of plants are capable of removing conventional and emerging contaminants due to the interaction between plants and microorganisms (García-Rodríguez et al. 2014; Gorito et al. 2017, 2022; Herrera-Melian et al. 2018; Osei et al. 2019; Dan et al. 2020; Kaur et al. 2020; Hassan et al. 2021; Chowdhury et al. 2022; Patyal et al. 2022; Sharma and Malaviya 2022). 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, e.g., wetland configuration, soil/substrate matrix, plant species, and hybrid systems, and operational factors, e.g., operating mode and hydraulic residence time, affect their performance. In this system, physical, chemical and biological processes, such as volatilization, adsorption, sedimentation, photodegradation, plant uptake and microbial degradation, may occur simultaneously. The occurrence of these processes depends on various factors such as the physical and chemical characteristics of pollutants, e.g., hydrophobicity, vapor pressure, and pKa, the properties of soil or substrate for the growth of plants and microorganisms, the conditions used, e.g., pH, temperature, ionic strength, and oxygen, and the seasonal variation. A challenge for constructed wetland technology is the question of the presence of so-called emerging substances such as alkylphenols and their polyethoxylated derivatives.

A great deal of research has been carried out on this topic, showing promising results for the removal of emerging substances. 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. 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.

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: (+*p*-coumaric acid) > (+*p*-hydroxybenzoic acid) = (+ferulic acid) > (+caffeic acid) > (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.

Sequential anaerobic–aerobic digestion of sewage sludge

Alkylphenol ethoxylates entering wastewater treatment plants are subjected to biotransformations producing alkylphenols, mainly nonylphenols, and their short chained ethoxylates, e.g., 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 (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 (Bragaglia 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 at T = 37 °C (Tomei et al. 2016). Since anaerobically digested sludge is at mesophilic temperature at T = 37 °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) analyzed 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 2. The mean concentration of alkylphenol ethoxylates and related metabolites in secondary sludge throughout the experimental campaign was 2.66 ± 1.88 mg/kg_{dw}, while the concentration range of the alkylphenol ethoxylates and related metabolites analyzed (referring to the period when the tests were performed) is shown in Table 3 (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 at T = 37 °C and with a sludge retention time of 15 days. The dissolved oxygen concentration in the aerobic reactor was controlled at ~3 mg/L and the aerobic sludge retention time was 12 days. A scheme of the

Table 2 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 3 Range of concentration in µg/kg_{dw} of the analyzed alkylphenol ethoxylates and related metabolites

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

LOD limit of detection in µg/kg_{dw}, dw dry weight

sequential process, with additional detailed information on the laboratory-scale installation, is given elsewhere (Tomei and Carozza 2015). Tests were conducted for both configurations: anaerobic mesophilic-aerobic at T = 20 °C (AA20) and anaerobic mesophilic-aerobic at 37 °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, the concentration pattern in the feed sludge and in digested sludge after anaerobic and aerobic digestion for the two operating conditions AA20 and AA37, was studied. Table 4 reports the corresponding removal efficiencies. Despite the high removal of volatile solid, no accumulation is observed in the digested sludge 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 analyzed, 4-tert-nonylphenol remained below the limit of detection during

Table 4 Removal efficiencies, in percentage, 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-tert-octylphenol monoethoxylate	98.5	81.4	93.6
4-tert-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-n-octylphenol	~ 100	–	–
4-tert-octylphenol	~ 100	–	–
4-nonylphenol	88.3	32.1	63.8
4-tert-nonylphenol	–	–	–

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.

Advanced oxidation processes

Removal of alkylphenols from municipal wastewater by ozone combined with 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 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 virucide, with an efficiency that depends on process parameters such as pH, presence of other substances and type 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, except when an oxidation process is specifically designed to enhance the concentration of hydroxyl radicals in a solution, e.g., during advanced oxidation processes. 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.

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 primarily attack takes place on the polyethoxylate chain and not the aromatic ring.

Ning et al. (2007a, 2007b) 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.

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.

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, 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 are applied that 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 (Parag et al. 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 O₃-H₂O₂ 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 by-products was not excluded but was not explicitly investigated.

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% (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.. Activated carbon also serves as an initiator of ozone decomposition, which increases the formation of hydroxyl radicals (Hoigne 1998; Alvarez et al. 2006; Rivera-Utrilla et al. 2011). The mechanism of this

catalytic ozonation is not completely elucidated. Jans and Hoigne (1998) reported that the reaction of ozone with activated carbon was a catalytic reaction. However, the work of Sanchez-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.

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, e.g., sonochemical

methods, photolysis, photocatalysis, electrochemistry, and Fenton process, or membrane filtration (the price of membranes has decreased significantly) 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.

Electrochemical degradation

Electrochemical techniques are a realistic option to remove alkylphenols and polyethoxylates in wastewater. These can be broadly divided into classical, e.g., electrocoagulation, electrofiltration, and electrooxidation, and advanced processes, e.g., electro-Fenton, (photo)-electrooxidation, and combined approaches. In the following overview, the research in this field is presented, mainly for the last ten years.

Electrocoagulation was applied by Henriques et al. (2012) to remove nonylphenol monoethoxylate from synthetic solutions and hospital wastewater. The process was performed with two aluminum electrodes and NaCl as supporting electrolyte at 1.5 A and 60 °C. Pseudo-first-order kinetics was established; 95% of the pollutant was removed from synthetic and 89% from hospital wastewater after 30 min of treatment. Yet, chemical oxygen demand decreased in the latter only by 26%. Transformation products with shorter ethoxylate chain (1–2 units), e.g., alkyl-phenoxy ethoxyacetic acid and alkyl-phenoxy acetic acid, were identified. Biodegradability data obtained using a manometric respirometry test showed better results in the treated solution at the beginning, but after 28 days reached the initial level of untreated solutions, i.e., 32–36%, probably because only partial degradation occurred.

Cook et al. (2016) applied electrocoagulation using aluminum electrodes for the removal of six endocrine-disrupting chemicals from spiked influent wastewater and tertiary-treated effluent from a communal wastewater treatment plant. After 20 min of treatment, nonylphenol had the highest removal ratio, which was 81% in influent wastewater and 98% in tertiary-treated effluent wastewater. The study demonstrated high removal efficiency for nonylphenol. However, there was no attempt to elucidate the mechanism of its removal or possible transformation products.

Armijos-Alcocer et al. (2017) applied electrooxidation to degrade nonylphenol ethoxylate. The pollutant was treated either in acetate buffer or ammonia buffer. In the first electrolyte, regeneration of the pollutant occurred on cathode, as shown by cyclic voltammetry. In contrast, oxidation was irreversible in alkaline buffer at anodic potentials above 1.0 V. Both direct and indirect oxidation by hydroxyl radicals was proposed. The changes in UV spectra at 200–500 nm led authors to the conclusion that quinone and hydroquinone

were formed and subsequently degraded and this was confirmed by the decrease of the total organic carbon (10% after 8 h). Authors also calculated the operational cost analysis and concluded that electrooxidation could be used to remove nonylphenol ethoxylates from wastewater.

Electrooxidation of nonylphenol decaethoxylate in textile industry wastewater was studied by Vences-Benitez et al. (2017). After 4 h of reaction, total organic carbon dropped to 26.5% and 37% for boron-doped diamond and Cu cathode, respectively. The dissolved iron from Fe cathode reacted with hydroxide and phosphate ions from wastewater, making the process less efficient. The ratio biochemical oxygen demand/chemical oxygen demand of treated wastewater in all cases indicated decreased biodegradability. The energy consumption and cost were calculated as well.

Sivri et al. (2020) studied electrooxidation of nonylphenol ethoxylate in synthetic and real wastewater, using boron-doped diamond anode and stainless steel cathode. Supporting electrolyte, initial pH, current density, and electrolysis time were optimized by response surface methodology. At optimal conditions of initial pH 8 and current density 250 A/m², NaCl as electrolyte was more efficient and fitted to zero-order kinetic model. However, electrolyte Na₂SO₄ fitted to first-order kinetic model and was a better choice for real wastewater. In synthetic and real spiked wastewaters, around 85% of pollutant was degraded in 45 min. Although authors have chosen NaCl as better supporting electrolyte, it should be noted that no transformation products were monitored.

Bozyiğit et al. (2022) used a batch type lab-scale reactor for electrooxidation of 4-n-octylphenol and 4-n-nonylphenol with titanium oxide and graphite electrodes as anode and cathode, respectively. These two alkylphenols were two of seven compounds spiked into domestic wastewater collected from the effluent of the grit chamber in an advanced biological treatment plant. Only 10 min of treatment were required to completely remove alkylphenols, the initial concentrations of which were 3–6.5 µg/L (40 times the limit of quantification). Bozyiğit et al. (2022) stated that electrooxidation was an effective wastewater treatment that achieved satisfactory removal efficiency for the selected endocrine-disrupting compounds. However, the authors did not study oxidation by-products although they used NaCl as supporting electrolyte.

Electrooxidation can be improved by coupling with other oxidation processes. In the case of electrooxidation of nonylphenol ethoxylate-10 with boron-doped diamond anode with addition of hydrogen peroxide, greater efficiency is achieved as showed by Barrera et al. (2019). Even a small amount of hydrogen peroxide (0.25 mL 30% v/w per 1.1 L of solution) acts as a promoter for the formation of hydroxyl radicals in the solution by removing 94.3% of pollutant in 375 min of treatment. The process parameters (pH, current density, quantity of H₂O₂, and reaction time) were optimized

using 4-chlorophenol as model compound. Removal of nonylphenol ethoxylate (50 ppm) was also effective in another experiment where electrooxidation with boron-doped diamond anode and stainless steel cathode in a batch reactor was combined with gamma irradiation using H₂O₂ as catalyst (Barrera et al. 2021). The combined treatment reached complete degradation (100% chemical oxygen demand removal). The authors claimed that strong oxidative species ($\bullet\text{OH}$, SO_4^- , $\text{S}_2\text{O}_8^{2-}$) were generated in situ, which made the process efficient and reliable.

Mediated electrooxidation of nonylphenol in synthetic wastewater was studied by Rodriguez-Pena et al. (2019) on boron-doped diamond anode either alone or with the addition of a chemical oxidant (H₂O₂), while cathode was stainless steel and electrolyte H₂SO₄. A DiaClean® reactor was used in recirculation mode. The dose and consumption of H₂O₂ was adjusted for the maximal production of hydroxyl radicals and minimal production of less reactive hydroperoxyl radicals. At optimal conditions, the removal of pollutant was 97.6% after 2 h of treatment, as determined by chemical oxygen demand and total organic carbon. Applicability of the approach for wastewater treatment was justified by calculation of operational costs, although the process was tested only on synthetic solutions without interferences.

Setiyanto et al. (2018) studied mediated electrochemical oxidation of nonylphenol ethoxylate with and without addition of cerium ions. Ce(III) ions were oxidized to Ce(IV), which then oxidized the pollutant. The maximum removal of 80–90% (analytical method not given) was obtained with 0.015 M Ce(III) in 0.2 M H₂SO₄ after 1.5 h of treatment. However, the removal was even slightly higher without of Ce(III) ions, although authors haven't explained these results. In another work, the same technique was applied (Setiyanto et al. 2021), but with the addition of Ag(I) ionic catalyst. The results showed that in the absence of Ag(I) catalyst, the degradation of nonylphenol ethoxylate (1500 ppm in 0.4 M H₂SO₄) by mediated electrochemical oxidation using Ce(III) ionic mediator was 85.93%, but when Ag(I) catalyst was applied, the efficiency was improved to 95.12% within 35 min.

Khosravanipour Mostafazadeh et al. (2019) treated raw laundry wastewater containing nonylphenol ethoxylates of different chain lengths with a sequential system, e.g., ultra-filtration followed by adsorption onto granular activated carbon or polymeric resin, and electrooxidation application. Electrocoagulation and electrooxidation were also applied on the concentrate after ultra- or nanofiltration. Nonylphenol ethoxylates were most efficiently removed by adsorption on both types of adsorbents, nanofiltration, and electrooxidation of the nanofiltrate, and the concentrate after nanofiltration on boron-doped diamond electrode. Electrocoagulation was less efficient for longer-chain nonylphenol ethoxylates, because their hydrophobicity decreased the adsorption on

flocs. Regeneration of laundry wastewater was most successful (80%) with nanofiltration, while the concentrate with high concentration of nonylphenol ethoxylates could be successfully further electrooxidized.

Ji et al. (2022) published an interesting study with kinetic experiments and chemical analysis, stating that micelles were responsible for inhibition of the electrooxidation of nonylphenol ethoxylates on Ti_4O_7 anode. Regardless of the inhibition, degradation efficiency of 92% was achieved. During the entire process of electrooxidation, nonylphenol ethoxylates micelles constantly grown due to solubilization, which prevented nonylphenol ethoxylates inside the micelle from being attacked by hydroxyl radicals.

Niu et al. (2020) designed a molecularly imprinted high-index facet SnO_2 (MI- $\text{SnO}_{2,\text{HIF}}$) electrode and used it in three-electrode system as working electrode, together with Pt counter electrode, reference electrode, and Na_2SO_4 as supporting electrolyte. Three similar electrodes were also tested: non-imprinted high-index facet SnO_2 , molecularly imprinted sol-gel SnO_2 , and non-imprinted sol-gel SnO_2 . The process was designed to degrade toxic and non-biodegradable chemicals, including nonylphenol, from tannery wastewater to improve its biodegradability and decrease the estrogenicity. Treatment with MI- $\text{SnO}_{2,\text{HIF}}$ electrode was the most efficient and removed 95% of nonylphenol in 8 h. The postulated mechanism was adsorption on the electrode with subsequent oxidation. Degradation pathways leading to the mineralization were proposed. Biodegradability increased, as shown by increased biochemical oxygen demand/chemical oxygen demand ratio (from 0.186 to 0.412), while the estrogenicity dropped to zero after 5 h of treatment (determined by enzyme-linked immunosorbent assay). Selective electrooxidation before biological treatment was confirmed as better option than more common reverse sequence.

Electrooxidation of industrial wastewater sludge containing an important concentration of recalcitrant pollutants, including nonylphenol, was studied by Barrios et al. (2015). Boron-doped diamond electrodes were used both as anode and cathode. Soluble chemical oxygen demand and UV/Vis spectra at 200–900 nm were measured, while concentration of pollutants was followed by gas chromatography–mass spectrometry preceded by extraction and clean-up. At optimal conditions, 89% of nonylphenol was degraded in 1 h. The same group also investigated the electrooxidation of sludge in a recirculation mode in a Diacell® reactor with boron-doped diamond electrodes (Barrios et al. 2016). Nonylphenol isomers, bisphenol A, and triclosan were among specifically monitored pollutants. The highest removal was achieved for nonylphenol isomers and was 69% after 3 h.

de Leon-Condes et al. (2017) coupled ozonation with electrooxidation to remove nonylphenol, bisphenol A, and triclosan from wastewater sludge. Each process was optimized separately. In the combined process, electrooxidation

was performed in a batch reactor with two boron-doped diamond electrodes and ozone continuously bubbled into solution. The best conditions for each process were contradictory, but the final conditions of the combined process achieved the best oxidation power and decreased soluble chemical oxygen demand by 62% and nonylphenol concentration by 68%. Degradation products were not monitored.

Barrera-Díaz et al. (2018) also studied a combination of ozonation and electrooxidation to remove nonylphenol from wastewater. It was compared to each process alone or to other advanced oxidation processes. Ozonation was the most effective at pH 7 due to formation of hydroxyl radicals. After 1 h of combined treatment, 70% removal was achieved, while the same time of ozonation alone removed only 30% of pollutant. Electrooxidation alone achieved the same removal after 2 h. Operational costs of the combined treatment were calculated and compared to UV/ozone treatment from the literature, finding that electrooxidation combination had lower costs, making it an attractive option.

Although electro-Fenton is popular for removal of pollutants from wastewater, only one paper was found for alkylphenols and their ethoxylates. Oturan et al. (2015) compared treatment of mature landfill leachates (> 10 years) by electro-Fenton and electrooxidation for removal of 55 pollutants with poor degradability, including alkylphenols and their ethoxylates. Total organic carbon removal of 87–93% was achieved in 18 h by electro-Fenton on a boron-doped diamond electrode, while on Pt electrode removal was 71–78%. Oturan et al. (2015) argued that hydroxyl radicals had increased availability on boron-doped diamond due to physisorption. Twice higher current increased the removal less than expected because of parasitic electrode reactions. The same observation was also made for electrooxidation on boron-doped diamond. Both electrochemical processes were efficient for the removal of alkylphenols and their ethoxylates: 85–100% by electrooxidation and 96–100% by electro-Fenton.

Combination of electrochemical and photolytic treatment, i.e., photoelectrooxidation, was applied by da Silva et al. (2015a) for nonylphenol ethoxylate degradation. Concentric dimensionally stable Ti/Ru $0.3\text{Ti}0.7\text{O}_2$ anode was used along with a Ti/TiO $_2$ cathode around the high-pressure mercury vapor lamp (254 nm), and Na_2SO_4 as supporting electrolyte. After 4 h of treatment, 83% of the pollutant was mineralized. Irradiation with a weaker lamp produced mainly more problematic nonylphenol. Intermediates alkylphenol and alkyl-alcohol were identified, but were later mineralized. Silva et al. (2015a) have also proposed the degradation pathway. The same group compared direct photolysis, heterogeneous photocatalysis, electrooxidation, and photo-assisted electrooxidation for degradation of nonylphenol ethoxylate from synthetic wastewater, made with commercial degreasing product ULTRANEX NP40® and with Na_2SO_4

as supporting electrolyte (da Silva et al. 2015b). After 4 h, the highest mineralization up to 83% was reached with photo-assisted electrooxidation system described previously (da Silva et al. 2015a). Phytotoxicity assays using *Lactuca sativa* and *Allium cepa* as bioindicators of treated and non-treated samples didn't show any difference. An exception were samples treated with a lower-intensity lamp, where a stable intermediate nonylphenol was formed, increasing the toxicity to *Lactuca sativa*. Cost analysis showed that the process was also economically feasible.

Fan et al. (2018) applied electrosorption and photoelectrocatalysis, which is a combination of photolysis and electrochemical catalysis, to removal of trace concentrations of nonylphenol. Three electrodes were synthesized: carbon aerogel, Bi_2WO_6 on carbon aerogel, and Bi_2WO_6 on F-doped SnO_2 . Three-electrode cell contained Na_2SO_4 as supporting electrolyte. Nonylphenol concentration was determined by extraction and high-performance liquid chromatography. In electrosorption, best adsorption was seen at potentials around 0.6 V (vs. saturated calomel electrode) and at $\text{pH} > 12$. Pseudo-first-order kinetics model of adsorption was established for $\text{Bi}_2\text{WO}_6/\text{F-doped SnO}_2$, and pseudo-second-order model for carbon aerogel and $\text{Bi}_2\text{WO}_6/\text{carbon aerogel}$. The latter electrode had the highest adsorption capacity. Nonylphenol was also degraded under simulated sunlight by photocatalytic and photoelectrocatalytic processes. Photoelectrocatalysis on the $\text{Bi}_2\text{WO}_6/\text{carbon aerogel}$ electrode was the most efficient and was therefore applied on real spiked wastewater. In spite of adsorption of matrix components, the concentration of nonylphenol still decreased to $< 1\%$ after 8 h, while total organic carbon decreased by 66.1%. Fan et al. (2019) prepared two novel electrodes: $\{0\ 0\ 1\}$ - TiO_2 electrode and TiO_2 modified with perfluoroalkyl groups, i.e., D- $\{0\ 0\ 1\}$ - TiO_2 electrode. Octyl-, nonyl-, and heptylphenol solutions were treated by photoelectrocatalysis in a three-electrode system consisting of a novel electrode, Pt counter electrode, reference electrode, and Na_2SO_4 supporting electrolyte. Xenon lamp was used to irradiate the working electrode. Fan et al. (2019) presented two experiments: static adsorption on the electrode for 2 h and photoelectrocatalytic degradation for 5 h. The perfluoroalkyl-modified electrode had similar polarity as pollutants and adsorbed them approx. twice better, as confirmed by infrared spectroscopy. Its photocatalytic current upon irradiation was also up to twice higher. Authors confirmed the possibility of selective pollutant degradation in wastewater.

Photocatalytic or photoelectrocatalytic degradation of 4-nonylphenol was performed by Xin et al. (2017) on novel WO_3/TiO_2 and TiO_2 nanotube array photoelectrodes. Electrochemical cell also contained Pt foil cathode, while anode was irradiated with a xenon lamp at 400–650 nm. Degradation was followed by high-performance liquid chromatography, and hydroxyl radical concentration was determined by

spectrofluorimetry. Effect of pH and inorganic anion addition (SO_4^{2-} , Cl^- , HCO_3^- , NO_3^-) was studied. After 2 h, removal was 80.1% and 92.3% with TiO_2 or WO_3/TiO_2 photoelectrode, respectively, while photocatalysis or electrocatalysis alone had inferior performance. The WO_3/TiO_2 photoelectrode performed better because of lower band gap of WO_3 and higher production of hydroxyl radicals. Although acidic or alkaline pH promoted the formation of hydroxyl radical, the degradation of the pollutant was the highest at neutral pH due to its decreased adsorption on electrode at alkaline pH and excess formation of oxonium ions at acidic pH. Anions inhibited the degradation of nonylphenol, mostly on TiO_2 photoelectrode, except for NO_3^- with increased negative effect on WO_3/TiO_2 . Reasons for the inhibitory effect could be hydroxyl radical scavenging, adsorption on the photoelectrode, and formation of new radical species with lower activity. The results showed that process efficiency would be different in real wastewater compared to model systems.

Nonylphenol adsorption on multi-walled carbon nanotubes was studied in a Na_2SO_4 without electricity, by applying electricity under open circuit conditions, and at different polarization potentials in a three-electrode system Li et al. (2014b). At optimal potential, a 7.9-fold increase in adsorption rate and 1.7-fold increase in adsorption capacity was achieved compared to adsorption alone. The best correlation and fit with the experimental data on adsorption was obtained with Langmuir model. Li et al. (2014b) concluded that non-electrochemical treatments for pollutant removal from wastewater can benefit from applying electricity.

Dai et al. (2017) applied electrochemical oxidation to regenerate carbon nanotubes with adsorbed nonylphenol. The best removal efficiency (mineralization to CO_2 and water) was 69% with NaCl electrolyte and RuO_2/Ti electrode. The established degradation mechanism was electroosmotic migration, followed by anodic oxidation with hydroxyl radical and hypochlorite ion in NaCl solution, or only the former in other electrolytes. Regenerated nanotubes maintained 96.2% of their initial adsorption capacity. Cost analysis was provided, accounting for electrode cost, power, and electrolyte consumption.

Electrokinetic treatment was applied to remove pollutants from solid samples, such as contaminated soil. Low direct current can cause electroosmosis, electromigration, and electrophoresis of pollutants. For example, Guedes et al. (2014) applied electrokinetic treatment to remove several contaminants, including nonyl- and octylphenol, from different soils. Electrochemical cell had two electrode compartments with platinized Ti electrodes. Soil saturated with deionized water and confined by filters was placed between them. Electrolyte NaNO_3 was percolated through compartments. Under galvanostatic conditions, hydroxyl radicals were produced. The remaining pollutants were at 17–50% or 27–48% of initial concentration for two different soils,

respectively. Nonylphenol showed slower degradation than octylphenol because of lower water solubility and lower mobility. However, the transformation products were not identified.

To conclude, electrochemical treatments showed good efficacy for the removal of alkylphenols and their ethoxylates from wastewater, landfill leachate, and contaminated soils. Electrooxidation alone or in combination with photolysis or addition of chemicals is the most popular approach due to its effectivity, speed, and cost-efficiency. The main shortcoming of the reviewed studies, however, is the lack of identification of transformation products. Mostly, it was simply assumed that the pollutants are mineralized, for example based on total organic carbon measurements.

Photocatalyst nanoparticles for the 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 and CdS/TiO_2 , 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 et al. 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) 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 benzyl dodecyl dimethyl ammonium chloride (Serpone and Pellizetti 1989; Hidaka et al. 1990; Pellizetti 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 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 mol 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.

The photodegradation of phenol and nonylphenol ethoxylates was investigated initially using only the Hg discharge lamp first. 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. The post-reaction analysis of the catalyst 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 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.

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.

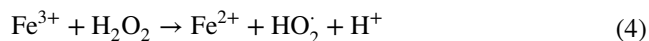
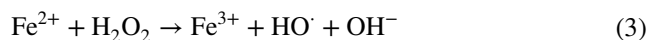
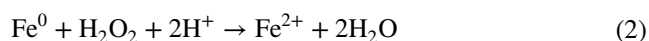
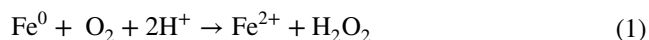
Among the advanced oxidation processes, in particular Fenton, Fenton-like and photo-Fenton processes have gained more attention due to their superior reaction kinetics and treatment efficiencies (Safarzadeh-Amiri et al. 1996; Nadochenko and Kiwi 1998; Arslan-Alaton and Teksoy 2007). Since iron-based 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 readjustment) 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 is available. 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 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, Fe²⁺ ions released from the zero-valent iron surface to the reaction bulk react with the in situ formed hydrogen peroxide and produce HO[•] and HO₂[•] 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⁺/O₂ treatment system are given in Eqs. 1–4 (Bergendahl and Thies 2004; Fu et al. 2014). Figure 9 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;

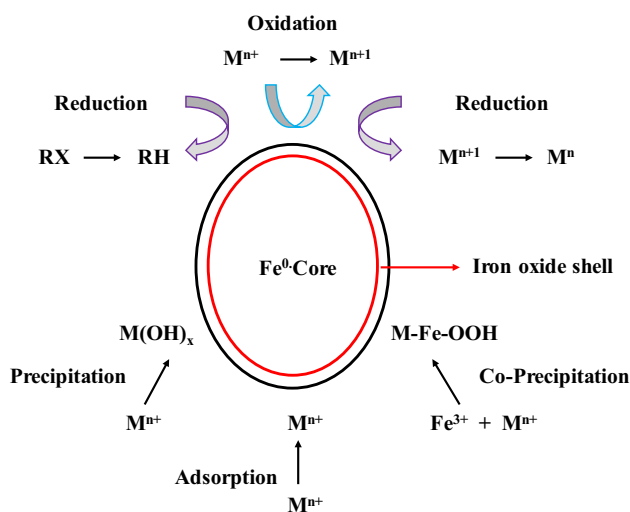
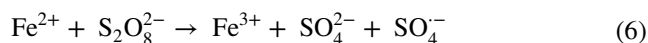
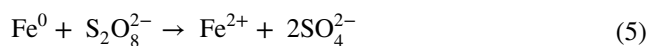


Fig. 9 Zero-valent iron surface reactions. This schematic illustration lists basic reactions of the zero-valent iron/H⁺/O₂ treatment system

Wang et al. 2011; O’Carroll et al. 2013; Trujillo-Reyes 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 U.S. Environmental Protection Agency.

Peroxydisulfate (S₂O₈²⁻) 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 (SO₄⁻) radicals which are very strong and hence reactive oxidizing agents. SO₄⁻ 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 Fe²⁺ to peroxydisulfate, continuing with a homogenous Fenton-like reaction (Eq. 6) that results in SO₄⁻ 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. (5) and (6).



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 (≤ 15% Triton™ degradation; ≤ 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.

In Table 5, Triton™ and dissolved organic carbon removal efficiencies obtained for zero-valent iron-mediated peroxydisulfate treatment are summarized for different initial pH values. It is interesting to note that with 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.

Catalytic ozonation of alkylphenols

Catalytic ozonation, i.e., the combination of a catalyst with ozone, is a promising technology for application in water treatment because of its simplicity and efficiency. Catalytic ozonation shows great advantages in removing refractory organics in water. This technique can be used either in homogeneous phase, e.g., 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 technology to degrade pharmaceuticals such as diclofenac in water, see for example 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 degradation 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 highly vulnerable to ozone attack. However, introduction of catalyst improved the extent of mineralization of the pollutant since reactive oxygen species like hydroxyl radicals originated from catalytic dissociation of ozone 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.

Conclusion

During the last two decades, alkylphenols and alkylphenol polyethoxylates, as priority hazardous substances present in aquatic compartments, have become a relevant research topic for scientists interested in water engineering issues related to their treatment, with the objective of finding technologies that are efficient, economically viable, technologically simple, and without environmental impact. This review summarizes recent trends in proposed advanced technologies for alkylphenol removal including adsorption-oriented processes, biotechnological methods, and advanced oxidation processes. The techniques such as adsorption onto cyclodextrin polymers or molecularly imprinted polymer, biodegradation using algae-based methods or catalytic ozonation, are efficient but 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. The removal of alkylphenols by biodegradation in constructed wetlands represents another promising option to treat these contaminants (Hassan et al. 2021). However, advanced oxidation processes, in association with biodegradation and/or adsorption, seem to be the technique of the future due to their efficiency (Nabgan et al. 2022; Pandis et al. 2022). In addition, these techniques can also be integrated into existing 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. However, the high costs of advanced oxidation processes still prevent their widespread use.

Table 5 Percent Triton™ and dissolved organic carbon removal obtained for zero-valent iron-mediated peroxydisulfate treatment at varying pH values in un-buffered aqueous solution

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

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)

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Declarations

Conflict of interest The authors declare no conflict of interest.

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