Chapter 9
Radical Reactions and Their Application for Water Treatment

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Abstract Basic chemistry and water treatment of broad range of oxidants and related radical species are covered in this chapter. A general introduction to oxidants and radicals is followed by detailed sections on chlorine species, advanced oxidation processes, persulfates, and non-consensual radical mechanisms. Further, detailed information on oxidant applicability and activation, oxidant-specific recalcitrant pollutants and commonly formed by-products is provided. To assess the suitability of the specific oxidants for real water conditions, matrix components interferences are discussed. Considerable attention is paid to chemistry of innovative oxidants (persulfates) and to the controversial aspects of superoxide radical anion reactivity with carbon tetrachloride.

Keywords AOP · Hydroxyl radical · Sulfate radical · Superoxide radical · Ozone · Reactive chlorine · Persulfates · Carbon tetrachloride

9.1 Introduction

Free radicals are, from the chemistry point of view definition, atoms or molecules with one or more unpaired electrons in bonding orbitals whereby paramagnetic metal ions are not normally regarded as radicals (IUPAC 1997). This electron arrangement leads, apart from a few important exceptions (see below), to high reactivity of free radicals. Oxidants generally possess the ability to attract the whole bonding electron pair from their reaction counterparts. Free radicals, in contrast, often mediate one-electron transfer reactions. Basic instrumentation for researching radical-driven reactions is electron paramagnetic resonance (EPR) and stopped-flow spectroscopic techniques (Hayyan et al. 2016; Qian and Buettner 1999).

Water-stable free radicals—molecular oxygen (O_2) and chlorine dioxide (ClO_2)—are examples of such important exceptions. Both O_2 and ClO_2 are well

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J. Filip et al. (eds.), *Advanced Nano-Bio Technologies for Water and Soil Treatment*,
Applied Environmental Science and Engineering for a Sustainable Future,
https://doi.org/10.1007/978-3-030-29840-1_9

water-soluble gases. Oxygen, which is actually a bi-radical, is often employed as a cheap electron-pair acceptor for oxidation of undesirable inorganic water components like Fe^{2+} or Mn^{2+} ions. However, molecular oxygen oxidative capabilities towards organic pollutants are very limited. This feature is called spin restriction of oxygen. For the reaction with molecular oxygen, both electrons need to be of the same spin, which is the condition biomolecules or organic pollutants rarely satisfy (Halliwell and Gutteridge 1984). Dissolved ClO_2 has been researched for a growing number of water treatment applications (Aieta and Berg 1986; Huber et al. 2005), which will be further discussed in Sect. 9.2.

Some oxidants such as H_2O_2, O_3, or $S_2O_8{}^{2-}$ are precursors of a number of other free radicals. The umbrella term reactive oxygen species (ROS) also encompasses non-radical yet reactive oxygen moieties, e.g., singlet states of oxygen (Halliwell 2006). The formation of these short-living radical species is driven by specific reaction conditions among which the temperature and the pH play the key role by influencing the kinetics of each of the simultaneously running reactions. Another important parameter is the reactor exposure to light, especially to the light of shorter wavelengths (UV) (see also Chap. 10, which focuses on UV water treatment). UV light mechanism of action is multimodal. Besides direct organic compound photolysis, ROS are generated under oxygen saturated or oversaturated water conditions. In addition, UV is often used to initiate ROS production in advanced oxidation processes (AOPs) for drinking water supply since UV can provide the right portion of energy for symmetrical bond cleavage. Hydroxyl ($^{\bullet}OH$) and sulfate radicals ($SO_4{}^{\bullet-}$) are species that are directly responsible for transformation of organic pollutants and for water disinfection. This chapter focuses on describing the conditions for radical species generation, on radical reactivity with the target pollutants and radical scavenging by other water components, and on disinfection by-products (DBP). Some of the processes tend to be more employed in drinking water supply (chlorine and ozone), other find its application first in wastewater treatment and groundwater remediation (Fenton reagent and peroxydisulfate).

9.2 Chlorine Species

Chlorine species are traditionally used as drinking water disinfectants, which make water supply safe from microbiological point of view. Presence of organic compounds is generally unfavorable in the treated water (Ramseier 2010), as will be explained further. Therefore, chlorination is not a suitable technology for pollutant degradation.

Most usually, chlorine gas (Cl_2) or sodium hypochlorite (NaOCl) is dosed. In the USA, monochloramine (NH_2Cl) is still in use as residual disinfectant for water distribution systems. High natural organic matter (NOM) and bromide (Br^-) content

Table 9.1 Chlorine species overview

Name	Formula	Cl valence
Chloride/hydrochloric acid	Cl^-/HCl	−1
Free chlorine, chlorine atom	$Cl_2/Cl^\bullet$	0
Hypochlorite/hypochlorous acid	$OCl^-/HOCl^-$	+1
Chlorite/chlorous acid	$ClO_2^-/HClO_2$	+2
Chlorate/chloric acid	$ClO_3^-/HClO_3$	+5
Chlorine dioxide	ClO_2	+4
Monochloramine	NH_2Cl	+1

in the treated water can lead to formation of toxic DBPs. More than 600 DBPs are known today (Richardson et al. 2007). For chlorine species, most important DBPs are:

- NaOCl or Cl_2 – trihalomethanes (THMs), haloacetic acids, haloacetonitriles, chloral hydrates, trihalonitromethanes
- NH_2Cl – nitrosamines, cyanogen halides, iodinated THMs, haloacetaldehyde
- ClO_2 – chlorite, chlorate, organic acids

Chlorine dioxide (ClO_2) offers several advantages in comparison to other chlorine sources as it reacts directly as an electron acceptor rather than via chlorine substitution. Moreover, it is more efficient in protozoa deactivation; its efficiency is pH-independent and no malodorous DBPs are formed. However, in case of ClO_2 some relevant DBPs can also appear. As with other chlorine species, precise dosing with a feedback to matrix components concentrations is absolutely necessary to avoid the DBP formation. An overview of chlorine water species is provided in Table 9.1.

With the exception of ClO_2, which is a free radical, chlorine species act as electron pair transfer oxidants. Only under specific conditions, chlorine atom $Cl^\bullet$ (radical) can act in persulfate-based oxidation in turnover of $SO_4^{\bullet-}$ to $^\bullet OH$ (Lutze 2013; see also Sect. 9.4).

9.3 Ozone and Hydrogen Peroxide Related AOPs

There are two main oxidants used in AOP: ozone (O_3) and hydrogen peroxide (H_2O_2). Both oxidants react directly with some target pollutants and at the same time they are the source of set of reactive oxygen species. $^\bullet OH$ is the active substance produced in solutions of both oxidants.

Ozonation is probably the most common drinking water treatment that provides disinfection, color removal, iron and manganese oxides precipitation, and pollutant control (Lutze 2013). In groundwater and soil remediation, ozonation did not gain such popularity mainly because of the risk connected with gaseous ozone toxicity.

O_3 directly reacts with double bonds or aromatic ring containing compounds, reduced sulfur containing groups, and deprotonated amines (von Gunten 2003). $^{\bullet}OH$ can be formed either in the reaction of O_3 with NOM or, in the pH > 8 range, with OH^- ions. To support $^{\bullet}OH$ formation from O_3, H_2O_2 is sometimes added to make a mix called peroxon (Staehelin and Hoigne 1982) or the pH is adjusted to higher values (Ramseier 2010).

In propagation reactions of $^{\bullet}OH$ and O_3 with NOM and carbonates, other ROS, e.g., perhydroxyl ($HO_2^{\bullet}$) or its deprotonated version superoxide radical anion ($O_2^{\bullet -}$) emerge and make the reaction system even more complex. $HO_2^{\bullet}/O_2^{\bullet -}$ are poorly reactive with organic compounds in water medium, i.e., react very slowly (Gutteridge and Halliwell 1989). This is in contradiction to the reaction mechanisms proposed by some authors; details will be discussed in Sect. 9.5. Superoxide easily undertakes termination reactions, e.g., in the one with ozone in which oxygen is formed. Two superoxide molecules can reconstitute H_2O_2 in dismutation reaction ($2O_2^{\bullet -} + 2H^+ \rightarrow H_2O_2 + O_2$). In termination reactions, O_2 (mainly from $O_2^{\bullet -}$) or H_2O/OH^- (from $^{\bullet}OH$) are formed.

H_2O_2 additions to ozone are also used to avoid by-products formation. In case of ozone, the most relevant DBP is bromate BrO^-, which could be formed if bromide (Br^-) is present in treated water (von Gunten and Hoigne 1994). Avoiding bromate formation is a challenging task, which exceeds single ozone treatment technology. Regarding the presence of ozone recalcitrant pollutants together with bromide and NOM concentration, it might be either more efficient to enhance ozone dosing in some cases or to optimize H_2O_2 addition or to leave ozone AOP and switch over to using UV/H_2O_2 (Lutze 2013; von Gunten and Oliveras 1998). Ozonation is a fairly established technology with solid knowledge foundation coming from water radiochemistry, with many full-scale applications and comprehensive literature, e.g., von Sonntag and von Gunten (2012).

Changing the basic oxidant to H_2O_2, we move from potable water treatment towards wastewater treatment technologies. Diluted H_2O_2 itself is not a sufficiently strong oxidant to treat dissolved TOC or specific organic pollutants. However, various iron species are known to initiate $^{\bullet}OH$ generation from H_2O_2 in homogeneous or heterogeneous Fenton reaction (Eq. 9.1) derived processes, as reviewed by (Navalon et al. 2010, 2011; Pignatello et al. 2007).

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \tag{9.1}$$

Since the presence of iron in the technological unit inevitably leads to the need for sludge management, there are often other methods employed for H_2O_2 one electron reduction (i.e., $^{\bullet}OH$ formation). Gamma radiation, electrolysis, and ultrasound (including cavitation) are examples of the means that can mediate it (Brillas et al. 2009; Ince et al. 2001). Unlike the case of persulfates, heating cannot break the peroxygen bond of H_2O_2.

Subsurface applications of H_2O_2 (so called *in situ* chemical oxidation, ISCO) for contaminated groundwater and soil treatment are a very complex mix of physical and chemical processes that are well reviewed in (Siegrist et al. 2011). In brief, H_2O_2 instantly and exothermically decomposes to oxygen and water ($H_2O_2 \rightarrow H_2O + 1/2O_2$) once in contact with iron and manganese oxides surfaces of aquifer materials. Therefore, organic acids (e.g., citric acid, EDTA) additions are widely studied for H_2O_2 ISCO (Engelmann et al. 2003). This way, via iron and manganese oxide dissolution and chelation by organic acids, the unfavourable exothermic reaction may be slowed down. However, with the addition of organic acids, the question of other (toxic) metals mobilization arises. Even if metals Cu^+, Cr^{2+}, Co^{2+} (Tarr 2003) can substitute iron in $^•OH$ formation, their presence has to be monitored to exclude the possibility of mobilisation. Many studies have shown that the mobilisation of heavy metals is a time and space limited process in case of joint applications of chelators and H_2O_2 (Bennedsen et al. 2012).

As pollutants recalcitrant to $^•OH$ attack, perhalogenated aliphatic hydrocarbons are reported (Siegrist et al. 2011), especially chlorinated methanes and ethanes. Small kinetic constants were also found for long chain petroleum hydrocarbons.

9.4 Non-consensual Radical Mechanisms

We provide basic information on two non-consensual radical mechanisms: Involvement of superoxide radical anion ($O_2^{•-}$) in tetrachloromethane (CCl_4) degradation and ferryl (FeO^{2+}) specie reactions.

Carbon tetrachloride is an established toxicity model substance (Weber et al. 2003), its transformation mechanism is well described in mammalian hepatic cells. Decades of CCl_4 toxic action research on cellular, tissue, and animal model levels brought postulation of its free radical nature: Liver cell cytochrome P450 initiates the transformation of CCl_4 to trichloromethyl radical ($^•CCl_3$) (McCay et al. 1984), which may form trichloromethylperoxyl radicals ($^•OOCCl_3$) in the presence of oxygen (Mönig et al. 1983). Both radicals were identified as the species being responsible for the specific toxic effects of CCl_4. Several hundreds of in-vitro and in-vivo studies have been conducted in order to clearly understand the variability of CCl_4-induced toxic effects, including dose-response dependence, preventive or potentiating impact of other compounds (e.g., antioxidants), oxygen partial pressure, or age of model animals (Vulimiri et al. 2011). Chloroform, hexachloroethane, phosgene, and alkanes/alkanals/alkenals belong to CCl_4 metabolism intermediates while carbon monoxide, carbon dioxide, and hydrochloric acid are its metabolic endproducts (Plaa 2000).

In complex scientific coverage of molecular mechanisms in CCl_4-induced toxic effects, no evidence is given for the $O_2^{•-}$ involvement in the initial step of the CCl_4 transformation, even though $O_2^{•-}$ is ubiquitously present in living cells (McCord and Fridovich 1988). Instead, the initial step is attributed to NADPH-cytochrome *P*-450 reductase. Furthermore, hyperbaric oxygen conditions are claimed to prevent the initiation of CCl_4 metabolism via trichloromethyl radical mechanism (Manibusan et al. 2007; Reiner et al. 1972).

In the aquifer, CCl_4 undergoes degradation, which is driven by biotic and abiotic factors (Shao and Butler 2009), whereby oxygen poor conditions are essential. Microbial transformations of CCl_4 are either accomplished by extracellular coenzyme exudates (Hashsham and Freedman 1999) or by extracellular mineral secretion (McCormick and Adriaens 2004). In abiotic degradation pathways, reduced species of iron and sulfur such as pyrite (Kriegman-King and Reinhard 1994), sulfides (Devlin and Müller 1999), adsorbed Fe^{II} (Amonette et al. 2000; Elsner et al. 2004; Kenneke and Weber 2003), or zero-valent iron (ZVI) (Johnson et al. 1998), were identified as reactants for reductive CCl_4 degradation. The half-life of CCl_4 in the aquifer is reported to range from a few days to hundreds of days (Howard 1991). For more information on the degradation of CCl_4 in the aquifer see Pecher et al. (2002) and Elsner and Hofstetter (2011).

Major products of CCl_4 aquifer degradation are chloroform, formate, carbon monoxide, and carbon dioxide. Similarly to CCl_4 mammalian metabolism, the initial step in the aquifer-related CCl_4 degradation—one electron reduction to trichloromethyl radical—is supposed for all identified intermediates and products (Elsner et al. 2004). However, in the degradation mediated by *Pseudomonas stutzeri* KC only traces of chloroform has been reported, with most of the carbon mass being transformed to carbon dioxide (Criddle et al. 1990).

Under oxygen-rich conditions, represented by oxidative water treatment such as ozone and hydroxyl radical based advanced oxidation processes (AOP), CCl_4 is claimed to exhibit chemical stability (von Sonntag 2008).

On the other hand, contrary to the above-mentioned literature, there is a series of studies (Che and Lee 2011; Furman et al. 2009; Howsawkeng et al. 2010; Smith et al. 2004; Stoin et al. 2015; Teel and Watts 2002; Watts et al. 2005) that describe CCl_4 degradation proceeding under peroxide-based conditions. Similar CCl_4 degradation reactions are believed to occur in peroxydisulfate systems, which was reported by (Xu et al. 2014a, b). Moreover, $O_2^{\bullet -}$ was identified as an oxygen species initiating CCl_4 transformation in both oxidative systems. Furthermore, a technique employing CCl_4 was established to prove the $O_2^{\bullet -}$ presence (Corbin III 2008; Watts 2011; US EPA 2014).

We conclude that the CCl_4 reactivity with $O_2^{\bullet -}$ in oxidative systems remains controversial. Both peroxide- and peroxydisulfate-based systems are a very complex interplay of several simultaneous reactions. Since gaseous oxygen is one of the reaction products in oxidative systems, it is extremely uneasy to conduct CCl_4 degradability experiments in a methodologically correct way. We suggest that it is the CCl_4 volatilisation loss rather than its degradation that might be the process leading to the CCl_4 decrease in the reaction systems reported in the previous paragraph. The CCl_4 degradation in oxidative systems is still questionable, so is its initiation by $O_2^{\bullet -}$.

The other non-consensual species, which is often discussed in studies of Fenton-like reaction systems, is ferryl ion FeO^{2+}. Reaction mechanisms in AOP are perceived as radical ($^{\bullet}OH$) based by most of the scientific community. However, there is an alternative to $^{\bullet}OH$—FeO^{2+}. High valent (4+, 5+, and 6+) iron-oxo species chemistry is thoroughly described in Chap. 8. Four-valent iron-oxo complexes are proposed to participate in enzymatic reactions of living cell systems. Ferryl ion is proven to be a part of non-heme iron metalloenzymes (Groves 2006; Krebs et al. 2007), which provide substrate hydroxylation. Some authors propose its equivalent presence in H_2O_2 systems with Fe^{2+} activation (Lee and Sedlak 2009) and its presence is also supposed in zero-valent iron corrosion systems, where H_2O_2 is generated as an intermediate species (Keenan and Sedlak 2008). Calculations of Bossmann et al. (1998) have shown higher thermodynamic favourability for the formation of FeO^{2+} rather than of $^{\bullet}OH$ under the assumption that the Fe^{2+} ion is present as $Fe(H_2O)_5(OH)^+$ at circumneutral pH and H_2O_2 must first be incorporated into this complex to form $Fe(OH)(H_2O_2)(H_2O)4^+$. Let's conclude with Barbusiński (2009) it is possible that both $^{\bullet}OH$ and FeO^{2+} can coexist in Fenton chemistry and, depending on the operating parameters, one of them predominates.

9.5 Persulfates Chemistry

Persulfates arouse enormous research interest. Over the course of the last 2 years about ten review papers have been published on sulfate radical-based advanced oxidation techniques (Boczkaj and Fernandes 2017; Brienza and Katsoyiannis 2017; Ghanbari and Moradi 2017; Hu and Long 2016; Ike et al. 2018; Liu et al. 2018; Matzek and Carter 2016; Oh et al. 2016; Wacławek et al. 2017; Wang and Wang 2018; Wang et al. 2016; Xiao et al. 2018; Ye et al. 2017; B.-T. Zhang et al. 2014).

There could be several different reasons why persulfates generate interest in recent scientific publication that has also been reflected in the number of citations. One of the reasons could be related to the simultaneous development of the heterogeneous catalysis field, which is directly interconnected with the persulfates one (Oh et al. 2016). Another reason could be that some time ago a cheaper method was developed for peroxydisulfate large scale production, which in combination with its cheaper and safer transport due to the solid state (powder) consequently makes it one of the most often used oxidants in ISCO (Ike et al. 2018; Wacławek et al. 2017). Another explanation could be the fact that the sulfate radicals (generated in the PS system) have different oxidation mechanism in comparison to the hydroxyl ones (Boczkaj and Fernandes 2017) and possess a very high redox potential, which consequently makes SO_4^{-} radical more suitable for degradation of several substances that are immune to standard AOP techniques, e.g., perfluorooctanoic acid (PFOA) (Wacławek et al. 2017). Sulfate radical oxidation mechanism was broadly described in a recent work of Ye et al. (2017) as shown in Fig. 9.1.

Persulfates are a group of two oxidants namely peroxydisulfate (PDS) and peroxymonosulfate (PMS); the main difference between them is that in the PDS molecule, the peroxide group bridges two sulfur atoms, whereas PMS is a type of an S-inorganic hydroperoxide. Both of these oxidants are not very reactive when non-activated, i.e., when they are not generating radical species. The main aim of the catalytic activation is to weaken the O–O bond of the persulfates (which can result in homolytic or heterolytic cleavage of the peroxide bond) (Wacławek et al.

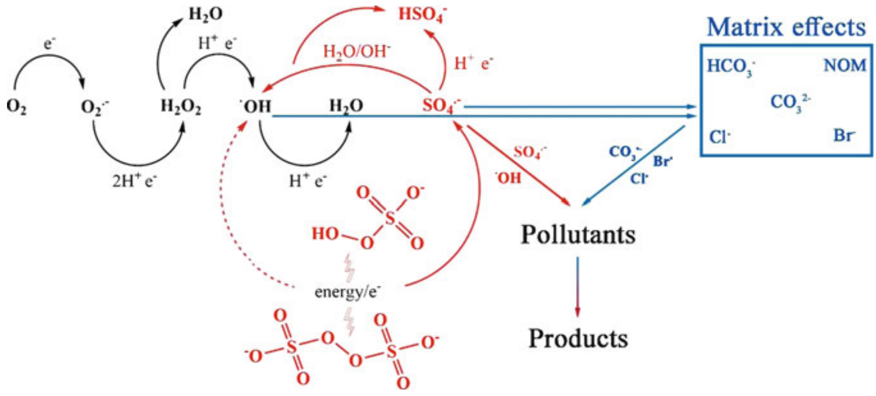


Fig. 9.1 Black arrows—scheme of oxygen molecule reduction to water; red arrows—radical formation and behaviour in a persulfates system; blue arrows—water matrix effects on the persulfates chemistry (dashed arrow—only valid for homolysis of the PMS peroxide bond). This figure is reprinted with a kind permission from Elsevier published paper (Wacławek et al. 2017)

2017), similarly to the Fenton chemistry discussed in the previous sections. In order to activate persulfates, several approaches that are homogeneous (catalyst is in the same phase as PS, e.g., dissolved cation) and heterogeneous (catalyst is in a different phase than PS, e.g., solid metal particles) can be adopted.

The homogeneous (as well as homolytic) activation of persulfates was critically reviewed and discussed by almost all the above-mentioned reviews (Ghanbari and Moradi 2017; Matzek and Carter 2016; Wacławek et al. 2017; Wang and Wang 2018; T. Zhang et al. 2014) and book (Siegrist et al. 2011). Because of this fact, only small part of this chapter will be devoted to these types of reaction. Persulfates can be activated by UV (Yang et al. 2010), heat (Ghauch et al. 2012; Yang et al. 2010), ultrasounds (Wei et al. 2017), and by homogeneous (B.-T. Zhang et al. 2015) and heterogeneous (Hu and Long 2016; Oh et al. 2016) approaches, whereas an example of a chemical element that can be used as a persulfates activator either as homogeneous and heterogeneous catalyst is iron (Fränzle et al. 2010; Fu et al. 2014; Hrabák et al. 2016; Kang et al. 2018; Wacławek et al. 2015).

A very good comparison of various homogeneous activators of PDS was provided by Anipsitakis and Dionysiou who determined Ag(I) as the best activator for PDS compared to other commonly available transition metals (Anipsitakis and Dionysiou 2004); however, there have been more reports published on persulfates catalysed by iron in its various valence states. Iron overall was identified as one of the best catalytic materials for persulfates activation, especially for PDS; as for PMS, divalent cobalt was determined to be the most efficient catalyst according to Anipsitakis and Dionysiou (2003) and Fernandez et al. (2004). The different reasons to explain the dominance of iron may include its price, biocompatibility, and capability of activating PS efficiently.

However, there are also several problems with the homogeneous iron activation of PS, i.e., the selection of an appropriate dose and the type of the iron catalyst since, when it is applied in excess, scavenging of sulfate radicals may become problematic (Zhao et al. 2014).

Moreover, Fe(II) can be quickly oxidized to Fe(III); although there are several researchers claiming that the Fe(III)/PS process can be efficient, the activation mechanism is still being questioned and investigated. For example, an interesting theory proposed by Ike et al. (2017) explains that a possible reaction considering the E^0 of PDS/Fe may involve Fe(III) oxidation to higher valence iron, i.e., ferrates. However, the main problem is the low solubility of Fe(III) in the absence of suitable complexation. Literature data indicates that, under standard conditions, the concentration of Fe(III) in solution can be less than 1.8×10^{-4} mmol/L. This is due to the strong tendency of Fe(III) to hydrolyse and form hydroxide complexes (that have a low solubility in H_2O).

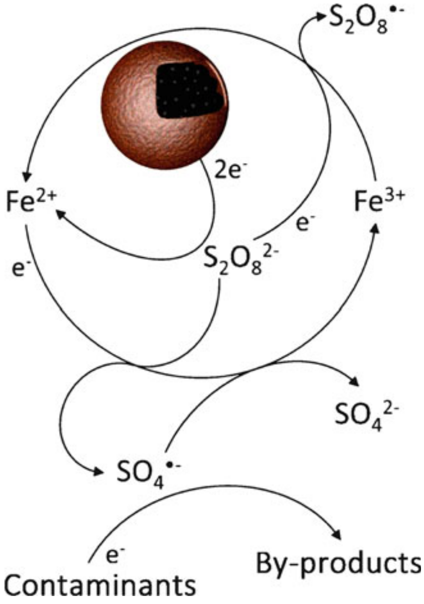
During the last eight years these problems have been thoroughly investigated and several solutions have been found, e.g.,:

- chelation of iron for effective control of the amount of Fe(II) available to react with PS (Rastogi et al. 2009)
- regeneration of Fe(II) by electrolysis. This technique may be very effective and may be competitive where sustainably generated electricity is abundant and cheap (Wacławek et al. 2016; Yuan et al. 2014)
- heterogeneous catalysis of persulfates that (in case of the zero-valent iron) provides slow release of Fe(II) (Oh et al. 2016; Xiao et al. 2018)

Especially the last point has aroused significant interest lately since the heterogeneous catalyst can often be easily separated from the reactant solution and have other interesting properties (Oh et al. 2016; Xiao et al. 2018). Moreover, carbonaceous catalysis of PS (Chen and Carroll 2016; Duan et al. 2015; Lee et al. 2015) was found very popular recently, however, this topic still remains controversial (Lee et al. 2017). Several oxidants can also be heterogeneously activated by subsurface minerals (Ahmad et al. 2010), which makes their application for, e.g., groundwater remediation more facile.

As mentioned before, iron is one of those elements that can be incorporated to the heterogeneous catalysis of PS. Adopting the use of solid iron particles where the release of iron species being responsible for the activation of PDS occurred smoothly without the risk of sulfate radical quenching was reported by Naim and Ghauch (2016). On the other hand, Ayoub and Ghauch (2014) demonstrated that the activation of PDS can be sustained better in solution especially while using bimetallic and trimetallic iron-based particles, which make the process more efficient in long-term application. Such great efficiency of heterogeneous activation by solid iron has led to investigating this material also in smaller dimensions, i.e., nanoscale zero-valent iron (nZVI). nZVI is not a new material in the environmental chemistry field and has already been applied to many contaminated sites *in situ*, where it can

Fig. 9.2 Scheme presenting mechanism of peroxydisulfate activation with nZVI. (Adapted from Kim et al. 2018)



not only adsorb and reduce contaminants but also enhance bioremediation processes (Krol et al. 2013; Němeček et al. 2016). It has been recently found that nZVI can be successfully applied as a heterogeneous catalyst for peroxydisulfate (Kang et al. 2018; Kim et al. 2018) and peroxymonosulfate (Tan et al. 2018; Wang et al. 2017). Especially Kim et al. (2018) focused on the mechanism of the reaction (Fig. 9.2).

For example, it was determined that the $SO_4^{\bullet-}$ yield per mole of PDS was more than two times higher in the PDS/nZVI system in comparison to the PDS/Fe(II) one (Kim et al. 2018). It could be therefore assumed that the radicals were produced more efficiently in the heterogeneous system because aqueous Fe(II) was supplied more slowly, preventing scavenging of $SO_4^{\bullet-}$ by excess Fe(II).

Therefore, a relatively low oxidant dose could be used when nZVI rather than Fe (II) is used as an activator.

Moreover, it should be noted that various coatings of nZVI can alter these processes, making it a real challenge worth solving (Diao et al. 2016). The influence of inorganic coating of nZVI was the subject of a recent study (Rayaroth et al. 2017) wherein the sulfidation of nZVI was investigated leading to the increased applicability of nZVI (efficiency of degradation was extended to alkaline pH).

To the best of our knowledge, the only oxidation state of iron that has not been reported in combination with persulfates is the iron in high oxidation states (i.e., ferrates). In the light of the preliminary experiments that have not been published yet (Wacławek, Hrabák, Filip, Černík, unpublished data), it is believed that ferrates can have a synergistic effect with persulfates (Fig. 9.3).

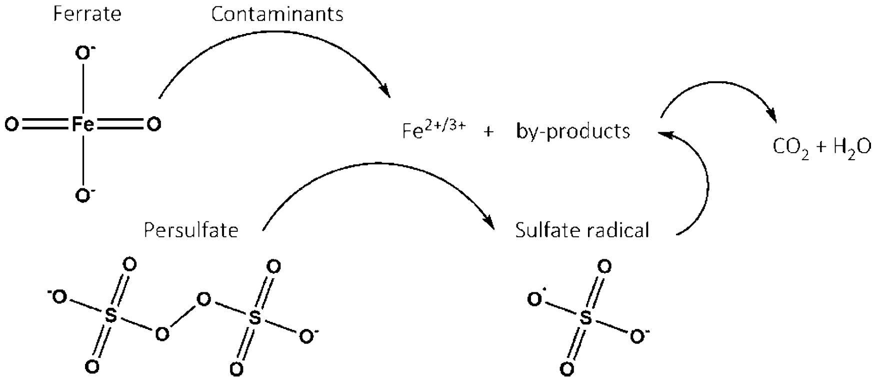


Fig. 9.3 Scheme of possible synergistic effect between ferrates and persulfates

However, this process will strongly depend on the solution pH as well as on many other parameters; therefore it should be thoroughly investigated in the future.

Overall, investigating the influence of the pH on the persulfate decomposition can be considered as another serious challenge. The oxidation of substances by persulfate depends strongly on the concentration of hydronium and hydroxyl ions. Especially PMS is affected by the pH since it reacts differently when the molecule is fully protonated or deprotonated (i.e., H_2SO_5, HSO_5^-, or SO_5^{2-}). Further, a very interesting topic that has not been carefully investigated yet is the rate of the formation of radicals in various pH values. Generally, PS reactions at acidic pH most frequently improve the degradation kinetics, however, the improved removal rates were also observed at neutral pH (between 6 and 8) and slightly basic pH (between 9 and 10, which can be often associated with interchanging of the radical species—sulfate to hydroxyl) depending on the contaminant and activation type (Matzek and Carter 2016).

Another challenging concept involves the PDS activation with hydrogen peroxide, which was studied by several authors (Zhao et al. 2013). However, its exact mechanism remains unknown, but there are several researchers that believe the activation process depends only on the heat generated from the hydrogen peroxide exothermic reactions.

It should be noted that because of several undesirable characteristics, like post-contamination with sulfate ions and reaction with chlorine/bromine species with further chlorination/bromination of the water matrix (both of those processes can lead to the increase in the toxicity), sulfate radical-based systems are not considered the best candidates for drinking water treatment. However, it is possible that a new technology in combination with the membrane techniques will be developed to serve the purpose in the future.

Acknowledgement The authors appreciate kind support of laboratory of Instrumental Analytical Chemistry at University Duisburg-Essen, namely of Prof. Torsten Schmidt, in elucidation of carbon tetrachloride degradability.

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