4. Sulfate radical based advanced oxidation processes for the removal of endocrine disrupting compounds

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Abstract. The discharge of recalcitrant organics particularly those classified as micropollutants from different industrial processes, domestic households and agricultural activities could pose serious risks to human health and ecological systems. Micropollutants such as alkylphenols, bisphenol A, dioxins, furans, pesticides, phthalate plasticizers, polycyclic aromatic hydrocarbons, certain polychlorinated biphenyls and synthetic steroids belong to the class of endocrine disrupting compounds (EDCs) and can cause adverse effects on humans and wildlife via interactions with the endocrine system. Due to the increased awareness of the risks involved with the presence of EDCs, public authorities are questioning the ability of current and developing treatment processes for effectively removing these chemicals from water and wastewater. The sulfate radical (SO$_4^{2-}$)-based advanced oxidation processes have promising potentials to be implemented for the effective treatment of organic micropollutants. In the last decades, 

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activation of persulfate (PS) to generate $\text{SO}_4^{\cdot-}$ has exhibited a great potential in the oxidative treatment of EDCs. Enhancing the effectiveness of activated PS includes manipulation of traditional methods and development of novel techniques. The present chapter summarizes basic principles and capabilities of the activated PS treatment systems for the degradation of EDCs belonging to three important industrial pollutant categories, namely bisphenol A, alkylphenols and phthalates.

**List of abbreviations and symbols**

2,4-DCP : 2,4-dichlorophenol  
AC : Activated carbon  
AO7 : Acid orange 7  
AOP : Advanced oxidation processes  
BA : Benzoic acid  
BC : Biochar  

b-CNTs : Magnetic bamboo-like carbon nanotubes  
BHA : Butylated hydroxyanisole  
BPA : Bisphenol A  
BPF : Bisphenol F  
CCD : Central composite design  
CNT : Carbon nanotubes  
COD : Chemical oxygen demand  

D : Dimensional  
DBP : Dibutyl phthalate  
DEP : Diethyl phthalate  
DES : Diethylstilbestrol  
DMP : Dimethyl phthalate  
DW : Drinking water  
EC : Electrogenerated ferrous ion  
EDCs : Endocrine disrupting compounds  
EE/O : Electrical energy per order  

$\text{E}^\circ$ : Redox potential under standard conditions  
EOF : Electroosmotic flow  
EPR : Electron paramagnetic resonance  

ETOH : Ethanol  
FTIR : Fourier transform infrared spectroscopy  
GC-MS : Gas chromatography-mass spectrometry  
GO : Graphene oxide  
HA : Humic acid  
HO$^\cdot$ : Hydroxyl radical  
HO$_2$ : Hydroperoxyl radical
1. Introduction

The presence of toxic and/or recalcitrant chemicals in the aquatic and terrestrial environment is increasingly becoming a challenging and multidisciplinary problem as new and complex-structured chemicals are
frequently being introduced into the environment. Water pollution due to the presence of recalcitrant organics particularly those classified as emerging contaminants and micropollutants (pharmaceuticals and personal care products, endocrine disrupting compounds, disinfection by-products, pesticides, etc.) lead to serious ecological and health-related impacts. Of these, an emerging group of contaminants of concern, known as endocrine disrupting compounds (EDCs) are chemicals that interfere with normal hormone activities by acting as hormone mimics, receptor agonist/antagonists, altering the synthesis and metabolism of natural hormones or modifying hormone receptor levels [1,2]. Recent estimates indicate that there are more than 80,000 chemicals currently require testing to confirm or deny their disrupting action to endocrine system [3]. To identify the list of compounds with endocrine activity, the volume of production, durability and the possibility of exposure to suspect compounds have been considered. In particular, alkylphenols used in the production of surfactants and plastics, bisphenol A (BPA) and phthalates used as plasticizers have aroused an enormous interest in the scientific community due to worldwide production, extensive use in industrial, agricultural and household applications and toxicological as well as physicochemical properties [4]. Several studies reported the frequent detection of EDCs in wastewater, surface waters, groundwater as well as in the drinking water sources [5]. Wastewater treatment plants are a well-known source and one of the most significant pathways for their transfer to the aquatic environment [6]. It is well evidenced that most of the EDCs are only partially removed through conventional water and wastewater treatment processes and therefore being detected in secondary effluents [6]. As such, advanced treatment methods including advanced oxidation processes (AOPs) have been explored and developed recently. In particular, sulfate radical (SO$_4^{\cdot -}$)-based AOPs are increasingly gaining attention as an effective solution to the destruction of recalcitrant organics in water. These processes use highly reactive SO$_4^{\cdot -}$ to oxidize organic contaminants to CO$_2$, H$_2$O and other mineralization end products. It was demonstrated that SO$_4^{\cdot -}$-based oxidation systems are also effective in a variety of applications including disintegration of activated sludge, disinfection and decontamination of groundwater and swimming pools. Most commonly, persulfate (PS) can be applied to generate SO$_4^{\cdot -}$ by either homogeneous or heterogeneous activation. Homogeneous catalysis applies thermal radiation, alkaline, ultraviolet light irradiation or transition metal ions to activate PS, while heterogeneous catalysis employs zero-valent
metals for the activation of PS. More recently, new methods i.e. electrochemical, ultrasound, microwave irradiation and the use of nonmetal carbon-based catalysts have received great deal of attention for PS activation. This chapter presents a review of the previous literature as well as an update on the latest developments in the application of PS activated treatment systems for the degradation of EDCs, with a focus on BPA, alkylphenols and phthalates as representative endocrine disruptors.

2. Activation of persulfate
2.1. Basic principles and general overview

Without activation, the common oxidant peroxydisulfate or persulfate (S$_2$O$_8^{2-}$; PS) will react with some organic chemicals, but the degree of removal would be less than that obtained using “activated persulfate” because of the relatively low oxidation potential ($E^o = 2.01$ V vs. NHE) of PS [7]. Being relatively stable at room temperature, PS can be activated by heat, transition metals, ultraviolet (UV) light, or other means, forming the highly reactive sulfate radicals (SO$_4^•$);

$$S_2O_8^{2-} + \text{activator} \rightarrow SO_4^• + (SO_4^•^- \text{ or } SO_4^{2-})$$

(1)

Alternately, PS can undergo an oxidation-reduction reaction with an electron donor from a transition metal or the radiolysis of water, generating a single SO$_4^•$;

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^-$$

(2)

Like hydroxyl radicals (HO•, $E^o = 1.89$-2.72 V vs. NHE), SO$_4^•$ have a high oxidation potential ($E^o = 2.60$ V vs NHE). Compared to HO• ($t_{1/2} = < 1$ µs), the freely-diffusible SO$_4^•$ has a longer lifetime ($t_{1/2} = 30$-40 µs) allowing excellent mass transfer and contact between SO$_4^•$ with the target pollutants [7,8]. SO$_4^•$ react with water at all pH values forming HO• which are the primary reactive species under basic conditions [9]. At pH < 7, SO$_4^•$ are the dominant reactive species; however, HO• and SO$_4^•$ participate equally in reactions at neutral pHs;

$$SO_4^•^- + H_2O \rightarrow SO_4^{2-} + HO^• + H^+$$

(3)

$$SO_4^•^- + OH^- \rightarrow SO_4^{2-} + HO^•$$

(4)
The reaction between $\text{SO}_4^{\bullet-}$ with the organic molecule is very fast, typically near diffusion controlled rate with second-order rate constants between $10^5$ to $10^9 \text{ M}^{-1} \text{s}^{-1}$ [10]. $\text{SO}_4^{\bullet-}$ react with organic molecules through hydrogen abstraction, addition on double bonds and electron transfer [9]. As $\text{SO}_4^{\bullet-}$ is electrophilic, it prefers to react with electron-donating groups such as amino- (-NH$_2$), hydroxyl- (-OH), alkoxy- (-OR) functional groups, $\pi$ electrons present on aromatic molecules and other organic compounds that contain unsaturated bonds [9]. The reaction of $\text{SO}_4^{\bullet-}$ with electron-withdrawing groups such as nitro- (-NO$_2$) and carbonyl- (C=O) substitutes is generally slower [11].

PS will also react with some organics directly, forming $\text{SO}_4^{\bullet-}$ that propagate secondary reactions or may create organic radicals, progressively decomposing the intended contaminant. Overall contaminant degradation rates are dependent on a complex series of $\text{SO}_4^{\bullet-}$-induced chain reactions;

\[
\text{S}_2\text{O}_8^{2-} + R \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{\bullet-} + R^* 
\]

\[
\text{S}_2\text{O}_8^{2-} + R \rightarrow 2\text{SO}_4^{\bullet-} + R^* 
\]

\[
\text{SO}_4^{\bullet-} + \text{HO}^* \rightarrow \text{HSO}_5^- 
\]

$\text{SO}_4^{\bullet-}$ can be scavenged by PS, $\text{SO}_4^{\bullet-}$ or transition metals (e.g. Fe$^{2+}$ and Co$^{2+}$) present in the reaction medium [12-14].

\[
\text{S}_2\text{O}_8^{2-} + \text{SO}_4^{\bullet-} \rightarrow \text{SO}_4^{2-} + \text{S}_2\text{O}_8^{\bullet} \quad k = 6.1 \times 10^9 \text{ M}^{-1} \text{s}^{-1} 
\]

\[
\text{SO}_4^{\bullet-} + \text{SO}_4^{\bullet-} \rightarrow \text{S}_2\text{O}_8^{2-} \quad k = 3.7 \times 10^8 \text{ M}^{-1} \text{s}^{-1} 
\]

\[
\text{M}^{n+} + \text{SO}_4^{\bullet-} \rightarrow \text{M}^{n+1} + \text{SO}_4^{2-} 
\]

### 2.2. Persulfate activation methods

As mentioned above, in order to enhance and facilitate reactions with contaminants, PS has to be activated with i) reduced metals (transition metals), ii) alkaline/high pH, iii) heat (thermally), iv) hydrogen peroxide (HP) and other (alternative) methods. Once activated; several types of pollutants including reduced organics (chlorinated phenols, trihalomethanes, chlorinated volatile organic carbons, chlorinated biphenyls, nitrobenzene, azo dyes, etc.), chlorinated ethenes (tetrachloroethylene, trichloroethylene, cis-dichloroethylene and vinyl chloride), oxygenates (methyl tert-butyl ether, 1,4-Dioxane, etc.) and perfluorinated acids (perfluorooctanoic acid,
heptafluorobutyric acid, etc.) can be easily degraded with SO$_4^{\bullet^-}$. Some activation methods are briefly described below.

### 2.2.1. Activation with Ultraviolet light irradiation

UV photolytic PS activation to produce two SO$_4^{\bullet^-}$ exhibits great potential for the degradation of organic pollutants [15]. The UV energy breaks the O-O bond and a quantum yield of unity has been proven for acidic, basic, and neutral conditions [12, 16]. Herrmann [17] has reported that the extinction coefficients of UV photolytic PS activation at 248, 308, and 351 nm are 27.5±1.1, 1.18±0.05, and 0.25±1.01 mol$^{-1}$ cm$^{-1}$, respectively. The formation of photo fragments (e.g., SO$_4^{\bullet^-}$) decreases as the wavelength increases due to the following reasons: UV light could provide sufficient energy to crack the peroxo bond and PS absorbs is in the UV region [18]. The most commonly utilized wavelength is 254 nm due to decreased reaction time requirements compared to other wavelengths [19-21]. The combinations of photochemical and photocatalytical oxidation show synergetic effects in TiO$_2$-, ZnO-, and WO$_3$-mediated treatment systems to maximize the degradation rate [22-25]. PS can serve as an electron scavenger in semiconductor-mediated photocatalysis system to accelerate the oxidation by increasing the quantum efficiencies through scavenging conduction band electrons and the formation of SO$_4^{\bullet^-}$ [26]. It was proven in most cases that PS was more efficient than other inorganic oxidant electron scavengers, such as H$_2$O$_2$, ClO$_3^-$, BrO$_3^-$ and IO$_4^-$ [27-30].

### 2.2.2. Activation with transition metals

PS can be activated through one-electron transfer using metals such as silver, copper, iron, zinc, cobalt and manganese forming SO$_4^{\bullet^-}$ [31-39];

\[
S_2O_8^{2-} + M^{n+} \rightarrow M^{n+1} + SO_4^{\bullet^-} + SO_4^{2-} \tag{11}
\]

(where M represents the metal ion)

The most common transition metal used for the PS activation is ferrous ion (Fe$^{2+}$). Fe$^{2+}$ can rapidly activate PS to form SO$_4^{\bullet^-}$ at a high rate constant (k) of 2.7×10$^1$ M$^{-1}$ s$^{-1}$. However, the high reduction potential of Fe$^{2+}$ ions and the high oxidation potential of the generated SO$_4^{\bullet^-}$ may initiate even stronger interaction (k=4.6×10$^9$ M$^{-1}$ s$^{-1}$) between Fe$^{2+}$ and SO$_4^{\bullet^-}$ [40];

\[
S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet^-} \quad k = 2.7\times10^1 \text{ M}^{-1} \text{ s}^{-1} \tag{12}
\]

\[
Fe^{2+} + SO_4^{\bullet^-} \rightarrow Fe^{3+} + SO_4^{2-} \quad k = 4.6\times10^9 \text{ M}^{-1} \text{ s}^{-1} \tag{13}
\]
Various chelating agents have been also used for Fe-activated PS systems due to the limited solubility of Fe$^{2+}$ at pH > 4.5. At neutral pH conditions, EDTA, citric acid or other chelates help keep Fe in solution and initiate the Fenton-like reaction. Citric acid was found to be the most effective chelating agent in applications with Fe-activated PS [41]. The real-scale application of Fe-activated PS oxidation system is well-established. However, the potential formation of trihalomethanes and Fe$^{2+}$/Fe$^{3+}$ hydroxide precipitation can be mentioned as the major limitations of this activation method [42].

2.2.3. Activation at elevated pH

PS can also be activated when the solution pH is raised to >10.5-11.0. Under these conditions, sufficient base needs to be added to account for buffering capacity of the reaction medium (water, soil) and the acids being generated during the decomposition of PS [43,44];

\[
S_2O_8^{2-} + 2H_2O \rightarrow HO_2^- + 2SO_4^{2-} + 3H^+ \quad (14)
\]

\[
HO_2^- + S_2O_8^{2-} \rightarrow SO_4^{2-} + SO_4^{2-} + H^+ + O_2^- \quad (15)
\]

\[
SO_4^{2-} + HO^- \rightarrow HO^- + SO_4^{2-} \quad (16)
\]

The reaction results in the formation of several transient oxygen species of such as SO$_4^{2-}$, HO$, ^{\bullet} O_2$, and HO$_2^-$. This activation method is relatively cost-effective and can be easily implemented. However, pH control of the reaction medium, additional costs and handling risks of alkaline reagents are the main drawbacks of this activation method [43].

2.2.4. Thermal activation

PS forms two SO$_4^{2-}$ through scission of the peroxide bond resulting from absorption of heat (>35°C for SO$_4^{2-}$; >80°C for a mixture of reactive oxygen species; ROS) energy;

\[
S_2O_8^{2-} + \text{heat} \rightarrow 2SO_4^{2-} \quad (17)
\]

The activation energy for the reaction is 119-129 kJ mol$^{-1}$, 134-139 kJ mol$^{-1}$ and 100-116 kJ mol$^{-1}$ under neutral, basic and acidic conditions, respectively [31]. It is a simple and highly efficient activation technique which allows the remediation of contaminants in a shorter period of time
Sulfate radical based advanced oxidation processes for the removal of EDCs [45-50]. Depending on the application pH, either $\text{SO}_4^{2-}$ ($<7, 8$) or $\text{HO}^{\cdot}$ become dominant in the reaction medium [51]. Before considering the application of heat treatment, it should be taken into account that many organic contaminants have higher solubility at elevated temperatures and high temperature can also accelerate volatilization processes [7,49]. Cost, health and safety issues related with heat sources should also be taken into account prior to implementation [7,8].

2.2.5. Activation with heterogeneous catalysts

The heterogeneous oxidation system is advantageous over the homogeneous one because (i) the solid heterogeneous catalyst can be easily separated from the treated water and reused, (ii) a secondary treatment method to remove dissolved metal ions from the effluent is not required and (iii) it is more tolerant towards extreme operating conditions. The heterogeneous system is effective over a broader pH (typically in the range of pH 2-9), whereas in the homogeneous system, the dissolved catalyst may precipitate at neutral to basic pH thereby decreasing its performance [52,53].

PS activation by a heterogeneous catalyst, most commonly zero-valent iron (ZVI, Fe$^{0}$), consumes the catalyst through the irreversible conversion of Fe$^{0}$ (ZVI) to Fe$^{2+}$ and Fe$^{3+}$. The mechanism of PS activation via ZVI involves direct electron transfer from the ZVI or surface-bound Fe$^{2+}$ to PS, continuing with a homogenous Fenton-like redox reaction that involves $\text{SO}_4^{2-}$ production in the reaction bulk [54]. Other iron compounds were also used as heterogeneous catalysts for PS activation (ie. core-shell Fe-Fe$_2$O$_3$ nanostructure, Fe$_3$O$_4$, polyhydroquinone/Fe$_3$O$_4$, FeS$_2$) [35,40,42,55-57]. Some other metals such as zero-valent aluminum (ZVA) or copper oxide (CuO) have also proven to be efficient catalysts for PS activation [58-61];

$$2\text{Al}^{0} + \text{S}_2\text{O}_8^{2-} + 6\text{H}^{+} + 1.5\text{O}_2 \rightarrow 2\text{Al}^{3+} + 2\text{SO}_4^{\cdot} + 3\text{H}_2\text{O} \quad (18)$$

However, metal ion leaching from heterogeneous catalysts during PS activation poses a serious concern since many metals are toxic and potentially carcinogenic [62]. In order to avoid leaching and other ecotoxicological risks, the research has more recently shifted towards the use of alternative, non-metal catalysts. Today, the investigation of non-metal catalysts has mainly focused on carbon-based materials because they are relatively abundant and have tremendous potential for practical application. Non-metal, carbon-based catalysts such as activated carbon (AC), graphene oxide (GO), reduced graphene oxide (rGO), and carbon nanotubes (CNTs) provide a potential solution to the metal leaching problem [30,62-65].
It has been suggested that AC containing oxygen functional groups may act as a catalyst of the electron-transfer mediator [18];

\[
\text{AC}_{\text{surface}} - \text{OOH} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{AC}_{\text{surface}} - \text{OO}^* + \text{SO}_4^{2-} + \text{HSO}_4^- \tag{19}
\]

\[
\text{AC}_{\text{surface}} - \text{OH} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{AC}_{\text{surface}} - \text{O}^* + \text{SO}_4^{2-} + \text{HSO}_4^- \tag{20}
\]

Recently, it has been demonstrated that pristine multi-walled CNTs (MWCNTs) could effectively activate PS to produce \(\text{SO}_4^•\) [66];

\[
\text{CNT-C}=\text{O} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{CNT-C} - \text{O}^* + \text{SO}_4^{2-} + \text{SO}_4^{2-} \tag{21}
\]

The effective catalytic active sites for rGO are the oxygen functional groups such as the nucleophilic ketonic and quinoidic groups which both have a high electron density and can mediate redox reactions. Comparing different pristine nanocarbon materials, it was reported that the 3-D hexagonally-ordered mesoporous carbon was superior over other nanocarbon materials with different structural dimensions (i.e. 0-D fullerence, 1-D single-walled carbon nanotube, 2-D graphene nanoplate, and cubically-ordered mesoporous carbon) owing to its higher surface area and edge defects with high density of electronic states, which as a key factor to electron transfer reactions [7, 8]. Nanocarbons with various kinds of active sites and networks present different capabilities for PS activation, water, and organic pollutant adsorption and electron transfer, thus presenting different performances in PS activation and organic matter degradation [67].

2.2.6. Activation with electrochemical methods

The electrochemical activation of PS by electrically produced Fe using sacrificial Fe or stainless steel electrodes has recently emerged as an inexpensive alternative to generate \(\text{SO}_4^•\). Electrochemical reactions generate the \(\text{SO}_4^•\) at the cathode following the same mechanism as the one-electron transfer redox reaction for Fe-activated PS [68]. Solid iron produces \(\text{Fe}^{2+}\) through chemical and anodic reactions, activates the PS, and can be regenerated at the cathode for additional PS activation [69]. It has been also suggested that PS could be regenerated at the anode after completion of an activated PS degradation reaction [70-74]. In conjunction with cathodic activation, this would perpetuate a source of \(\text{SO}_4^•\) [73]. The advantages of continuous generation of \(\text{Fe}^{2+}\) and \(\text{SO}_4^•\) via electrochemical and
electrocoagulation methods has been reported by some authors for the degradation of phenol and pentachlorophenol.

\[ \text{SO}_4^{2-} + \text{SO}_4^* \rightarrow \text{S}_2\text{O}_8^{2-} + e^- \]  \hspace{1cm} (22)

Combining electrochemistry and electrochemically-activated PS may achieve superior removal results compared to each technique alone, thus reducing PS and/or electricity usage [75]. However, additional studies are needed in order to elucidate which electrode materials, including those commonly used for the degradation of organic pollutants (boron-doped diamond, Ti/RuO_2-IrO_2 and Ti/SnO_2-Sb), are best suited for the activation PS, as well as the relationship between current density and activation.

### 2.2.7. Activation with ultrasound

Among several AOPs, ultrasound (US; 20-1000 kHz) can serve as source of HO^* and other ROS through the cyclic formation, growth and implosive collapse of microbubbles in a liquid resulting in an unusual reaction environment within and in the vicinity of bubbles [76-78]. The bubble collapse causing temperatures of several thousand Kelvin and pressures of several hundred atmospheres therein which induces the pyrolysis of water vapor, oxygen molecules and volatile organic compounds that can be present in the gas phase [79-81]. Pyrolysis of water vapor yields HO^* and hydrogen atoms. These active species can recombine, react with other gaseous species present in the cavity to form other ROS such as HO_2^*, O_2^*, or diffuse out of the bubble into the bulk liquid to serve as oxidants [80,82]. More recently, the combination of US and PS has received much attention as a potential alternative for the treatment of recalcitrant hazardous compounds [83]. US/PS using low frequency US (20-100 kHz) has been widely investigated and proved to be effective for removing several kinds of pollutants such as dyes, pharmaceuticals, EDCs, chlorinated aliphatic hydrocarbons, aromatic hydrocarbons, heavy metals, etc. [84-90]. In the presence of PS and the pollutant in the sonicating medium, cavitationally generated HO^* and hydrogen atom can react with PS and produce highly reactive SO_4^* [83,91]. In addition, PS can also undergo homolytic cleavage at the bubble liquid interface by the heat generated during bubble collapse. This interface temperature (estimated to be at 1900 K) is largely above temperatures necessary for PS decomposition (generally > 50°C). Once it
forms, $\text{SO}_4^{\cdot\cdot}$ can further react with $\text{H}_2\text{O}$ to produce more $\text{HO}^{\bullet}$ in the solution [91,92]. Therefore, PS is a source of both $\text{SO}_4^{\cdot\cdot}$ and $\text{HO}^{\bullet}$ in the US/PS treatment system [80], which simultaneously enhances micropollutant degradation and induces a new degradation pathway, which are the chain reactions involving $\text{SO}_4^{\cdot\cdot}$.

### 2.2.8. Activation with microwaves

Activation via microwave (MW) irradiation is another form of thermal PS activation [93]. The primary step occurring in MW-activated PS is the production of $\text{SO}_4^{\cdot\cdot}$ by MW radiation involving the thermal rupture of the O-O bond which was reported to be 33.5 kcal mol$^{-1}$ (140.2 kJ mol$^{-1}$) [9]. Besides $\text{HO}^{\bullet}$ may be produced because of the interaction of $\text{SO}_4^{\cdot\cdot}$ with OH$^{-}$ or $\text{H}_2\text{O}$ depending upon the pH. Both $\text{SO}_4^{\cdot\cdot}$ and $\text{HO}^{\bullet}$ may participate in the degradation of organic molecules.

### 3. Case studies for activated persulfate-mediated AOPs

#### 3.1. Bisphenols

Girit et al. [94] investigated the use of a commercial, air-stable ZVI powder, consisting of Fe$^0$ surface stabilized nanoparticles for the treatment of 20 mg/L, aqueous BPA solutions. In their study the influence of reaction pH (3, 5 and 7), addition of HP and PS oxidants (0.0, 1.25 and 2.5 mM) as well as temperature (25 and 50°C) was studied for BPA treatment with ZVI. ZVI coupled with PS provided an effective treatment system as a consequence of rapid $\text{SO}_4^{\cdot\cdot}$ formation by a Fenton-like reaction between the released $\text{Fe}^{2+}$ and PS. Complete BPA degradation (in 5 min) accompanied with a significant TOC removal (88% in 120 min) was achieved with ZVI/PS treatment (BPA =20 mg/L; TOC= 16 mg/L; ZVI=1 g/L; PS =1.25 mM; pH=5.0; T = 50°C).

In the study of Huang and Huang [95] a two-stage oxidation (UV-$\text{Na}_2\text{S}_2\text{O}_8$/$\text{H}_2\text{O}_2$-$\text{Fe(II,III)}$) process was applied to mineralize BPA at initial pH of 7. They took advantage of the high oxidation potential of $\text{SO}_4^{\cdot\cdot}$ and use PS as the first-stage oxidant to oxidize BPA to less complex compounds. Afterwards, the traditional photo-Fenton process was used to mineralize those compounds to CO$_2$. During the second-stage reaction, other oxidants (HP and Fe alone) were also employed to observe the extent of enhancement of photo-Fenton. Experimental results for the qualitative identification of both $\text{HO}^{\bullet}$ and $\text{SO}_4^{\cdot\cdot}$ indicated that such a small dosage of
oxidant $([S_2O_8^{2-}]_0/[BPA]_0 = 1)$ was sufficient to produce $SO_4^{\cdot}$ which can be detected from electron paramagnetic resonance (EPR) treatment (with 5,5-dimethyl-1-pyrroline-N-oxide, DMPO) after few minutes ($\approx$6min), directly verifying that these expected strong radicals ($SO_4^{\cdot}$ and $HO^{\cdot}$) were both present in the reaction solution to oxidize BPA. In this study the effects of temperature and the activation energy of the investigated BPA degradation system were also studied. BPA degradation rates was improved under thermally enhanced conditions resulting in the degradation of BPA after 1 h being $\approx$88% at 25°C, $\approx$96% at 35°C, and $\approx$99% at 50°C, respectively ($[BPA]_i = 0.05\text{mM, } [PS]_i = 0.05\text{mM}$). The BPA degradation by UV/PS process formulated a pseudo-first order kinetic model well, with a rate constant of approximately 0.038 min$^{-1}$ (25°C), 0.057 min$^{-1}$ (35°C), and 0.087 min$^{-1}$ (50°C), respectively. The single use of the PS process reached the efficacy of total decomposition of BPA, but very rarely for TOC removal. The addition of HP (or Fe(II,III)) contributed to a $\approx$25% TOC removal (or 25-34% TOC removal). This was due to the additional UV/HP process, or the additional activator (Fe(II,III)) for decomposing remaining PS to $SO_4^{\cdot}$ more completely as in the second-stage processes ($[BPA]_i = 0.05\text{mM, 5mM, } [Fe(II,III)]_i = 0.045\text{mM, and } [HP]_i = 0.1579\text{mM}$. $T = 25$°C). High TOC removals (87-91%) was achieved in the Fe(II,III)/HP promoted second-stage process: it indicated that the photo-Fenton (UV/Fe(II,III)/HP) could proceed successfully from initial pH 7 by the combination of the PS process. Only a minimum molar ratio of $[S_2O_8^{2-}]_0/[BPA]_0 = 1$ is required from the neutral initial pH (=7) condition to promote the traditional Fenton’s reagents $([Fe(II,III)]_0/[H_2O_2]_0 < 1$ and a theoretical oxygen demand (ThOD) of $[H_2O_2]_0/[BPA]_0$ utilized during the proposed 2$^{nd}$-stage oxidation process as pH< 4. Final TOC removal levels of BPA by the use of such two-stage oxidation processes were 25-34%, 25%, and 87-91% for additional Fe(II,III) activation, HP promotion, and Fe(II,III)/HP promotions, respectively.

The removal of BPA by a novel "electro/Fe$^{3+}$/ peroxydisulfate’’ process was studied by Lin et al. [96]. In their study the effects of initial pH (3.0, 6.0 and 9.0), electrolyte (sodium sulfate, Na$_2$SO$_4$) concentration (50, 100 and 200 mM), Fe$^{3+}$ concentration (1, 2 and 4 mM), PS concentration (1, 5, 10 and 20 mM) and current density (8.4, 16.8 and 33.6 mA/cm$^2$) were investigated. BPA removal efficiency decreased with an increase of initial pH and electrolyte concentration, while it increased with the increase of Fe$^{3+}$ concentration and current density. The BPA
degradation efficiency was improved significantly when PS concentration increased from 1 to 10 mM, but a further increase in PS concentration did not enhance BPA removal anymore. In order to investigate the mineralization efficiency of BPA during the EC/Fe\(^{3+}\)/PS process, the change of TOC concentration was also examined (BPA=0.22 mM, Na\(_2\)SO\(_4\)=50 mM, Fe\(^{3+}\)=4 mM, PS=20 mM, current density=33.6 mA/cm\(^2\), pH=3.0). The TOC removal efficiency was 83.1\% at 60 min compared with 99.8\% of BPA degradation efficiency. By extending the reaction time to 120 min, the TOC removal efficiency increased to 94.3\% but never reached 100\% due to the presence of highly recalcitrant organic acids.

In the study of Olmez-Hanci et al. [97], thermally activated PS oxidation process was investigated to treat aqueous BPA (20 mg/L, 88 \(\mu\)M) solution. The effect of temperature (40-50-60-70°C), initial pH (pH = 3.0, 6.5, 9.0 and 11.0) and PS concentration (0-20 mM) on BPA and TOC removals was examined. After optimization of the treatment performance, BPA degradation products that were formed during hot PS oxidation were quantified via gas chromatography-mass spectrometry (GC-MS) to examine the relationship between PS oxidation products and acute toxicity patterns. Increasing the treatment temperature (40-70°C) resulted in a significant enhancement of BPA and TOC removals. The activation energy for hot PS oxidation of BPA was calculated as 184 \(\pm\) 12 kJ mol\(^{-1}\). Acidic and neutral pH values were found to be more favorable for BPA oxidation than basic pH values. TOC removals did not exhibit a specific pattern with varying initial pHs. Several aromatic and a few aliphatic compounds could be detected including benzaldehyde, p-isopropenyl phenol, 2,3-dimethyl benzoic acid, 3-hydroxy-4-methyl-benzoic acid, ethylene glycol monoformate and succinic acid. Acute toxicity tests conducted with Vibrio fischeri (V. fischeri) indicated that the inhibitory effect of 88 \(\mu\)M BPA solution originally being 58\%, increased to 84\% after 30 min and decreased to 22\% after 90 min hot PS treatment that could be attributed to the formation and subsequent disappearance of oxidation products.

Jiang et al. [98] evaluated the degradation of BPA with SO\(_4^{2-}\) which was generated by the activation of PS with Fe\(^{2+}\) and iron powder (Fe\(^0\); a slow-releasing source of dissolved Fe\(^{2+}\)). BPA removal efficiency was improved by the increase of initial PS or Fe\(^{2+}\) concentrations and then decreased with excess Fe\(^{2+}\) concentration. With the increase of PS concentration, BPA removal rate improved from 15\% (0.2 mM PS; S\(_2\)O\(_8^{2-}\)::Fe\(^{2+}\); molar ratio=1:1) to 45\% (2 mM PS; S\(_2\)O\(_8^{2-}\)::Fe\(^{2+}\); molar ratio=10:1) within 120 min reaction. The highest BPA removal rate (49\%) was observed when Fe\(^{2+}\)
concentration was 1.6 mM ($S_2O_8^{2-}$:Fe$^{2+}$, molar ratio=5:4). The addition mode of Fe$^{2+}$ had significant impact on BPA degradation and mineralization. BPA removal rates increased from 49% to 97% with sequential addition of Fe$^{2+}$, while complete degradation was observed with continuous diffusion of Fe$^{2+}$, and the latter achieved higher TOC removal rate. When Fe$^0$ was employed, 100% of BPA (80 µM) degradation efficiency was achieved and the highest removal rate of TOC (85%) was obtained at the initial pH of 5.9, 2 mM PS and 8 mg/L iron powder concentrations within 2 h reaction.

Wang et al. [99] examined nitrogen modified reduced graphene oxide (N-rGO) which was prepared by a hydrothermal method was used as a bifunctional material for the removal of BPA and bisphenol F (BPF). The synergistic effect between adsorption and catalysis was also investigated in this study. The results showed that the nitrogen modification enhanced the adsorption and catalysis ability of rGO. For an initial BPA and BPF concentrations of 0.385 mM, the adsorption capacity of N-rGO was found as 1.56 and 1.43 mmol g$^{-1}$ for BPA and 1.43 mmol g$^{-1}$ for BPF, respectively, both of which were about 1.75 times that (0.90 and 0.84 mmol g$^{-1}$, respectively) on N-free rGO. The heterogeneous system of N-rGO and PS was found to be efficiently adsorb and oxidize bisphenols. The apparent degradation rate constant of BPA on N-rGO was 0.71 min$^{-1}$, being about 700 times that (0.001 min$^{-1}$) on N-free rGO. A simultaneous use of N-rGO and PS yielded fast and efficient removal of bisphenols. The use of N-rGO (120 mg/L) and PS (0.6 mM) almost completely removed the added BPA and BPF (0.385 mM) at pH=6.6 within 17 min. It was found that the pre-adsorption caused a TOC removal of 50%, and the combination of the pre-adsorption (10 min) and the degradation (30 min) achieved a TOC removal of more than 90% at the above mentioned reaction conditions. The promoted adsorption and catalytic performances of N-rGO were attributed to the doping of N, which functioned as active sites for both the adsorption of bisphenols and the activation of PS, producing surface-bound SO$_4^{2-}$.

Sharma et al. [100] investigated the removal and mineralization of BPA at a concentration of 0.22 mM in aqueous solution using inorganic oxidants (HP and PS) under UV irradiation at a wavelength of 254 nm and 40 W power ($I_0 = 1.26 \times 10^6$ E s$^{-1}$) at natural pH conditions and a temperature of 29±3°C. In this study with an optimum PS concentration of 1.26 mM, the UV/PS process resulted in ~95% BPA removal after 240 min of irradiation (oxidant:BPA; molar ratio=5.7:1). The optimum BPA removal was found to be ~85% with a HP concentration of 11.76 mM.
(oxidant:BPA; molar ratio=53.4:1). The UV/PS oxidation system, even though having a 10 times lower PS:BPA molar ratio than that of UV/HP system, resulted in a 10% higher BPA removal. At higher concentrations, either of the oxidants showed an adverse effect because of the quenching of the HO• or SO₄•⁻ in the BPA solution. The mineralization of BPA in terms of TOC removal was found to be higher (55%) for UV/PS than that of UV/HP system (38%) at their respective optimum molar ratios. The UV/PS treatment system, thus, shows higher mineralization efficiency than the UV/HP treatment system. This was attributed to the higher stability of the SO₄•⁻ and their higher selectivity than that of HO• for BPA. The authors concluded that The SO₄•⁻-based oxidation process was found to be effective over a wider initial pH range of 3-12, on the other hand the HO•-based oxidation of BPA should be carried out in the acidic pH range only. The water matrix components bicarbonate, chloride and humic acid showed higher scavenging effect in HO•-based oxidation than that in the SO₄•⁻-based oxidation of BPA. UV/PS oxidation system utilized less energy (EE/O electrical energy per order of pollutant removed) in comparison to UV/HP system. The EE/O was found to be 307 kWh m⁻³ at an oxidant:BPA molar ratio of 5.7:1 for UV/PS system, with a cost of about 20 USD m⁻³. However, the UV/HP system required 509 kWh m⁻³ at an optimum molar ratio of 53.4:1 at a cost of 30 USD m⁻³.

In another study of Sharma et al. [101] photo-oxidation of BPA with HP and PS was explored. UV-C light (254 nm wavelength, 40 W power) was applied to BPA contaminated water at natural pH under room temperature conditions. Experiments were carried out with the initial BPA concentration in the range of 0.04 mM-0.31 mM and the oxidant:BPA molar ratio in the range of 294:1-38:1 for UV-C/HP and 31.5-4.06:1 for UV-C/PS systems. The degradation kinetics was well represented by pseudo-first-order rate equations and the rate constant (k) for both the oxidants was found to increase with a decrease in the BPA concentration, and was found to be 0.005 min⁻¹ for UV-C/HP (HP:BPA; molar ratio=53.4:1) and 0.009 min⁻¹ for UV-C/PS (PS:BPA; molar ratio=5.7:1) system. Competition of BPA for reaction with HO• or SO₄•⁻ at its higher concentrations resulted in a decrease in the removal of BPA. The degree of mineralization of BPA was also found to be more for UV-C/PS (55%) system than that for UV-C/HP (38.3%) system (HP=11.76 mM; PS=1.26 mM; T=29±3°C). Effective TOC removal by SO₄•⁻-mediated AOP revealed the selectivity and stability of these radicals and exemplified
Sulfate radical based advanced oxidation processes for the removal of EDCs

its efficacy over conventional HO•-based oxidation methods. During identification of intermediates and the end-products of the investigated oxidation systems, various compounds were observed in the reaction mixture. The hydroxylated by-products were observed for UV-C/HP system providing the evidence of hydroxylation reaction mechanism. In case of SO₄²⁻ (UV-C/PS)-based oxidation process, the formation of intermediates like quinone of monohydroxylated BPA (Q-MHBPA), quinone of dihydroxylated BPA (Q-DHBPA) and phenoxy phenols confirmed one electron transfer mechanism and the hydroxycyclo hexadienyl and phenoxy radical based degradation pathway for BPA.

Darsinou et al. [92] explored the combined effects of US and PS on the kinetics of BPA degradation in relation to various operating conditions such as US power, substrate concentration at the low µg/L level, solution temperature, pH and the water matrix. Experiments were performed at 110-450 µg/L BPA and 1-100 mg/L PS concentrations and an US power density between 4 and 60 W/L. The liquid bulk temperature was either kept constant at 30°C or left uncontrolled and gradually increased to 80°C. As the authors suggested, BPA degradation occurred due to the combined action of HO• generated by the US and SO₄²⁻ generated by PS sonolysis and this was confirmed with experiments with methanol (MA) and tert-butyl alcohol (TBA) as radical scavengers. Considerable thermal PS activation was also occurred at increased temperatures (60-80°C) although the enhanced formation of SO₄²⁻ compensated by a decrease in sonochemical activity. Pseudo-first order expression with the apparent rate constant (k_app, in min⁻¹) decreased with increasing BPA concentration. The BPA removal rate increased with increasing power density and PS concentration and decreased under alkaline conditions (i.e. pH=9). To assess the effect of water matrix, experiments were conducted in drinking water (DW), in ultra pure water (UPW) spiked with humic acid (HA) at two concentrations (17.5 and 35 mg/L), as well as in secondary treated wastewater (WW); in all cases, the BPA concentration was 225 µg/L, the PS concentration 10 mg/L and the power density 20 W/L at 30°C. BPA degradation was found to decrease in the order: UPW (54.8×10⁻³)>DW (30.7×10⁻³)>HA (22.2×10⁻³)>WW (9.4×10⁻³) with numbers in brackets corresponding to the apparent first order rate coefficient k_app (min⁻¹). Identification of oxidation intermediates was also carried in this study and liquid chromatography-time of flight-mass spectrometry (LC-TOF-MS) analysis revealed the formation of 12 transformation by-products. Based
on their evolution profiles, a reaction mechanism was proposed as: (i) hydroxylatation that could occur mainly in the aromatic ring through HO\(^*\), SO\(_4\)\(^*\) attack and to a lesser extent in methyl groups, through hydrogen abstraction by HO\(^*\), with subsequent O\(_2\) addition, and (ii) scission of the bond between the isopropylidene carbon and the phenyl group.

In the study of Akbari et al. [102], BPA was removed using electro-generated ferrous ion (EC) activated ozone (O\(_3\)), HP and PS. The effects of operating parameters such as pH (3.0-9.0) current density (0.2-1.0 mA/cm\(^2\)), oxidant concentration (2-8 mM for PS and HP, 122-189 mg/L for O\(_3\)) and time (0-50 min) were evaluated on three systems of EC/HP, EC/PS and EC/O\(_3\). The acidic conditions (pH = 3.0-5.0) was found to be suitable for all the processes. Increase in current density had an inhibition effect on EC/O\(_3\) and EC/HP systems while BPA removal efficiency was limited by excessive oxidant dosage in EC/PS system. Under optimum conditions, removal efficiencies of BPA were 97%, 72% and 84% for EC/O\(_3\) (pH = 5.0, 0.6 mA/cm\(^2\) current density and 162 mg/L O\(_3\)), EC/PS (pH = 5.0, 1.0 mA/cm\(^2\) current density and 6 mM PS) and EC/HP (pH = 3.0, 0.8 mA/cm\(^2\) current density and 8 mM HP), respectively. Electrochemical degradation of BPA in a divided cell proved that O\(_3\) was activated by both anode and cathode reactions while HP and PS were activated only in anode compartments endorsing HP and PS catalytic activation by ferrous ion. In addition, it was demonstrated that SO\(_4\)\(^*\) was the major oxidant in EC/PS while HO\(^*\) was the main agent in EC/HP and EC/O\(_3\) treatment systems. The results showed that EC/O\(_3\) exhibited the best performance in the degradation of BPA compared to others. Among the EC/oxidant systems, EC/O\(_3\) yielded the highest TOC removal efficiency (56.9%) and the sole application of O\(_3\) was more effective than sole application of other oxidants. The order of TOC removals was EC/O\(_3\) > EC/HP > EC/PS > O\(_3\) > EC > PS > HP. Moreover, the effects of chloride ion on the performance of three systems were investigated in this study by adding NaCl salt instead of Na\(_2\)SO\(_4\) as the supporting electrolyte (0.01 M) and the related results displayed a slight increase in BPA removal efficiencies. The electrochemical sludge generated was reused for activation of the oxidants as HP and PS were noticeably activated while no effect was observed on ozone application.

Degradation of BPA in aqueous solution was investigated by Yang [103] using the Fe(II)-activated PS oxidation process, electrochemical
process, electrochemical process with 2.5 mM PS without Fe(II), and electrochemical assistant Fe(II)-activated PS process. It was found that the electrochemical assistant Fe(II)/PS process performed best in the degradation of BPA. The variables considered to influence the degradation efficiency of BPA were the initial concentration of Fe\(^{2+}\), the initial concentration of PS, and the current density. More than 97% of the BPA removals were achieved within 120 min under the optimum operational condition (BPA=35 mg/L, Fe\(^{2+}\)=1.0 mM, PS=2.5 mM, current density=3.6 mA/cm\(^2\), pH=neutral, T=ambient). The degradation of BPA was accompanied by the formation of phenol, hydroquinone, and small-molecule compounds such as succinic acid. The electron transfer was found to be the principal step in the oxidation of BPA.

Zhao et al. [104] conducted a set of experiments in order to investigate simultaneous removal of BPA and phosphate in ZVI activated PS oxidation process. In their study, it was demonstrated that BPA and phosphate could be simultaneously removed via this system. BPA degradation was accelerated with increased ZVI dose and initial PS concentration. BPA degradation was slightly inhibited in the presence of phosphate due to scavenging of SO\(_4^{2-}\). Eight transformation products were identified using GC-MS. SO\(_4^{2-}\)-induced oxidative transformation of BPA included electron transfer and hydrogen abstraction mechanisms. Carbonate exhibited no obvious influence on the removal both of phosphate and BPA. Natural organic matter showed inhibitory effect on BPA degradation but had no appreciable negative effect on phosphate removal.

In the study of Wang et al. [105] novel magnetic bamboo-like carbon nanotubes (b-CNTs) were fabricated and applied as both the adsorbent and the catalyst for the removal of BPA. The obtained b-CNTs exhibited a large specific surface area (157.3 m\(^2\)/g), large pore volume (0.444 cm\(^3\)/g) and mesoporous structure (pore size of 3.8 nm). The b-CNTs showed excellent adsorption properties toward BPA with the maximum adsorption capacity of 328.6 mg/g at 303 K. The results of the study indicated that b-CNTs can act as the catalyst for the activation PS, producing a large number of highly reactive surface-bound SO\(_4^{2-}\). With the synergistic effect of adsorption and catalysis by the b-CNTs (0.2 g/L), BPA (70 mg/L) was almost completely removed (over 97%) at initial PS concentration of 0.4 g/L and pH 7.0 within 80 min after the adsorption-oxidative degradation process. Moreover, the b-CNTs also displayed an excellent
reusability for the catalytic oxidation of BPA (70 mg/L) with the degradation ratio remaining at 84% after 5 cycles.

A novel quinone-modified (AQS-NH-MIL-101(Fe)) metal organic frameworks (MOFs) composites using a mild chemical method were fabricated by Li et al. [106] and tested as a redox mediator to enhance the degradation of BPA via PS activation. AQS-NH-MIL-101(Fe) (k=0.107 min⁻¹, R²=0.99) exhibited better catalytic performance on degradation of BPA compared with NH₂-MIL-101(Fe) (k=0.012 min⁻¹, R²=0.99) and NH₂-MIL-101(Fe) with free AQS (k=0.014 min⁻¹, R²=0.99), revealing the immobilization of AQS on NH₂-MIL-101(Fe) had prominent impact on BPA degradation. The authors attributed this higher catalytic activity to the synergistic effect among AQS, Fe(III) and Fe(II). In order to further study the catalytic process for the degradation of BPA, the authors conducted experiments with active radicals quenching agents to acquire insightful information on the role of these radicals in the AQS-NH-MIL-101(Fe)/PS system. Based on the results of the quenching experiments, it was concluded that SO₄•⁻, HO• and O₂•⁻ were all responsible for the degradation of BPA and SO₄•⁻ was found to be the dominant radical specie.

In the study of Mokhtari et al. [107] mineralization of BPA from aquatic environments by the application of novel UV/PS/H₂O₂/Cu system and optimization and modelling of its removal using central composite design (CCD) from response surface methodology was explored. A six-variable, three-level CCD in combination with response surface modelling and quadratic polynomial were used to determine of the effects of initial PS concentration (25-105 mg/L), initial HP concentration (5-15 mg/L), initial pH (3-11), initial Cu²⁺ concentration (5-30 mg/L), reaction time (5-240 min) and BPA initial concentration (10-40 mg/L) on the degradation of BPA as the response variable. Analysis of response surface plots showed a considerable impact of all six selected variables which BPA and Cu²⁺ initial concentrations have been the highest and the least impact on the process, respectively. The optimum values of the operation parameters were determined as: initial PS concentration=69.57 mg/L, initial HP concentration=9.85 mg/L, initial pH=10.91, initial Cu²⁺ concentration=20.76 mg/L, reaction time=140.38 min and initial BPA concentration=39.33 mg/L leading to 99.99% of BPA 70% TOC removals.
Recently, HP and PS-activated nanoscale ZVI (nZVI) and zero-valent aluminum (nZVAL) heterogeneous treatment systems (nZVI/HP-PS and nZVAL/HP-PS) were investigated for the removal of 20 mg/L (88 μM) aqueous BPA [59]. Oxidation with HP and PS in the absence of nanoparticles did not cause BPA degradation, whereas the nZVI/O₂/H⁺ and nZVAL/O₂/H⁺ treatment systems (in the absence of oxidants) resulted in 33-38% BPA and 2-7% TOC removals at an initial reaction pH of 3, respectively. Activation of nZVI and nZVAL with HP or PS improved BPA and TOC removals due to the enhancement of HO⁻ and sSO₄⁻ generation. Removal efficiencies decreased upon increasing the reaction pH from 3 to 5, while a remarkable enhancement in BPA (from 84% to 100%) and TOC (from 69% to 89%) removals was evident when nZVI was activated with PS. Complete BPA removal was achieved by using 1 g/L nanoparticle activated with 2.5 mM HP or PS at pH=3 for the nZVI/HP and nZVAL/HP-PS treatment combinations, whereas 84% BPA removal was obtained for nZVI/PS treatment. Highest TOC removal was achieved as 90% for nZVI/PS treatment at pH=5 and nZVAL/PS treatment at pH=3. HP and PS consumptions proceeded faster for the experiments conducted at pH=3, which was attributable to the more efficient interaction between oxidant, nanoparticle and dissolved metal ion specie at the more acidic pH value.

Advanced oxidation of aqueous BPA by O₃/Na₂S₂O₈ (PS) was investigated by Yang et al. [108]. It was demonstrated that the degradation rate of BPA fitted to the pseudo-first order kinetics model and was strongly affected by several factors including the initial concentrations of O₃ and PS, dosage of BPA and the pH value. Optimum conditions were obtained as a reaction pH=9, 1.0 mg/L O₃, 1:50 BPA:PS “on molar basis” and 2.0 mg/L BPA. The removal of BPA went up to 62.43 % after reacting 20 min. Free radical species in the O₃/PS system were identified by using TBA and ethanol (ETOH) as two probes, and the results showed that the major free radical was SO₄⁻ at acidic condition (pH=3), while the quantity of HO⁻ increased with the pH increased. Eight intermediates were identified using liquid chromatography-mass spectroscopy (LC-MS) analysis, most of which were quinonoid derivants and some cleavage products indicating the incomplete mineralization.

Although an overview of the performances of various methods for PS activation have already been presented in this section, a comparative list of recent applications has also been provided in Table 1.
Table 1. Treatment with activated PS: Case studies with BPA.

<table>
<thead>
<tr>
<th>PS Activation Method</th>
<th>Experimental Conditions</th>
<th>Main Results</th>
<th>Reference</th>
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</table>
| Zero valent copper (nZVC)/PS          | BPA=20µM  
PS=1 mM  
nZVC=40 mg/L  
(size: 10-30 nm)  
pH=3  
V=500 mL  
T=12±1°C | • BPA was rapidly degraded in the initial phase of the nZVC/PS process  
• With nZVC/PS, 82.3% BPA reva at t=25 min  
• pH (≤4) was found to be a critical factor for the activation of PS by nZVC.  
• PS accelerated the corrosion of nZVC to release Cu⁺ in both aerobic and anaerobic conditions and the released Cu⁺ was the main effective copper species to activate PS to produce reactive radicals | [110]     |
| Electro/Fe³⁺/peroxydisulfate (EC/Fe³⁺/PS) | BPA=0.22 mM (50 mg/L)  
PS=1, 5, 10, 20 mM  
pH=3.0, 6.0, 9.0  
Anode=Ti/RuO₂-IrO₂ (5.0cm×11.9cm)  
Cathode=Stainless steel (5.0cm×11.9cm)  
Parallel arrangement with a distance of 4.0 cm.  
Electrolyte (Na₂SO₄) =50, 100, 200 mM  
Fe³⁺ =1, 2, 4 mM  
Current density=8.4, 16.8, 33.6 mA/cm²  
V=200 mL  
T=20°C | • 76.5% and 34.3% BPA removals were achieved at t=60 min at pH 3.0 and 9.0  
• BPA removal decreased from 76.5% to 26.2% with increasing electrolyte concentration from 50 to 200 mM  
• BPA removal increased from 48.6%, 76.5% to 99.4% with increasing Fe³⁺ concentration from 1, 2 to 4 mM, respectively at t=60 min  
• BPA removal increased from 57.5% to 99.2% at t=90 min with increasing PS concentration from 1 to 10 mM. Further increase to 20mM did not improve the degradation efficiency  
• BPA removal increased from 63.2%, 84.2% to 98.4% with increasing the current density from 8.4, 16.8 to 33.6 mA/cm², respectively at t=60 min  
• 94.3% TOC was removed at BPA=0.22 mM, Na₂SO₄=50 mM, Fe³⁺=4 mM, PS=20 mM, current density=33.6 mA/cm², pH=3.0, t=12 min | [96]     |
| Nitrogen modified reduced graphene oxide (N-RGO)/PS | BPA= 0.385 mM (≥88 mg/L)  
BPF=0.385 mM (≥77 mg/L)  
PS=0.6 mM  
N-RGO=120 mg/L (average particle size=579 nm)  
PH=6.6 (not controlled during the experiments)  
V=50 mL  
T=298 K | • N-RGO was prepared by hydrothermal treatment of graphene oxide with ammonia at 180°C.  
• In the N-RGO/PS system, both the adsorption of N-RGO and the oxidation of PS activated by N-RGO contributed to BPA removal  
>97% of the added bisphenols removed within 17 min  
• An apparent rate constant (k) was found as 0.71 min⁻¹ for the degradation of BPA in the N-RGO/PS system.  
• N doping promoted treatment performance, which functioned as active sites for both the adsorption of bisphenols and the activation of PS, producing surface-bound SO₄²⁻ | [99]     |
Table 1. Continued

<table>
<thead>
<tr>
<th>PS Activation Method</th>
<th>Experimental Conditions</th>
<th>Main Results</th>
<th>Reference</th>
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<tr>
<td>O₃/PS</td>
<td>BPA=2, 5, 10 mg/L</td>
<td>• BPA removal was enhanced with increasing O₃ conc. and decreasing the initial BPA conc.</td>
<td>[108]</td>
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<td>BPA/PS mol ratio=1:10, 1:25, 1:50</td>
<td>• The obtained optimum conditions for the removal of 2 mg/L BPA were pH 9, 1.0 mg/L O₃, and 1:50 BPA/PS.</td>
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<td>O₃=0.5, 1.0, 2.0 mg/L</td>
<td>• The major free radical of the O₃/PS process was SO₄⁻ at pH 3, while the quantity of HO• increased with increasing pH.</td>
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<td>pH=3, 7, 9</td>
<td>• Eight intermediates were identified using HPLC-DPD-MS, most of which are quinonoid derivants and some cleavage products indicating the incomplete mineralization.</td>
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<td>V=500 mL, 200 rpm</td>
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<td>T=293 K</td>
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<td>PS/UV-C</td>
<td>BPA=0.04 mM-0.31 mM</td>
<td>• As the BPA/PS molar ratio increased, the removal of BPA decreased.</td>
<td>[101]</td>
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<td>PS/BPA molar ratio=31.5:1-4.06:1</td>
<td>• The TOC removal was found to be 55% with UV-C/PS system (BPA=0.22 mM, PS=1.26 mM)</td>
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<td>V=450 mL, T= 29±3°C L=1.26 µE⁴</td>
<td>• The rate of reaction in UV-C/PS system was found to be higher than that in UV-C/HP system.</td>
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<td>• The main route of BPA degradation was the hydroxylation followed by dehydration, coupling and ring opening reactions.</td>
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<td>Quinone-modified metal-organic framework (AQS-NH-MIL-101(Fe))/PS</td>
<td>BPA=60 mg/L PS=10 mM</td>
<td>• The obtained performance of BPA adsorption and degradation over AQS-NH-MIL-101(Fe) was compared to those of NH₂-MIL-101(Fe) and NH₂-MIL-101(Fe)/AQS.</td>
<td>[106]</td>
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<td>NH₂-MIL-101(Fe) modified by 2-anthraquinone sulfonate (AQS)</td>
<td>• The adsorption removal of BPA was 23.1% and 27.9% for AQS-NH-MIL-101(Fe) and NH₂-MIL-101(Fe), respectively.</td>
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<td>Average particle size=500-800 nm AQS-NH-MIL-101(Fe)=0.2 g/L Initial pH=5.76 V=25 mL T= 25°C</td>
<td>• AQs-NH-MIL-101(Fe) was demonstrated to be the most efficient in that more than 97.7% of BPA was removed after 180 min, increased approximately 22.8% over NH₂-MIL-101(Fe) as catalyst.</td>
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<td>• The immobilization of AQS on NH₂-MIL-101(Fe) had prominent impact on BPA degradation.</td>
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<td>• The AQS-NH-MIL-101(Fe) catalyst exhibited excellent stability and can be used several times without significant deterioration in performance.</td>
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<td>• Two cycles were built up in the AQS-NH-MIL-101(Fe)/PS process, one quinone unit (Q)/hydroquinones (HQ) cycle, another cycle of Fe(III)/Fe(II) caused by Q, and the two cycles greatly facilitated the SO₄²⁻ production.</td>
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<td>• The semiquinones (SQ) produced in the reaction can directly react with PS, promoting the degradation of BPA by SO₄²⁻.</td>
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3.2. Phthalates

Diethyl phthalate (DEP), a plasticizer widely used in chemical industry, has been classified as an endocrine disruptor. Therefore, it is urgent to develop methods for degradation of DEP to minimize its ecological risk. Zhang et al. [65] prepared copper ferrite decorated multi-walled carbon nanotubes magnetic nanoparticles (CuFe$_2$O$_4$/MWCNTs MNPs) by a sol-gel combustion method as catalysts for the degradation of DEP. The catalysts were characterized by scanning electron microscope, transmission electron microscope, Fourier transform infrared spectroscopy (FTIR), nitrogen gas uptake-BET, X-ray diffraction and X-ray photoelectron spectroscopy (XPS). The catalytic degradation of DEP with PS was investigated at varying reaction conditions including catalyst loading, PS concentrations, temperature and pH. CuFe$_2$O$_4$/MWCNTs MNPs exerted a high catalytic activity, stability and recyclability during DEP removal. Metal ion leaching from reused CuFe$_2$O$_4$/MWCNTs was negligible (concentration < 0.4%), indicating their resistance to oxidation. The electron paramagnetic resonance analysis confirmed that the addition of CuFe$_2$O$_4$/MWCNTs could accelerate the generation of HO$^\cdot$ and SO$_4$$^{2-}$ of PS and the quenching experiments further certified the catalytic reaction was predominated by SO$_4$$^{2-}$. Degradation intermediates were identified and reaction pathways were proposed. Overall, this study provided practical knowledge for DEP removal by CuFe$_2$O$_4$/MWCNTs activated PS at ambient temperature.

The degradation of dimethylphthalate (DMP) by PS at ambient temperature (T=20–40°C) was examined by Wang et al. [109] in aqueous solutions and soil slurries to assess the feasibility of using PS to remediate DMP-contaminated soil and groundwater. The effects of temperature, initial oxidant concentration, initial DMP concentration and initial solution pH on the removal of aqueous DMP and TOC were studied. PS could effectively mineralize DMP at 40°C. Furthermore, dimethyl 4-hydroxyl phthalate, maleic acid and oxalic acid were identified as the degradation intermediates, and degradation pathways were proposed. Lastly, PS was applied at 40°C to remediate soil spiked with DMP at 600 mg/kg. Results indicated that PS treatment at 40°C was highly effective for the remediation of DMP-contaminated soil.

Zhou et al. [110] employed nano-scale zero-valent copper (nZVC) particles as activators for PS to degrade organic contaminants. Benzoic acid (BA) was almost completely degraded in 25 min and the nZVC/PS process also exhibited a good oxidizing capacity on acid orange 7 (AO7), nitrobenzene (NB), DMP, diethylstilbestrol (DES), BPA and
2,4-dichlorophenol (2,4-DCP). The degradation rates of AO7, DMP, NB, DES, BPA and 2,4-DCP in 25 min were 93.2%, 82.1%, 84.6%, 90.3%, 82.3%, and 100%, respectively ([substrate]₀=20 mM, [PS]₀=1 mM, [nZVC]₀=40 mg/L, pH₀=3.0). It could be demonstrated that PS can accelerate the corrosion of nZVC to release Cu⁺ in acidic aqueous conditions and ROS were generated through activation of PS by intermediate Cu⁺ via a Fenton-like reaction. Both SO₄⁺ and HO· were considered as the primary ROS involved in the nZVC/PS treatment process according to scavenging test carried out with MA and TBA. Moreover, the degradation rate of BA increased gradually with an increase of nZVC dosage and a pH decrease from 5.4 to 2.0.

Cotillas et al. [111] studied the advantages and drawbacks of the combination of PS, UV irradiation with electrolysis to question their feasibility for the reclamation of conventionally-treated wastewater. The oxidation of synthetic solutions containing five complex model pollutants indicated that UV irradiation improves the results of electrolysis for progesterone, metoprolol and caffeine and deteriorates the performance for the degradation of sulfamethoxazole and DMP. In terms of mineralization differences in treatment performance became smaller showing that the effects of UV irradiation are diluted when a mixture of species is oxidized. Results suggested that high ThOD:TOC ratios improve the synergy of the proposed treatment processes while low ratios lead to a clear antagonistic effect. The observed effect on mineralization was much lower than in the oxidation of the original molecule. Opposite to this effect, the improvement in the performance of the disinfection by coupling UV to electrolysis was more apparent. UV irradiation modified significantly the chlorine speciation and helped to prevent the formation of hazardous compounds such as chlorate and perchlorate during the electrochemical processes.

Fe/S doped granular activated carbon (Fe/SGAC) was synthesized with ferric nitrate, Na₂S₂O₃ and (NH₄)₃(2)S₂O₈ via an impregnation-precipitation, reduction-oxidation combination with an aqueous-phase synthesis method [64]. Surface density of functional groups, surface area changes as well as the chemical state inside Fe/SGAC catalyst were determined by Boehm titration, N-2 adsorption and XPS, respectively. The reactivity of the catalysts was tested by degrading the model pollutants Orange G (OG) and DEP. The Fe/SGAC catalyst could significantly enhance the removal rate of OG as compared to PS alone and PS/GAC. The catalytic capacity was also improved by S doping. However, the degradation of DEP was inhibited by adsorption because of the different hydrophobicities of OG and DEP molecule. Fe₂O₃/FeOOH (Fe³⁺; representing ferrihydrite) together with FeO/Fe₃O₄ (Fe²⁺) and Fe₂O₃-satellite providing new active sites for PS, were found to be the major components of Fe in the Fe/SGAC catalyst. The
existence of FeS$_2$(S-) for S verified the assumption that the doped S promoted the electron transfer between PS and Fe- oxides at the interface. Chemical oxygen demand (COD) removals confirmed that the major contaminant removal was owed to Fe/SGAC-catalyzed PS oxidation.

The main objective of Yang et al. [112] was to evaluate the suitability of coupling nano-Fe$_3$O$_4$/S$_2$O$_8^{2-}$ oxidation process and electrokinetic remediation for degradation of phthalate esters (PAEs) in Taiwan river sediment. In the test run of injecting nanoscale Fe$_3$O$_4$ slurry and PS solution into the anode reservoir, the derived radicals and oxidant were transported into the sediment compartment by electroosmotic flow (EOF) to oxidize PAEs; an increase of the electric potential gradient from 1 V/cm to 2 V/cm was found to enhance the removal of PAEs in control runs with no addition of chemicals to the EK remediation system; Fe$^{2+}$ and Fe$^{3+}$ originated from nano-Fe$_3$O$_4$ dissociation and/or naturally occurring iron in the river sediment. These formed precipitates in the pores of sediment near the cathode rendering a decrease of the EOF rate; a prolonged treatment period resulted in an enhanced removal of phthalates from sediment. It appeared that the EK-assisted nano-Fe$_3$O$_4$/S$_2$O$_8^{2-}$ oxidation process is a viable technology for the in-situ remediation of PAEs-contaminated river sediments.

Li et al. [113] studied the effect of initial pH on the degradation of dibutyl phthalate (DBP), the formation and evolution of iron corrosion products and the role of iron oxides on the degradation of DBP in ZVI activated PS treatment system. The half-lives for DBP removal by ZVI/PS were 30-176 min at pH=3.0-11.0. The constituents and the morphology of the iron coating formed on ZVI at different initial pH and over reaction time were measured with Raman spectroscopy, XPS and Scanning electron microscopy (SEM). Magnetite (Fe$_3$O$_4$), wustite (FeO), hematite (alpha-Fe$_2$O$_3$) and goethite (alpha-FeOOH) were identified as the corrosion products on ZVI surface. In alkaline and neutral solutions, the inner layer of iron oxides was mainly composed of alpha-Fe$_2$O$_3$ with some alpha-FeOOH, while the outer layer mostly consisted of Fe$_3$O$_4$ and alpha-FeOOH. Oppositely, the Fe oxides formation in acidic solution mainly consisted of Fe$_3$O$_4$, alpha-FeOOH and a small amount of alpha-Fe$_2$O$_3$ and FeO in the inner layer, the outer layer was mostly composed of alpha-Fe$_2$O$_3$ and some alpha-FeOOH. These iron corrosion coatings exhibited an inhibitory effect on the degradation of DBP hindering effective electron transfer from the ZVI core to the solid-liquid interface.

The removal of DMP was also examined by Sun et al. [114] using PS catalyzed by Ag$^+$ combined via MW irradiation. Effects of PS concentration, reaction time, MW power and Ag$^+$ on the degradation efficiency of DMP by PS were examined in batch experiments. The optimum PS and Ag$^+$
concentrations were 0.083 mM and 0.042 mM, respectively. Increasing the MW irradiation time, PS concentration or Ag\(^+\) concentration accelerated DMP degradation. Catalytic Ag\(^+\) combined with MW irradiation was a rapid method to activate PS. About 80% of DMP and 70% of COD could be degraded in 140 s at a MW power of 800 W.

Li et al. \cite{115} investigated the reaction pathway and oxidation mechanisms of DBP by ZVI/PS treatment. DBP degradation was studied at three pH values (acidic, neutral and basic) in the presence of different organic radical scavengers. Using a chemical probe method, both SO\(_4^–\) and HO\(^•\) were found to be primary oxidants at pH=3.0 and pH=7.0, respectively while HO\(^•\) was the major specie to oxidize DBP at pH=11.0. A similar result was found in an experiment of electron spin resonance spin-trapping where in addition to HO\(^•\), superoxide radical (O\(_2^–\)) was detected at pH=11.0. The transformation of degradation products including DMP, DEP, phthalic anhydride, and acetophenone exhibited diverse variation during the reaction processes. The phthalic anhydride concentration appeared to be maximum at all pHs. Eleven intermediate products were found at pH=3.0 by GC-MS and high performance liquid chromatography (HPLC) analysis and their degradation mechanisms and pathways were proposed as dealkylation, hydroxylation, decarboxylation and hydrogen extraction at pH=3.0.

A facile and simple one-step thermal oxidation method was recently proposed by Li et al. \cite{116} to prepare core-shell Fe-0@Fe\(_3\)O\(_4\) composites as efficient heterogeneous activators of PS for DBP oxidation under neutral pH. The effects of temperature (T) and reaction time were investigated. The Fe-0@Fe\(_3\)O\(_4\) composites were characterized using SEM, X-ray diffraction patterns, Raman spectra and XPS. Activity testing showed the Fe-0@Fe\(_3\)O\(_4\) composites prepared at 400°C for 40 min achieved the highest activity towards PS, which suggested that Fe\(_3\)O\(_4\) played an important role in the catalytic activity. Increasing PS and Fe-0@Fe\(_3\)O\(_4\) dosages enhanced DBP oxidation. 94.7% degradation of DBP was achieved when PS and Fe-0@Fe\(_3\)O\(_4\) concentrations were increased to 1.8 mM and 0.5 g/L, respectively. Fe-0@Fe\(_3\)O\(_4\) also exhibited excellent reusability according to six consecutive reaction cycles with no obvious loss of catalytic activity. More interestingly, the DBP degradation rate increased in the first three cycles. The mechanism for activating of PS by Fe-0@Fe\(_3\)O\(_4\) composites involved an efficient electron transfer process that initiated SO\(_4^•\) formation by a Haber-Weiss mechanism.

Three distinctive phases of butylated hydroxyanisole (BHA) reactivity toward UV/PS at acidic, neutral, and basic pH range were examined, where 80-100% mineralization has been observed within 60 min of irradiation at
UV=254 nm [117]. A reduction in solution pH during the reaction was observed mainly due to the complete conversion of PS to SO$_4^{2-}$ together with proton generation. Seven measurable intermediates were found via an oxidation and dimerization process at all tested pH levels. There were three unique intermediates detectable at pH=3 via two additional pathways due to the generation of weaker ROS resulting in slower degradation of the BHA. Hence, these intermediates accumulated at detectable levels. The rate of BHA decay generally increased from low to high pH levels; however, the corresponding mineralization at higher pH due to radical recombination and the involvement of intermediates. Therefore, a neutral pH was suggested to be the optimum pH in terms of highest mineralization and BHA removal.

3.3. Alkylphenols

Yamazaki et al. [118] studied the photocatalytic degradation of 4-(tert-octyl)phenol (4-OP) by recirculating the aqueous solution through a packed-bed reactor with TiO$_2$. The first-order rate constant k and activation energy for the degradation of 4-OP was found as 5.40×10$^{-3}$ min$^{-1}$ and 18.6 kJ mol$^{-1}$, respectively. The rate constant k was not dependent on the flowrate but a decrease in TOC became smaller as the flowrate increased. A treatment time of 6 h at the flowrate of 28.5 ml min$^{-1}$ resulted in 83.2% of 4-OP and 39.3% TOC removals. LC/MS analysis using electrospray ionization revealed the formation of byproducts with molecular weights of 136, 178, 192, 220 and 222. The degradation rate of 4-OP was remarkably accelerated by the addition of PS; 4-OP completely disappeared under irradiation of 4 or 2 h in the presence of 4×10$^{-3}$ or 2×10$^{-2}$ M PS, respectively. In the latter case, the TOC decreased to 34.6% by continuing the irradiation even after 4-OP completely disappeared. In the presence of PS, 4-OP was degraded without TiO$_2$, which was attributable to SO$_4^-$.$^*$. The UV/TiO$_2$/S$_2$O$_8^{2-}$ system was more appropriate than the UV/S$_2$O$_8^{2-}$ for decontamination of 4-OP in water.

Olmez-Hanci et al. [119] comparatively treated the nonionic surfactant Triton X-45 (TX-45), an octylphenol polyethoxylate, by the PS/UV-C process and the well-known HP/UV-C treatment process. Complete and rapid TX-45 oxidation required extended treatment periods (>30 min) and high oxidant concentrations (≥2.5 mM). Several degradation products could be qualified via GC–MS and HPLC analyses. Inspection of the identified degradation products indicated that the reaction mechanism of TX-45 was a combination of various pathways; (i) progressive shortening of the ethoxylate chain leading to relatively short-chain TX-45 and ultimately
octyphenol, (ii) ω-carboxylation of the terminal alcoholic groups yielding octyphenol ethoxy carboxylates (OPECs) and (iii) central fission of the ethoxy chain resulting in the formation of polyethylene glycols (PEGs). Continued oxidation of the primary degradation products resulted in mono- and di-carboxylated PEGs. Degradation products bearing a smaller number of ethylene oxide units (≤3) were generated during H$_2$O$_2$/UV-C treatment, whereas OPECs was only detected during PS/UV-C treatment of TX-45. Acetic and succinic acids were quantitatively identified during PS/UV-C treatment, whereas oxalic and fumaric acids were also detected during H$_2$O$_2$/UV-C oxidation. Degradation products indicated that SO$_4$$^\cdot$- and HO$^\cdot$-induced reaction pathways were similar.

Triton X-100 is one of the most widely-applied non-ionic surfactants. This detergent can hardly be degraded by biological treatment. Hence, a more efficient degradation method is indispensable for the total mineralization of this pollutant. The efficiency of TiO$_2$/UV treatment may be improved by the addition of various reagents. Hegedus et al. [120] have examined the photocatalytic degradation of Triton X-100 and the efficiencies of ozonation and PS treatment were compared under similar reaction conditions. Besides, the AOPs were also combined with each other. Changes in TOC, pH as well as absorption and emission spectra of the reaction mixture were monitored. An ultra-high-performance liquid chromatography (UHPLC) method was developed and optimized for monitoring the degradation of Triton X-100. Intermediates were detected by GC-MS analysis to elucidate the degradation mechanism. This non-ionic surfactant could be efficiently degraded by TiO$_2$-mediated heterogeneous photocatalysis. However, its combination with AOPs that were applied in this study did not enhance the rate of the mineralization. Moreover, the presence of PS inhibited the photocatalytic degradation.

The photolytic degradation of 4-tert-butylphenol (4-t-BP) in aqueous solution was examined by Wu et al. [121] using direct UV(-C), UV/HP and UV/PS treatment systems. The degradation rate of 4-t-BP was in the decreasing order of UV/PS>UV/HP>UV-C. The increase of PS concentration enhanced the 4-t-BP degradation rate that was inhibited when the concentration of PS exceeded 4.0 mM. The highest efficacy in 4-t-BP degradation was obtained at pH=6.5. The oxidation rate of 4-t-BP could be accelerated by increasing the reaction temperature and irradiation intensity. The highest rate coefficient of $8.4 \times 10^{-2}$ min$^{-1}$ was achieved at 45°C. The optimum irradiation distance was 10 cm. Moreover, the preliminary mechanism of 4-t-BP degradation was studied. The bond scission of the
4-t-BP molecule occurred by the oxidation of \( \text{SO}_4^* \), which dimerized and formed two main primary products. Under the conditions of room temperature (25°C) and low concentration of \( \text{K}_2\text{S}_2\text{O}_8 \) (0.5 mM), 35.4% of the original TOC was removed after 8.5-h irradiation.

Arslan-Alaton et al. [61] studied nZVA1-activated HP, PS and PMS oxidation of TX-45. Treatment performances were evaluated in distilled water (DW), raw surface water (SW), tap water (TW) and effluent from a domestic wastewater treatment plant (WW). Two different acute toxicity tests as well as the UMU-Chromo assay were undertaken to evaluate the ecotoxicological effects of TX-45 and its oxidation products. Poor TX-45 removals in the absence of nZVA1 (HP, PS and PMS only and oxidants (nZVA1/O\(_2\)/H\(^+\) treatment) were obtained (5%-38%). Activation of HP, PS and PMS with nZVA1 resulted in complete TX-45 removal in DW with the nZVA1/PS and nZVA1/PMS treatment systems after 90 min and 60 min, respectively, whereas only 76% TX-45 removal was obtained with nZVA1/HP after 120 min (TX-45=2 mg/L; nZVA1=1 g/L; HP-PMS=0.25 mM; PS=0.5 mM; pH=3). In DW, the decreasing order of TX-45 removal efficiencies was obtained as follows; nZVA1/PS = nZVA1/PS > nZVA1/HP and as nZVA1/PS > nZVA1/HP > nZVA1/PS in SW and WW. The nZVA1/PS-treated TX-45 samples did not exhibit toxic effects on \( V. \text{fischeri} \); the relative inhibition increased from 15% to 26% in DW and decreased to practically non-toxic levels (<8%) in SW after 120 min treatment. During the early stages of nZVA1/PS treatment, \( \text{Pseudokirchneriella subcapitata} \) (\( P. \text{subcapitata} \)) toxicity of TX-45 increased from 35% to 44% and from 39% to 52% in DW and SW samples, respectively. After 120 min treatment, it dropped back to 40% and 25% in DW and SW samples, respectively. The original and nZVA1/PS-treated TX-45 neither exhibited cytotoxic nor genotoxic effects.

Pokhalekar et al. [122] carried out ultrasonic and photocatalytic degradation of BPA and OP by optimizing different parameters such as the effects of pH, US frequency and power as well as PS (oxidant) and TiO\(_2\) photocatalyst concentrations. The highest degradation of BPA and OP was obtained at a pH value of 5, an US frequency of 45kHz, 500 W and with 100-200 mg/L PS under bubbling with air. For the photocatalytic treatment system, the highest degradation was observed at a pH=5, with 50-150 mg/L TiO\(_2\). Photocatalytic degradation was found to be more efficient and cost-effective than ultrasonic degradation.

TX-45 (TOC=14 mg/L), a commercially important alkylphenol polyethoxylate, was subjected to PS oxidation activated with nZVI by Temiz et al. [123]. After optimization of the ZVI/PS treatment combination
(1 g/L ZVI; 2.5 mM PS at pH=5) in terms of pH (3-9), ZVI (0.5-5 g/L) and PS (0.5-5.0 mM) concentrations, TX-45 could be efficiently (>90%) degraded within short treatment periods (<60 min) accompanied with significant (>40%) TOC removals. A positive correlation existed between TX-45 removals and ZVI-activated PS consumption rates accompanied with a parallel Fe release. The acute toxicities significantly decreased from an original value of 66% relative inhibition to 21% and from 16% relative inhibition to non-toxic values according to *V. fischeri* and *P. subcapitata* bioassays, respectively. The photobacterium *V. fischeri* appeared to be more sensitive to TX-45 and its degradation products than the microalgae *P. subcapitata*.

Arslan-Alaton et al. [124] explored the potential use of a SO$_4^*$-based photochemical oxidation process to treat the nonionic surfactant TX-45. For this purpose, the effect of initial PS and octylphenol polyethoxylate (OPPE) concentrations on OPPE and its TOC removal was investigated. PS/UV-C oxidation of OPPE was also compared the more conventional HP/UV-C oxidation process. The reactivity and selectivity of SO$_4^*$ and HO* was also examined by employing competition kinetics with aqueous phenol solution. Experimental results indicated that the treatment performance of PS/UV-C was comparable to that of HP/UV-C for the degradation and mineralization of OPPE. The selectivity of SO$_4^*$ was found to be significantly higher than that of HO*.

As aforementioned, nonylphenol (NP) is an endocrine disrupting chemical which is capable of interfering with the hormonal system of various organisms in the environment. In a study conducted by Hussein et al. [62], nZVI supported on biochar (BC) nanocomposite (nZVI/BC) was synthesized using low-cost rice husk through reduction of ferrous iron with sodium borohydride as a reductant under N$_2$ atmosphere. The morphology and structure of nanocomposite was characterized by X-ray diffraction, SEM, FTIR and Brunauer-Emmett-Teller (BET) studies. nZVI/BC nanocomposite was used to activate PS for NP degradation. The oxidation efficiency of NP (20 mg/L) was 96.2% within 120 min using 0.4 g/L nZVI/BC$_3$ and concentrations of 5 mM PS. The effects of initial pH, PS and nZVI/BC nanocomposite concentrations were also investigated. The presence of oxygen functional groups on the surface of BC and large surface area, nZVI/BC nanocomposite increased ROS generation and hence NP degradation. The radical scavenger experiments and EPR studies revealed that both SO$_4^*$ and HO* were responsible for NP degradation. The findings of this study provide new insights into the mechanism of nZVI/BC activation of PS and potential treatment applications.

Table 2 presents some major applications of PS activation for the treatment of alkylphenols and phthalates.
Table 2. Treatment with activated PS: Case studies with alkylphenols and phthalates.

<table>
<thead>
<tr>
<th>Micropollutant</th>
<th>PS Activation Method</th>
<th>Experimental Conditions</th>
<th>Main Results</th>
<th>Reference</th>
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<tr>
<td>Triton X-100 (TX-100)</td>
<td>PS/air, UV PS/air/UV PS/air/TiO&lt;sub&gt;2&lt;/sub&gt;/UV</td>
<td>TX-100=2×10&lt;sup&gt;-4&lt;/sup&gt; M (126 mg/L) PS=1 Mm TiO&lt;sub&gt;2&lt;/sub&gt;=1 g/L V=2.5 L t=4 h 40 W, λ&lt;sub&gt;max&lt;/sub&gt;=350 nm I=4.3×10&lt;sup&gt;-4&lt;/sup&gt; mol photon dm&lt;sup&gt;-3&lt;/sup&gt;·s&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>•76% TX-100 removal at t=4 h for PS/UV with an initial rate of 8×10&lt;sup&gt;-7&lt;/sup&gt; mol·dm&lt;sup&gt;-3&lt;/sup&gt;·min&lt;sup&gt;-1&lt;/sup&gt;.</td>
<td>[120]</td>
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<td>•54% TX-100 removal at t=4 h for UV</td>
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<td>•22% TX-100 removal at t=4 h for PS</td>
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<td>•The initial rate and TOC removal were 1.75 mol·dm&lt;sup&gt;-3&lt;/sup&gt;·min&lt;sup&gt;-1&lt;/sup&gt; and 55%, respectively for PS/TiO&lt;sub&gt;2&lt;/sub&gt;/UV</td>
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<td>•For TiO&lt;sub&gt;2&lt;/sub&gt;/UV the initial rate was 1.07 mol·dm&lt;sup&gt;-3&lt;/sup&gt;·min&lt;sup&gt;-1&lt;/sup&gt; and TOC removal 40%.</td>
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<td>•The presence of TiO&lt;sub&gt;2&lt;/sub&gt; did not increase the initial TX-100 removal rate and TOC removal</td>
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<td>Triton X-45 (TX-45)</td>
<td>PS/nZVA HP/nZVA PMS/nZVA</td>
<td>TX-45=2 mg/L (4.7 µM) PS=0.50 mM (96 mg/L) HP=0.25 mM (8.5 mg/L) PMS=0.25 mM (28.25 mg/L) nZVA (BET=10–20 m&lt;sup&gt;2&lt;/sup&gt;/g; particle size=100 nm)</td>
<td>•TX-45 was efficiently removed by nZVAI-activated HP, PS and PMS treatments.</td>
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<td>TX-45 removal was followed in real effluent samples V=500 mL T=25±2°C</td>
<td>•nZVAI/oxidant treatment was affected by water/wastewater characteristics.</td>
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<td>•nZVAI/PMS treatment exhibited highest TX-45 removal.</td>
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<td>•Acute toxicity was affected by water quality and type of test specie.</td>
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<td>•No cytotoxic/genotoxic effects were evident for original and nZVAI/PS-treated TX-45.</td>
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<td>•The highest TX-45 removals were 20, 11 and 38% for oxidation with PS, HP and PMS only, respectively.</td>
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<td>•Only 22% TX-45 removal was obtained with nZVAI/O&lt;sub&gt;2&lt;/sub&gt;/H&lt;sup&gt;+&lt;/sup&gt; treatment at t=120 min.</td>
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<td>•TX-45 was completely removed at t=90 min and 60 min treatments with nZVAI/PS (0.50 mM) and nZVAI/PMS (0.25 mM), respectively, whereas 76% TX-45 removal was achieved with nZVAI/HP (0.25 mM) at t=120 min.</td>
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<td>•During nZVAI/PS treatment inhibition was observed for TX-45 removal that it decreased from 100% in pure water at t=90 min to 58% and 12% in surface water and tertiary treated wastewater, respectively.</td>
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<td>•Poor DOC removals were obtained for the nZVAI/HP, nZVAI/PS and nZVAI/PMS treatments (2–22%).</td>
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<td>•Toxicity decreased to practically non-toxic levels (&lt; 8%) after 120 min treatment of surface water</td>
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**Table 2. Continued**

<table>
<thead>
<tr>
<th>Micropollutant</th>
<th>PS Activation Method</th>
<th>Experimental Conditions</th>
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</table>
| Nonyl Phenol (NP)       | PS/nZVI/BC          | NP=2-20 mg/L, PS=0-10 mM nZVI/BC (biochar) nanocomposite was synthesized and characterized with different mass ratios of nZVI to BC at 1:1, 1:2, 1:3 and 1:4, respectively. BC was produced by pyrolysis of rice husk nZVI=0.4 g/L BC=0.4 g/L pH=3-11 V=100 mL 125 rpm T=25°C | • NP removal increased from 23.5% to 38.52% with an increase in nZVI/BC mass ratio from 1:1 to 1:3.  
• In the nZVI/PS system, NP removal increased to 61.72% compared to 28.3% to the BC/PS system.  
• NP removals were 68.4%, 78.3%, 96.2% and 88.6% for the nZVI/BC mass ratios of 1:1, 1:2, 1:3 and 1:4, respectively.  
• NP removal increased from 54.5% to 96.2% at t=120 min with increasing nZVI/BC from 0.1 to 0.4 g/L.  
• NP removal decreased to 85.7% when nZVI/BC was increased to 0.5 g/L.  
• NP removal increased from 42.5% to 96.2% with increasing PS from 1 mM to 5 mM. NP removal decreased with the further increase of PS to 10 mM.  
• Order of NP removals was pH3>pH5>pH7>pH9>pH11  
• NP removals increased from 55.9% to 99.15% as the solution pH decreased from 11.0 to 3.0.  
• 72% and 96.2% of NP was removed at t=120 min for T=15 and T=25°C, respectively.  
• Complete NP removal occurred at t=120 and 30 min at 35 and 45°C respectively.  
• Gibbs free energy (ΔG) was calculated as 75.53 kJ mol⁻¹.  
• According to stability experiments (2mg/L NP, 0.4g/L nZVI/BC, 5mM PS, t=120 min) NP removal for every recycle steadily decreased from 96.2% to 75.4% after 5 cycles.  
• For 20 mg/L NP, PS=5 mM, pH=7.0, nZVI/BC=0.4 g/L and T=25°C, NP removal was 78% at t=30 min with 31% TOC removal. TOC removal was 73.4% at t=120 min. | [62]       |
| 4-tert-Butylphenol (4-T-Bp) | PS/UV               | 4-t-BP=0.1 mM PS=0.5-5.0 mM pHs=2.1, 3.2, 5.6, 6.7, 8.3 and 10.9; 9 W medium-pressure mercury lamp (254 nm/312 nm/365 nm/405 nm/435 nm; I=14.22 Wm⁻²) T = 15, 25, 35 and 45°C | • 24.4% 4-t-BP removal with UV photolysis at t=50 min  
• 98.0% 4-t-BP removal with HP/UV at t=50 min  
• 100% 4-t-BP removal with PS/UV at t=40 min  
• Removal rate increased with increasing PS conc.  
• Highest 4-t-BP removal occurred at pH 5.6  
• 4-t-BP removal was enhanced with increasing T  
• 35.4% TOC was removed after 8.5-h PS/UV treatment at T=25°C, pH = 6.5 and 0.5 mM PS | [121]     |
<table>
<thead>
<tr>
<th>Micropollutant</th>
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<th>Main Results</th>
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<tr>
<td>4-(Tert-Octyl)Phenol (4-Op)</td>
<td>PS/TiO&lt;sub&gt;2&lt;/sub&gt;/UV</td>
<td>4-OP=5×10&lt;sup&gt;-5&lt;/sup&gt; M PS=2×10&lt;sup&gt;-2&lt;/sup&gt; - 5×10&lt;sup&gt;-5&lt;/sup&gt; M Packed bed system with immobilized ceramic TiO&lt;sub&gt;2&lt;/sub&gt; balls (total V=28 cm&lt;sup&gt;3&lt;/sup&gt;) 6 W fluorescent black light bulb lamp T=30°C</td>
<td>With TiO&lt;sub&gt;2&lt;/sub&gt;/UV, 83.2% of 4-OP and 39.3% TOC was removed at t=6 h With PS/TiO&lt;sub&gt;2&lt;/sub&gt;/UV, 100% 4-OP removal at t=2 h 34.6% TOC removal at t=4.5 h With PS present, 4-OP was also removed without TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>[118]</td>
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<tr>
<td>Dibutyl Phthalate (DBP)</td>
<td>PS/ZVI</td>
<td>DBP=5 mg/L (0.018 mM) PS=43 mg/L PS/DBP molar ratio=10/1 (fixed) ZVI=0.3 g/L V=100 mL 180 rpm T=25±0.2°C</td>
<td>The DBP degradation at different initial pH ranked as 3&gt;5&gt;7&gt;9&gt;11. The iron oxide was mostly composed of α-Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; in acidic solution. The oxidation layers consisted of Fe&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;, α-FeOOH in alkaline and neutral solutions and exhibited an inhibitory effect on DBP degradation. 80% DBP removal at t=120 min and pH3 Only 23% at pH11. Dissolved Fe&lt;sup&gt;2+&lt;/sup&gt; reached 30.8 mg/L for pH3.0 (highest at pH5) SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt; was the main ROS</td>
<td>[113]</td>
</tr>
<tr>
<td>Dimethyl Phthalate (DMP)</td>
<td>PS/T</td>
<td>DMP=10 - 40 mg/L PS=1.03×10&lt;sup&gt;-2&lt;/sup&gt; M, 5.15×10&lt;sup&gt;-3&lt;/sup&gt; M, 1.03×10&lt;sup&gt;-2&lt;/sup&gt; M pH=3.1, 7.0, 9.0 V=1000 mL T=20-40°C Soil samples were typical lateritic red soils obtained from Guangzhou, China at a depth of 20-40 cm, (66% well graded sand (&lt;2 mm), 14% silt and 20% clay)</td>
<td>PS at 40°C can effectively mineralize DMP. Dimethyl 4-hydroxyl phthalate, maleic acid and oxalic acid were identified degradation products PS at 40°C was applied to remediate soil spiked with DMP at ~600 mg/kg. PS at 40°C is highly effective for the remediation of DMP contaminated soil.</td>
<td>[109]</td>
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<tr>
<td>Phthalate Esters (PAEs) in Taiwan River Sediment</td>
<td>PS/Nano-Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;+ electrokinetic remediation</td>
<td>Houjing river water was used as the electrolyte for all EK tests. Constant voltage mode (1 Vcm&lt;sup&gt;−1&lt;/sup&gt; and 2 Vcm&lt;sup&gt;−1&lt;/sup&gt;) was employed to supply the electric field for operating the EK Daily injection of Houjing River water + 3.14 g Na&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;8&lt;/sub&gt; solution + 0.63 g nano-Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt; slurry into different electrode compartments in the river sediment</td>
<td>93.87% removal of Di-n-butyl phthalate-DnBP and 53.87% removal of Di(2-ethylhexyl) phthalate -DEHP When the treatment time was extended from 14 d to 28 d, DnBP and DEHP removals increased to 97.92% and 68.79%, respectively</td>
<td>[112]</td>
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| Dibutyl Phthalate (DBP) | PS/core-shell Fe$_0$@Fe$_3$O$_4$ | DBP=0.018 mM  
PS=0.54 mM  
Fe$_0$@Fe$_3$O$_4$=0.5 g/L  
pH=7  
V=100 mL  
180 rpm  
T=25±0.2°C | • The Fe$_0$@Fe$_3$O$_4$ posed a superior catalytic performance towards PS for degradation of DBP at neutral pH values compared with Fe$_2^+$/PS and Fe$_0$/PS systems.  
• No loss of the catalytic activity of Fe$_0$@Fe$_3$O$_4$ composites was observed for DBP removal after 5 cycles. DBP removal was enhanced with increasing the cycle run from 1 to 3.  
• Both involves homogeneous Fe$_2^+$ activation reactions and heterogeneous activation reactions on the Fe$_0$@Fe$_3$O$_4$ composites solid surfaces  
• SO$_4^-$ was the main ROS | [116] |
| Diethyl Phthalate (DEP) | PS/CuFe$_2$O$_4$/MWCNTs/MNPs ("copper ferrite decorated multi-walled carbon nanotubes magnetic nanoparticles") | DEP=5 mg/L;  
DEP:PS=1:50, 1:100 and 1:200 (w/w)  
CuFe$_2$O$_4$/MWCNTs (BET=38 m$^2$/g)  
pH=7.0±0.2.  
V=150 mL  
T=25.0±0.2°C | • 100% DEP removal in the presence of CuFe$_2$O$_4$/WMCNTs at t=30 min  
• PS without catalyst (control experiment) resulted in only 10% DEP removal during the same time.  
• Adsorption of DEP by CuFe$_2$O$_4$ was 19%  
• DEP removal was increased from 75% to 100% by increasing CuFe$_2$O$_4$/MWCNTs dosage from 50 mg/L to 200 mg/L.  
• The adsorption amounts onto DEP removal was complete at the DEP:PS ratio of 1:200 at t=30 min.  
• The efficiency of DEP degradation decreased from 100% to 28% when pH was increased from 3.0 to 11.0  
• DEP was completely removed at t=25 min at 40 °C  
• DEP removal efficiency remained at 87% and the recovery yield of the catalyst after five runs  
• SO$_4^-$ was the main ROS | [65] |

4. Concluding remarks

Activated PS-mediated AOPs have promising potentials to be implemented for the effective treatment of recalcitrant and/or toxic pollutants present in soil, water or wastewater. Activated PS/PMS is an
exciting treatment system that has been successfully applied in the environmental remediation field for several years. In this book section, several conventional and alternative methods to activate PS have been discussed. Major treatment applications have been comparatively described. It is suggested that future studies can be extended to investigate novel reactor design for heterogeneous catalytic activation systems based on batch or continuous flow (e.g. completely mixed or plug flow) reactor configurations featuring catalyst recovery or immobilization of catalysts used to activate PS on supports including inert 1/2/3-D materials, metal oxides, molecular sieves and/or adsorbents. The supported catalysts generally have better catalytic activity, improved dispersion, reduced metal ion leaching, better separation/recovery potential from the treated water, and added functionality (antibacterial, photocatalytic, etc.). Combination with conventional treatment methods and more classical AOPs to alter/enhance treatment efficiencies and reaction kinetics could also be advised for future work.

References

Sulfate radical based advanced oxidation processes for the removal of EDCs

75. Matzek, L.W., and Carter, K.E. 2016, Chemosphere, 151, 178-188.