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VYUŽITÍ PERSULFÁTU PRO ODBOURÁVÁNÍ ORGANICKÝCH LÁTEK

USE OF PERSULFATES FOR DEGRADATION OF ORGANIC POLLUTANTS

Autoreferát disertační práce

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Autor práce:	Mgr Inż. Stanisław Wacławek
Školitel:	Prof. Dr. Ing. Miroslav Černík, CSc.

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Abstract

Peroxydisulfate (PDS) and peroxymonosulfate (PMS) are among the strongest and newest oxidants used in environmental studies. Furthermore, they can form free radicals analogous to the hydroxyl radical pathways generated by Fenton's chemistry. Sulfate radicals are also very strong aqueous oxidizing species with a redox potential estimated to be 2.6 V, similar to that of the hydroxyl radical, 2.7 V. These radicals can be used for the remediation of a wide range of contaminants, including chlorinated olefins, BTEXs, phenols, pharmaceuticals, inorganics and pesticides. Moreover, the reactivity of persulfates is extremely dependent on the related activation techniques and the composition of the treated matrix. Non-catalysed persulfate reactions have drawbacks in the form of slow reaction rates and the formation of stable disinfection by-products, which reduce natural attenuation. Activation can be achieved by heat, UV radiation, radiolysis, where two radicals are generated from each molecule of oxidant, or by either homogenous or heterogeneous chemical methods. Treatment with a generated sulfate radical is effective for almost all known types of contamination, but depending on reaction conditions, hydroxyl, superoxide radicals or singlet oxygen can be the dominant radical. In addition to the activation process, the water quality parameters are of great importance, especially pH and concentrations of halogens or natural organic matter.

Part of the work was focused to evaluate the efficacy of two persulfate-based oxidants: peroxydisulfate and peroxymonosulfate activated in various ways to treat HCH-impacted environmental media. Results from batch treatment showed positive results for electro-activated PDS but only negligible effectiveness for electro-activated PMS. However, cobalt-mediated activation of PMS had shown good effect on HCH oxidation. Furthermore, tests investigating decomposition of both persulfates were done and the optimal conditions for decontamination (applied current, molar ratio between oxidant and activator) were found. To follow PMS decomposition rate, simple, sensitive and accurate spectrophotometric method has been developed and validated for the determination of it.

Furthermore, it was demonstrated that elevated temperatures from meso- or thermophilic digestion could activate persulfates and oxidize toluene and other organic matter in anaerobically digested sludge thereby improving its dewaterability. Furthermore, supernatant obtained after oxidation treatment was conditioned by struvite precipitation in order to remove ammonium nitrogen and phosphates. The results of this study indicate large improvements in ADS properties after PDS treatment in comparison to PMS or temperature conditioning alone.

To summarize, this work has shown persulfates applicability for the treatment of HCH-contaminated water and anaerobically digested sludge. It has been shown, that properly activated PDS and PMS can efficiently degrade HCH isomers as well as remove toluene and improve properties of anaerobically digested sludge.

The introduction of this thesis is a significant part of a review paper entitled “Chemistry of persulfates in water and wastewater treatment: a review” which is submitted in an impact factored journal.

Keywords: oxidation, remediation, persulfates, peroxydisulfate, peroxymonosulfate, persistent organic pollutants

Abstrakt

Peroxodisíran (PDS) a peroxomonosíran (PMS) patří mezi nejnovější a nejsilnější oxidanty používané v životním prostředí. Tyto oxidanty mohou tvořit volné radikály analogické k radikálům hydroxylovým vytvořeným ve Fentonově reakci. Sulfátové radikály jsou také velmi silné vodné oxidační činidla s oxidačně-redukčním potenciálem cca. +2,6 V, podobným hydroxylovým radikálům (+2,7 V). Tyto látky mohou být použité pro širokou škálu kontaminantů, např. chlorované olefiny, BTEX, fenoly, léčiva, anorganické látky a pesticidy. Navíc, reaktivita peroxosíranů je velmi závislá na použitých aktivačních technikách a na složení upravované matrice. Nekatalyzované reakce peroxosíranu mají nevýhody, jako je nízká reakční rychlost a tvorbu toxických produktů s dlouhou životností. Aktivace se může provádět zvětšením teploty, UV zářením, radiolýzou (kde se vytvářejí dva moly radikálů na každý mol molekuly oxidantu), nebo homogenními či heterogenními chemickými metodami. Generované sulfátové radikály jsou účinné pro téměř všechny známé typy polutantů, ale v závislosti na reakčních podmínkách ostatní radikály kyslíku (hydroxylové, superoxidové, singletový kyslík) mohou být silnějšími oxidanty. Kromě toho, proces aktivace a parametry kvality vody (zejména pH, obsah halogenů a organických rozpuštěných látek) jsou důležité pro průběh oxidačních procesů.

Část práce byla věnována hodnocení účinnosti těchto dvou oxidantu (peroxodisíranu a monoperoxosíranu), aktivovaných různými způsoby, na degradovatelnost hexachloro-cyklohexanů (HCH). Velmi rychlá kinetika dekontaminace HCH byla pozorována u peroxodisíranu aktivovaného elektrolýzou při zanedbatelné účinnost pro monoperoxosíran aktivovaný stejným procesem. Nicméně, aktivace monoperoxosíranu kobaltem měla pozitivní vliv na oxidace HCH. Kromě toho byly provedeny testy pro stanovení kinetiky úbytku peroxodisíranů a optimálních podmínek pro oxidaci (intenzita proudu, molární poměr oxidačního činidla do aktivátoru). Pro sledování rychlosti reakce byla vyvinuta a použita jednoduchá, přesná a citlivá spektrofotometrická metoda pro stanovení monoperoxosíranu mj. v aktivovaném kalu.

Dále bylo ukázáno, že zvýšená teplota (v rozmezí od mezo- do termofilních podmínek) může být účinná pro aktivaci peroxosíranu pro oxidaci toluenu a dalších organických látek ke zlepšení vlastnosti a odvodnění kalu. Ze supernatantu získaného po oxidaci byl vysrážen struvit pro odstranění amoniakálního dusíku a fosfátu. Výsledky této studie ukazují výrazné zlepšení vlastností kalu po oxidace peroxodisíranem ve srovnání s oxidací monoperoxosíranem nebo zvýšením teploty.

Stručně řečeno, tato práce ukázala, že peroxosírany jsou vhodné pro zlepšení vlastností kalu, jakož i pro remediaci podzemní vody kontaminované vysoce toxickým HCH. Byly rovněž zjištěné aktivační metody PMS a PDS pro účinnou degradaci izomerů HCH, toluenu a zlepšeni vlastnosti kalu po fermentaci.
Teoretická část této práce je součástí přehledového článku "Chemistry of persulfates in water and wastewater treatment: a review", který je připraven pro publikaci v časopise s impakt faktorem.

Klíčová slova: oxidace, sanace, persulfáty, peroxodisíran, peroxomonosíran, perzistentní organické polutanty

Streszczenie

Nadsiarczan (PDS) oraz mononadsiarczan (PMS) są jednymi z najnowszych i najmocniejszych utleniaczy stosowanych w badaniach środowiskowych. Ponadto, mogą one tworzyć wolne rodniki, analogicznie do sposobu generowania rodników hydroksylowych w reakcji Fentona. Rodniki siarczanowe są bardzo silnymi utleniaczami o potencjale redoks szacowanym na 2,6 V, podobnym do potencjału rodnika hydroksylowego, który wynosi 2,7 V. Rodniki te mogą być wykorzystywane do oczyszczania szerokiego zakresu zanieczyszczeń, w tym chlorowanych węglowodorów, BTEX, fenoli, farmaceutyków, związków nieorganicznych i pestycydów. Ponadto, reaktywność nadsiarczanów w wysokim stopniu zależy od zastosowanych technik aktywujących oraz składu matrycy, w którym zostały one użyte. Reakcje niekatalizowanego nadsiarczanu mają wady w postaci niskiej szybkości reakcji i tworzenia trwałych produktów ubocznych. Aktywacja owej reakcji może zostać przeprowadzona za pomocą ciepła, promieniowania UV, radiolizy (gdzie z każdego mola cząsteczki utleniacza generowane są dwa mole rodników) albo metod chemicznych (jednorodnych lub niejednorodnych). Wygenerowany rodnik siarczanowy jest skuteczny wobec niemal wszystkich znanych rodzajów zanieczyszczeń, ale- w zależności od warunków reakcji- rodnik hydroksylowy lub nawet tlen singletowy mogą być dominującymi utleniaczami. Poza tym w procesie utleniania niezwykle istotne są: sposób aktywacji i parametry jakości wody (zwłaszcza pH, stężenie halogenów i rozpuszczonych substancji organicznych).

Część pracy została poświęcona ocenie skuteczności dwóch utleniaczy: nadsiarczanu i mononadsiarczanu, aktywowanych różnymi sposobami, w celu uzyskania degradacji hexachlorocyklohexanów (HCH). Bardzo szybka kinetyka rozkładu HCH została zaobserwowana u nadsiarczanu aktywowanego procesem elektrolizy, natomiast znikomą skuteczność wykazywał mononadsiarczan aktywowany tym samym procesem. Jednakże, aktywacja mononadsiarczanu kobaltem wywarła pozytywny wpływ na utlenianie HCH. Ponadto, zostały przeprowadzone testy określające kinetykę redukcji nadsiarczanów, w wyniku których odkryto optymalne warunki dla utleniania (takie jak natężenie prądu czy stosunek molowy utleniacza do aktywatora). Aby śledzić szybkość redukcji mononadsiarczanu, opracowano i zastosowano łatwą, wrażliwą i dokładną metodę spektrofotometryczną oznaczania tego związku m.in. w osadzie czynnym i wodach podziemnych.

Ponadto, wykazano, że podwyższone temperatury występujące w procesie fermentacji (w zakresie od mezo- do termofilowych) mogą skutecznie aktywować nadsiarczany doprowadzając do utlenienia toluenu i polepszenia własności osadu przefermentowanego, jednocześnie poprawiając również jego odwadnialność. Dodatkowo, w supernatancie otrzymanym po przeprowadzonym procesie utleniania został wytrącony struwit, co spowodowało tym samym usunięcie azotu amonowego i fosforanu z cieczy nadosadowej. Wyniki tego badania wskazują na dużą poprawę własności osadu po procesie utleniania nadsiarczanem, w porównaniu do utleniania mononadsiarczanem czy użycia wyłącznie podwyższonej temperatury.

Podsumowując, w pracy tej wykazano, że nadsiarczany skutecznie wpływają na polepszenie własności osadów przefermentowanych, jak również na oczyszczanie wód podziemnych zanieczyszczonych silnie toksycznymi HCH. Odkryto i opisano także odpowiednie metody aktywacji PDS i PMS, której celem jest rozpoczęcie procesu degradacji izomerów HCH, usunięcia toluenu oraz poprawienia własności przefermentowanego osadu.

Rozdział teoretyczny przedstawionej pracy jest częścią artykułu przeglądowego pod tytułem "Chemistry of persulfates in water and wastewater treatment: a review", który zostanie opublikowany w impaktowanym czasopiśmie.

Słowa kluczowe: utlenianie, rekultywacja, nadsiarczany, nadsiarczan, mononadsiarczan, trwałe zanieczyszczenia organiczne

Contents

1. Introduction

Over the last few decades, ubiquitous contamination with various inorganic and organic substances has caused serious problems all over the world (Crutzen and Wacławek, 2014). One example can be the misuse or overuse of antibiotics e.g. for agricultural purposes, which enrich the population of resistant microorganisms that are able to infect humankind (Martinez, 2009). In many countries with a low human development index (HDI), particularly in Africa and Asia, surface- and groundwater contamination can be a direct cause of water scarcity. It is important, therefore, to develop cheap and efficient water and wastewater treatment methods (Larsen et al. 2016).

There are many different water and wastewater decontamination methods, which can be universally divided into biological (Phillips et al. 2005), physical (Bass et al. 2000) and chemical methods (Sonntag and von Gunten, 2012). From the chemical methods, we can distinguish processes focusing on the exchange of electrons between reagents and contaminants, which involve either reduction (e^- donation) or oxidation (e^- acceptance) from the point of view of the contaminant.

Persulfates, namely peroxydisulfate (PDS) and peroxymonosulfate (PMS), belong to the peroxide group and are gaining tremendous popularity in water and wastewater treatment (Xu et al., 2012; Tsitonaki et al., 2010; Zhang et al., 2014). Many studies have shown that they are capable of degrading highly toxic pollutants e.g. PCBs (Fan et al., 2014), stable in the environment (Yen et al., 2011), and relatively cheap in comparison to other oxidants (Duan et al., 2015) (Table 1).

My PhD study resulted in 8 scientific papers, on degradation of various contaminants by PDS and PMS, of which I am mostly first (or corresponding) author.

1.1 Thesis goals

The main aim of the thesis was to develop and assess feasible methods for decontamination of organic pollutants with the use of activated persulfates. Thus activated persulfates were used for degradation of persistent organic pollutants and anaerobically digested sludge. In order to deeper understand the reaction mechanisms, one of the goals was to develop simple, rapid and accurate determination method for peroxymonosulfate.

Since persulfates are relatively new oxidants used *in situ*, there are many unknown reactions taking part in their chemistry. Therefore, another goal of the thesis was to determine the reaction pathways of catalysed persulfates with hexachlorocyclohexanes and to examine tested methods on contaminated water from site or anaerobically digested sludge from wastewater treatment plant.

2. Chemistry of persulfates

2.1. Chemical and physical properties of persulfates

Persulfuric acid ($H_2S_2O_8$) was discovered by the French chemist Marcelin Berthelot in 1878 (Kolthoff et al., 1951). It can be produced by electrolysis of sulfate salt. The resulting PDS salt is almost non-hygroscopic and has a good longevity.

There are three salts of PDS (PDS): potassium, ammonia and sodium. The solubility of potassium PDS is very low for environmental applications, and the reaction of ammonium PDS results in residual ammonia, which is an undesirable reaction product. Therefore, sodium PDS ($Na_2S_2O_8$) is the most common and feasible form used to date in ISCO, with a high solubility (73 g/100 g H_2O at 25 ^oC) (Behrman and Dean, 1999; EPA/600/R-06/072).

PDS is cheap in comparison to other oxidants used in situ (0.74 USD/kg), but is still more expensive than hydrogen peroxide for large-scale applications. The bond distance and energy of $O_3SO\text{-}OSO_3$ bonding were estimated to be 1.497 Å and 140 kJ/mol, respectively (Kolthoff et al., 1951; Yang et al., 2010; Duan et al., 2015) and (Table 1).

Table 1. Various properties of common oxidants used *in situ*

Oxidant	**O-O bond-dissociation energy [kJ/mol]**	**Solubility in water in 25°C [g/L]**	**Average estimated lifetime in groundwater[4]**	**Price [USD/kg][2]**	**Price [USD/mol]**
H_2O_2	213	unlimited	hours to days	1.5	0.05
O_3	364	0.1	<1 hour	2.3	0.11
Potassium ferrate	-	0.7-3[3]	unstable in pH ≠9	2000	396
PDS[5]	92[6]	730	>5 months	0.74	0.18
PMS[1]	377[6]	298	hours to days	2.2	1.36

[1] PMS is herein considered as a triple salt with the trade name Oxone®

[2] Prices per kg are taken from: Duan et al. (2015); Langlais et al. (1991); http://www.labmanager.com/news/2010/04/new-battelle-process-slashes-price-of-useful-but-expensive-chemical?fw1pk=2#.Vu2SzOZxBqF; Zhang et al. (2014)

[3] (Bailie et al., 1996)

[4] Depends on water hardness, transition metal concentration, dissolved organic carbon (DOC) concentration, and many other factors

[5] Sodium PDS

[6] (Benson, 1978)

The remaining data was taken from Kolthoff et al., 1951; Yang et al., 2010

The symmetric structure of PDS molecules and relatively high bonding energy makes more difficult to break the O-O bond and generate free radicals without external activation.

Peroxymonosulfate (PMS) originates from the peroxymonosulfuric acid (H_2SO_5) also known as Caro's acid (Hussain et al., 2013). It possesses reactive oxygen closest to the hydrogen atom that carries the active power (Fig. 1b). Since the oxygen is readily reactive, $KHSO_5$ is usually found in a more stable form of a white triple salt, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (potassium hydrogen PMS). Commercially, the product goes under the trade-name of Oxone® and it is a water-soluble, safe to handle, strong and stable (but not as stable as PDS) oxidizing agent, thus having a good potential applicability (Shukla et al., 2010; Lente et al., 2009; Yao et al., 2015). In comparison to PDS, PMS has a shorter bond length (1.46 Å), which translates to a higher bond dissociation energy (377 kJ/mol). In other words, in theory, PMS requires even more energy in order to be activated.

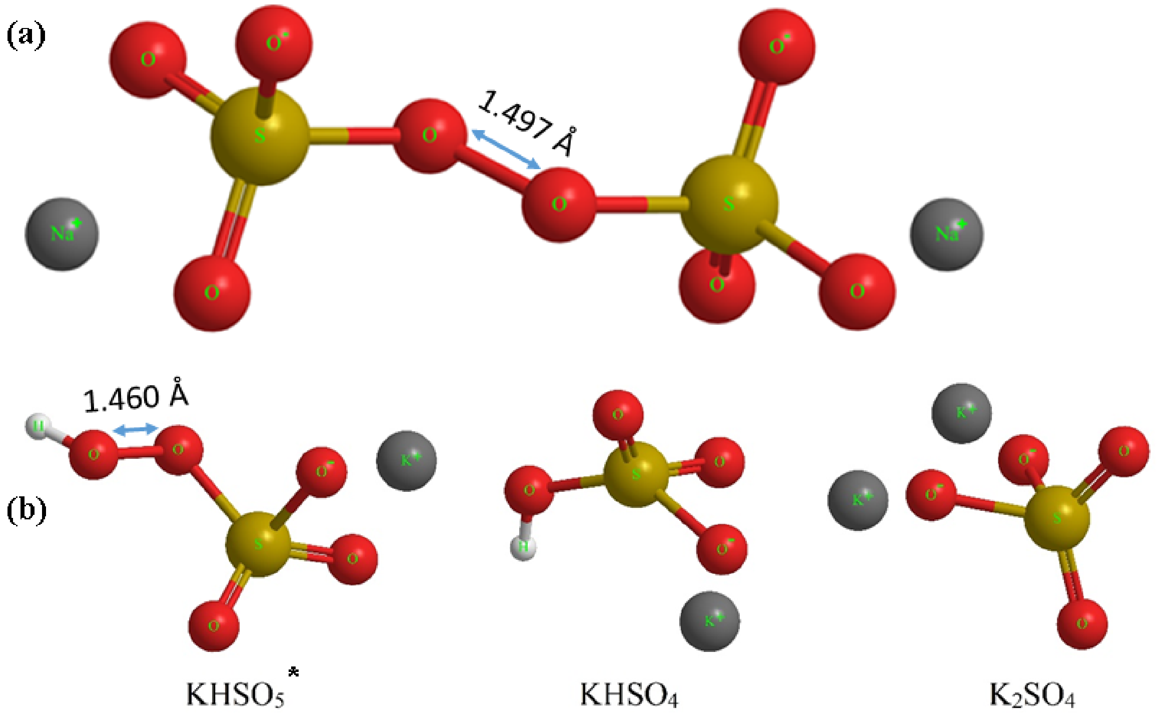

Figure 1. (a) Sodium PDS and (b) Oxone triple salt molecular structure (*potassium PMS ($KHSO_5$) - active part of Oxone). (Spivey et al., 2015).

The cost of Oxone is the highest of all of the conventionally used oxidants in ISCO, although it is still much cheaper than ferrates (Zhang et al., 2014).

Persulfates are very stable in the solid state and remain stable for several months in the aqueous phase. One of the advantages of PDS in comparison to the other commonly used ISCO reagents (hydrogen peroxide or ozone) is its much higher stability. This means fewer transportation drawbacks, it can be injected into the place of contamination at elevated concentrations, and can be moved through porous media by density driven dispersion (Siegrist et al., 2011).

Yen et al. (2011) determined that PDS anions can persist in the soil system for over five months. PMS does not show such a high persistence as PDS, although as long as it is stored under dry and cool conditions, it loses about 1% activity per month due to the release of oxygen and heat (http://www2.dupont.com/Oxone/en_US/index.html). Decomposition to SO_2 and SO_3 takes place under the influence of heat (starting at 300 °C). Stability in the aqueous phase reaches a minimum at pH 9, whereby the mono anion (HSO_5^-) has the same concentration as the dianion (SO_5^{2-}) (http://www2.dupont.com/Oxone/en_US/index.html). More detailed information about the stability of PMS at various pH values can be found in Bouchard et al. (2009).

In addition to their high permanence, PDS and PMS are among the strongest oxidants used in environmental remediation applications. The standard oxidation-reduction potential (ORP) for the PDS reduction (Eq. 1) is 2.01 V, thus it is higher than the 1.4 V (Eq. 2) of PMS but lower than that of ozone (2.2 V) (Bajpai, 2012; Block et al., 2004).

$$S_2O_8^{2-} + 2H^+ + 2e^- \rightarrow 2HSO_4^- \quad (1)$$

$$HSO_5^- + 2H^+ + 2e^- \rightarrow HSO_4^- + H_2O \quad (2)$$

Moreover, persulfates can be activated by a cleavage of the O-O bond to form two types of radicals - sulfate and hydroxyl. These radicals exhibit higher ORP potential and are more suitable for radical reactions with organic contaminants. The activation process can be shown as:

$$S_2O_8^{2-} \xrightarrow{\text{initiator}} SO_4^{\bullet-} + (SO_4^{\bullet-} \text{ or } SO_4^{2-}) \quad (3)$$

$$HSO_5^- \xrightarrow{\text{initiator}} SO_4^{\bullet-} + (OH^{\bullet} \text{ or } OH^-) \quad (4)$$

where non-radical species are generated by electron transfer from a donor - activator.

2.2. Activation mechanism

As mentioned above, PDS and PMS are chemically stable, do not react with contaminants without external activation and can persist in the environment for a long periods of time. Their activation forms free radicals by splitting the peroxide bond. This can be initiated mainly by thermal (Ji et al., 2016; Johnson et al., 2008), photolytic (Zhang et al. 2015), sonolytic (Chen and Su, 2012), radiolytic (Criquet et al., 2011), magnetic spinel (Zhang et al., 2013; Ding et al., 2013), granular activated carbon (Yang et al., 2011), quinones (Fang et al., 2013), alkaline pH (Furman et al., 2010; Qi et al., 2016) ozone (Yang et al., 2015) or phenol (Ahmad et al., 2013) activation. In addition, sulfate radicals can also be formed via electron transfer by transition-metal activation of PDS (Zhao et al., 2014) or PMS (Anipsitakis and Dionysiou, 2004). Radiolysis, photolysis, or thermal activation of PMS precedes the evolution of both sulfate and hydroxyl radicals (Anipsitakis and Dionysiou, 2004; Guan et al., 2011). The formation of sulfate radicals as the major oxidizing species can be performed only via transition-metal catalysis (although the interchange of radicals in water solutions can be also notable and will be further discussed). Among the transition metal ions (Co^{2+}, Cu^{2+}, Ni^{2+}, Fe^{2+}, Ag^{+}, Ru^{3+}), cobalt was found to be the most efficient catalyst for PMS according to Anipsitakis and Dionysiou (2003) and Fernandez et al. (2004). As for PDS, similarly to the Fenton reaction, Fe^{2+} is the most commonly used metal for the homogeneous catalysis. The type and dose of the transition metal catalysis is of significant importance, since when it is applied in excess, it can become a double-edged sword, scavenging the radicals (Wacławek et al., 2016a).

A detailed breakdown of the activation methods of PDS and PMS is presented in Table 2 and 3, respectively.

Table 2. PDS activation methods

Method	Mechanism	Predominant radical species	Comments	Reference
Heat	Homolytic cleavage of O-O bond	Sulfate radical/Hydroxyl radical	Because of the low bond-dissociation energy, often low temperature increase can effectively cleave O-O bond	(Zhao et al., 2013)
UV radiation	Homolytic cleavage of O-O bond	Sulfate radical	Often used λ=254 nm	
Homogenous: Transition metals	One electron transfer	Sulfate radical	Often requires low pH to have metals in desirable oxidation state	(Zhao et al., 2014)
Heterogenous: Transition metals	One electron transfer	Sulfate radical	Preparation of catalyst is neither easy nor economical	
Chelated transition metals	One electron transfer	Sulfate radical	Can slow down oxidant decomposition, widely used in situ	(Rastogi et al., 2009)
Alkaline pH	Base-catalyzed hydrolysis of PDS to hydroperoxide, which later initiates radical formation	Sulfate radical/Hydroxyl radical/Superoxide radical	Often pH>11	(Furman et al., 2010)
Hydrogen peroxide	Initiation with heat generated from exothermic hydrogen peroxide reactions	Sulfate radical/Hydroxyl radical	According to Yan et al., (2015), PDS slowed the decomposition of hydrogen peroxide	(Yan et al., 2015)
Electrolysis	Fe^{2+} produced from the electrochemical and chemical corrosion of iron	Sulfate radical/Hydroxyl radical	Additional Fe^{3+} reduction on the cathode. Yuan et al., 2014 claim that OH radical contribution in this system is more significant	(Yuan et al. 2014)
Nanocarbons	O-O bond of persulfate is firstly weakened on the active sites of carbocatalysts, following by directly oxidizing the adsorbed water or hydroxyl groups	Hydroxyl radical	Single-walled carbon nanotubes, reduced mesoporous carbon and graphene oxide, displayed great catalytic activities for heterogeneous PDS activation, whereas nanodiamonds, fullerene and graphitic carbon nitride presented low efficiencies	(Duan et al., 2015; Lee et al., 2015)
Other organics	One electron transfer	Sulfate radical	Low molecular weight, anionic organic compounds	(Fang et al., 2013; Ahmad et al., 2013)
Radiolysis	Homolytic cleavage of O-O bond	Sulfate radical	-	(Criquet et al., 2011)

Table 3. PMS activation methods

Method	Mechanism	Predominant radical species	Comments	Reference
Heat	Homolytic cleavage of O-O bond	Hydroxyl radical/Sulfate radical	Higher temperatures are required to split the O-O bond, due to a higher bond-dissociation energy in comparison to $S_2O_8^{2-}$	(Anipsitakis and Dionysiou, 2004)
UV radiation	Homolytic cleavage of O-O bond	Hydroxyl radical/Sulfate radical	Often used λ=254 nm	(Anipsitakis and Dionysiou, 2004)
Homogenous: Transition metals	One electron transfer	Sulfate radical	Often requires a low pH to have the metals in a desirable oxidation state	(Anipsitakis and Dionysiou, 2004)
Heterogenous: Transition metals	One electron transfer	Sulfate radical	Preparation of the catalyst is neither easy nor economical	
Alkaline pH	Base-catalyzed hydrolysis of PMS to hydrogen peroxide	Superoxide radical	Apart from the superoxide radical, singlet oxygen can also be the primary reactive oxygen species	(Qi et al., 2016)
Electrolysis	One electron transfer from electrochemically/chemically produced Fe^{2+}	Sulfate radical	The contaminant degradation rate by an oxidant assisted with electrolysis was observed in the following order: PMS > PDS > H_2O_2	(Govidan et al., 2015)
Nanocarbons	One electron transfer	Sulfate radical	Graphene demonstrated greater activity than several carbon allotropes, such as activated carbon, graphite powder, graphene oxide, and multiwall carbon nanotubes	(Sun et al., 2012)
Organics	One electron transfer	Hydroxyl radical/Sulfate radical	Polyimide as an electron donor	(Tao et al., 2015)
Ozone	Formation of an $-O_3SO_5-$ adduct that decomposes into radicals	Hydroxyl radical/Sulfate radical	-	(Guan et al., 2011;Yang et al., 2015)
Radiolysis	Homolytic cleavage of O-O bond	Sulfate radical	-	(Anipsitakis and Dionysiou, 2004)

The application of PMS and PDS in oxidation treatment belongs to advanced oxidation processes (AOPs) due to the presence of hydroxyl radicals (Deng and Ezyske, 2011). AOPs can be either homogeneous or heterogeneous. Whilst homogenous AOPs are the most efficacious at an acidic pH (2.5-4.0), heterogeneous AOPs can function in a broad pH range (Zhang et al., 2009; Ahmed et al., 2010). Despite the fact that heterogeneous AOPs exhibit numerous benefits over homogenous AOPs, the fact that the preparation of the catalyst is neither easy nor economical should also be considered.

2.2.1. Homogeneous activation process

In the case of ISCO, the activation should be slow to allow the long-term generation of free radicals and the treatment of heterogeneously distributed contaminants. For homogenous AOPs, one of the most common methods is to use chelated transition metals, significantly decreasing the metal concentration required for the activation (Tsitonaki et al., 2010; Zhang et al., 2014). Rastogi et al. (2009) assessed the efficacy of three representative chelating agents (citrate, ethylenediaminedisuccinate and pyrophosphate) on Fe(II)-mediated activation of PMS and PDS under neutral pH conditions. They found that PMS was the most universal oxidant activated by all three iron-chelating agents, and citrate coupled with ferrous iron was the most universal chelating agent configuration.

2.2.2. Heterogeneous activation processes with metal catalysts

On the other hand, heterogeneous processes with material synthesized beforehand, often to a nano-scale, have drawn much attention recently due to their excellent performance. In addition, as mentioned above, cobalt was found to be the best homogenous activator for PMS. Therefore, there is no surprise in the fact that heterogeneous materials often also consist of this element. Co_3O_4 was used e.g. by Chen et al. (2008) and Muhammad et al. (2012) as an activator for PMS to decompose Acid Orange 7 and phenol, respectively. Interestingly, Zhang et al. (2016b) prepared nano-Co_3O_4 and successfully applied it as a heterogeneous catalyst for PDS activation. The highest degradation rate of Orange G (as a model compound) was at pH ~ 7, where the catalyst dissolution is very low. The authors also confirmed that the sulfate radicals and hydroxyl radicals were the main oxidative species.

One of the major problems of the activation of persulfates with Co_3O_4 is an excessive quantity of cobalt leaching. To enhance catalytic performance and reduce leaching, the cobalt can be immobilized on several metal oxide supports such as TiO_2, SiO_2, MgO or activated carbon/carbon aerogel or graphene. Yao et al. (2012) used bimetallic oxides $CoFe_2O_4$ and $CoFe_2O_4^-$ on graphene to activate PMS for the degradation of phenol. Su et al. (2013) successfully synthesized heterogeneous $Co_xFe_{3-x}O_4$ nanocatalysts and discovered that the intimate Fe-Co interactions are vital for effective heterogeneous activation of PMS. Lin et al. (2015) demonstrated an alternative path to synthesize a magnetic cobalt-graphene nanocomposite from carbonizing of a cobalt-based metal organic frameworks and graphene oxide and its application to activate PMS. In order to measure the long-run catalytic activity, a 50-cycle decolourization of Acid yellow 17 was performed and the regeneration efficiency remained at 97.6%, displaying its stableness and efficient catalytic activity. In their further study, a nanocomposite was prepared by the one-step carbonization of a cobalt-based zeolitic imidazolate (Lin and Chen, 2016). Higher cobalt/carbon nanocomposite loading, PMS dose, acidic conditions and temperature greatly ameliorated the degradation of caffeine. Based on the effects of inhibitors (i.e., methanol and tert-butyl alcohol), the process involves sulfate radicals over hydroxyl radicals. Shi et al. (2014) examined Co_3O_4/expanded graphite, developed in a solvothermal synthesis, as an extremely effectual heterogeneous catalyst of PMS. They concluded that the abatement of Orange II in water is due to sulfate radicals, and 100% removal can be achieved after 8 min. Ding et al. (2012) used cobalt nitrate and bismuth nitrate as forerunner salts and NaOH as a precipitation agent to create the Co_3O_4-Bi_2O_3 nanocomposite as a heterogeneous catalyst for the activation of PMS. The nanocomposite demonstrated substantial catalytic activity in the heterogeneous activation of PMS for the removal of organic pollutants. In addition, cobalt leaching was decreased to 43 μg/L, which is much less than that of Co_3O_4 (158 μg/L) under the equivalent conditions. Yang et al. (2009) reported that the heterogeneous oxide $CoFe_2O_4$ was capable to slowly-activated PMS for the degradation of 2,4-dichlorophenol at pH 7.0, and cobalt leaching was reduced to a very low extent. However, such a reduction in cobalt leaching requires the pH of the solution to be close to 7.0, which is problematic in the applicative treatment of water or wastewater due to substantial acidification during activation. Hence, it is still an important challenge to create an efficacious cobalt-carrying heterogeneous catalyst for PMS activation with low cobalt leaching. One way to overcome this problem was proposed by Rhadf et al. (2010), who determined that the partial replacement of cobalt in Co_3O_4 with Mn can be a strategy for decreasing the quantity of the harmful Co element. Mn is more abundant in nature, more environmentally friendly and is twenty times cheaper than cobalt (Zhai et al., 2013). Wang et al., 2014, provided an example of the PMS activation mechanism using a magnetic core/shell carbon nanosphere supported by manganese oxide nanoparticle catalysts. They found that sulfate radicals were the primary reactive species for phenol oxidation. The same authors also attempted to use 3D-hierarchically structured MnO_2 to activate PMS (Wang et al., 2015). The mechanism of the catalytic reaction for PMS activation was determined therein by electron spin resonance (ESR) spectra and showed that both hydroxyl and sulfate radicals are produced in the activation processes, and that sulfate radicals played a more critical role in oxidation of phenol. Similarly, Li et al. (2016a) synthesised three trivalent Mn (oxyhydr)oxides, namely bixbyite, hausmannite and manganite, from which only manganite showed good catalytic activity for PDS activation. Analogous to Wang et al. (2015), it was also shown that both hydroxyl and sulfate radicals are present during the treatment, although at pH 7 the oxidative intermediate formed between the manganite and the PDS could be the predominant oxidative species in phenol oxidation.

Similarly to the homogeneous systems, iron-based compounds are frequently used for persulfate activation due to their lower toxicity compared to cobalt. Tan et al. (2014) reported a nano-Fe_3O_4 catalyst in PMS activation process, whose stability decreased significantly from the first to the third run. In another study, authors of a recent paper concerning heterogeneous catalysis (Oh et al., 2016), fabricated $CuFe_2O_4$-Fe_2O_3 at a low temperature for the oxidation of bisphenol A via PMS activation (Oh et al., 2015). The performance of $CuFe_2O_4$-Fe_2O_3 was confronted with alternative catalysts and the results implied that the performance was in the following order: $CuFe_2O_4$-Fe_2O_3 > $CuFe_2O_4$ > $CoFe_2O_4$ > $CuBi_2O_4$ > $CuAl_2O_4$ > Fe_2O_3 > $MnFe_2O_4$. The $CuFe_2O_4$-Fe_2O_3 catalyst can be reused at least several times without a significant deterioration in performance. In addition, Zhang et al. (2016a) observed superior catalytic properties of nano-Fe_3O_4 as an activator for PMS. The levels of Fe_3O_4 coupled with hydroxylamine (a reducing agent that accelerates the conversion of Fe^{3+} to Fe^{2+}) soared gradually in the ten consecutive runs.

2.2.3. Heterogeneous activation with metal-free catalysts

Recently, metal-free catalysts are gaining popularity due to the many advantages of having no heavy metal pollution, good chemical stability and environmental friendliness

(Tao et al., 2015). It was confirmed that the oxygen-containing functional groups (especially the carbonyl group) of carbonaceous materials can effectively contribute to the initiation of persulfates (Wang et al., 2016). From the metal-free heterogeneous catalyst, Sun et al. (2012a) discovered that chemically reduced graphene oxide can work as an effective material to activate PMS in order to generate reactive radicals. Zhang et al. (2013) used granular activated carbon as a green catalyst to activate PMS to degrade Acid Orange 7 in an aqueous solution. Also, Saputra et al. (2013) reported that activated carbon powder can be an environmentally friendly catalyst for the efficient activation of PMS that later exhibited excellent potential for phenol degradation mediated by sulfate radicals.

Lee et al. (2015) found that carbon nanotubes could activate persulfates into reactive species. Similarly, Duan et al. (2015) evaluated the ability of various nanocarbons to initiate PDS for catalytic oxidation of phenolics and dyes as well as their degradation by-products. Single-walled carbon nanotubes, reduced graphene oxide and mesoporous carbon displayed superior catalytic activities for heterogeneous PDS activation, whereas fullerene, nanodiamonds and graphitic carbon nitride presented low efficiencies. Furthermore, the carbo-catalysts manifested much higher activity towards PDS activation in comparison to the universally applied activated carbon and metal oxides, such as Fe_3O_4, CuO, Co_3O_4, and MnO_2.

In a recent study, Lin and Zhang (2016) showed that not only carbons can act as metal-free initiators for persulfates. Orthorhombic α-sulfur was employed as a metal-free photo-catalyst to initiate PMS (under irradiation with visible light) and found it to be a promising process for chemical oxidation reactions.

Considering the fact that large amounts of solid waste that could be used for the activation of persulfates are produced from various industries there is no need to synthesize expensive catalysis. Fly ash from coal or oil and biomass combustion are major contributors to the production of solid waste and could be used to prepare (Co)-based catalysts for PMS activation (Muhammad et al., 2012). It was found that the fly ash does not adsorb phenol and cannot initiate PMS for the formation of sulfate radicals. Nonetheless, fly ash consists of cobalt oxide, which can be used for the activation of PMS. In another study, steel waste powder was applied as an activator for PDS (Oh and Kang, 2010).

Electron donor catalysis has various benefits but can also, as was stated before, become a new source of contamination. In addition, it is often much less efficient, e.g. only one mole of radical can be obtained from one mole of oxidant, in contrast to UV or heat activation (see Eq. 3 and 4). A detailed study of the UV and heat initiation of oxidants with peroxide bonds was performed by Yang et al. (2010). They found that the order for the degradation efficiency of heat-activated peroxides is: PDS > PMS > H_2O_2 and of UV (254 nm) activated peroxides: PDS > H_2O_2 > PMS. Surprisingly, they also determined that PMS can be induced by anions (such as HCO_3^-, HPO_4^{2-}, Cl^- and CO_3^{2-}) to form more reactive species.

2.2.4. Alkaline activation

Another persulfate activation technique often used *in situ* is alkaline activation involving an increase in pH (often >11) by the addition of concentrated sodium hydroxide (NaOH) or potassium hydroxide (KOH) (Siegrist et al., 2011). On the other hand, Cassidy et al. (2015) concluded that in-situ stabilization amendments, including fields containing $Ca(OH)_2$ and/or CaO, can effectively activate PDS by increasing the pH, and in the case of CaO also heat. upon their reaction with soil water (i.e. additional initiation). Activated PDS decreased concentrations of BTEX compounds and PAHs. The proposed mechanism of alkaline activation of PDS (Furman et al., 2010) relies on the hydrolysis of PDS to hydroperoxide anion (HO_2^-) and subsequent reduction of PDS by this anion with the production of sulfate and superoxide radicals. Very recently, Qi et al. (2016) proved a similar activation tendency for PMS, which can be initiated at high pH with base-catalysed hydrolysis of PMS to hydrogen peroxide. The superoxide radical was found to be the dominant radical species in this system, but the role of singlet oxygen was also found to be significant.

2.2.5. Electro-activation

Several studies have evaluated the “electro-activation” of persulfates. Yuan et al. (2014), conducted the activation of PDS using ferrous iron produced in an electrolytic system. Zhen et al. (2013b) determined that PDS is mainly decomposed by Fe^{2+} created in two steps - from the chemical and electro-chemical corrosion of Fe followed by the reduction of Fe^{3+} formed on the cathode. They also found the hydroxyl radical to be the predominant species in this system. Recently, Govidan et al. (2014) proved the efficacy of electrochemical activation for persulfates. Electrochemically activated PMS was the best oxidant for pentachlorophenol decontamination from PDS, PMS and hydrogen peroxide. Long and Zhang (2015) stated that the electro-activation of PDS can be effective for removing toluene from a surfactant flushing solution. The results indicated that Fe^{2+} is electro-regenerated on the cathode by the reduction of Fe^{3+}, which is in agreement with the studies conducted by Zhen et al. (2013b) and Yuan et al. (2014). Also, simultaneous use of electrolysis and UV process/geothite can enhance PMS and PDS initiation (Jaafarzadeh et al., 2015; Lin et al., 2016). Moreover, the great efficacy of electro-activation of PDS was shown in our recent study (Wacławek et al., 2016a).

2.2.6. Other activation methods

Recent work reported by Cong et al. (2015), focusing on the enhancement of ozonation on chlorobenzoic acid degradation with PMS, indicated that PMS may act in a similar way to H_2O_2 in the promotion of $OH^{\bullet}$ production in ozonation. This theory was confirmed by Yang et al. (2015), who demonstrated that the reaction between PMS and ozone is primarily responsible for promoting ozone consumption with a determined second-order rate constant of 2×10^4 M^{-1} s^{-1}. The formation of both $OH^{\bullet}$ and $SO_4^{\bullet-}$ radicals was confirmed by chemical probes and their yields ($OH^{\bullet}$ and $SO_4^{\bullet-}$) were determined to be 0.43 ± 0.1 and 0.45 ± 0.1 per mol of ozone, respectively. An adduct $-O_3SOO- + O_3 \rightarrow -O_3SO_5^-$, is assumed as the first step, which can further decompose into more reactive $SO_5^{\bullet-}$ and $O_3^{\bullet-}$ radicals. The subsequent reaction of $SO_5^{\bullet-}$ with ozone is assumed to generate $SO_4^{\bullet-}$, while $O_3^{\bullet-}$ converts to $OH^{\bullet}$.

2.3. Determination methods

Numerous methods for the determination of PDS and PMS can be found in the literature. These methods vary in their execution time and sensitivity of detection (Table 4 a 5).

Table 4. PDS determination methods

Method	Substance used	Time of measurement	Limit of quantification [M]	Reference
Titration	Ce^{4+}/Fe^{2+}	<20 min	$>10^{-4}$	(Boudeville, 1983)
Spectrophotometry	KI/HCO_3^-	15 min	7×10^{-2}	(Liang et al., 2008)
Spectrophotometry	H_2SO_4/NH_4SCN	~40 min	2.1×10^{-4}	(Huang et al., 2002)
Spectrophotometry	Methylene blue under microwave radiation	1 min	3×10^{-6}	(Zhao et al., 2015)
Spectrophotometry	N,N-diethyl-p-phenylenediamine	10 min	10^{-5}	(Gokulakrishnan et al., 2016)
Spectrophotometry	Alcian blue	120 min	8.8×10^{-8}	(Villegas et al., 1963)
Amperometry	-	-	10^{-5}	(Lin et al., 2012)
Amperometry	-	-	10^{-5}	(Roushani and Karami, 2014)
Amperometry	-	-	10^{-5}	(Roushani and Karami, 2014)
Voltammetry	-	-	5×10^{-5}	(Oliveira et al., 2000)
Ion chromatography	Mobile phase: 50 mM KOH; flow rate: 1 mL/min	18 min	5.2×10^{-8}	(Huang et al., 2014)

Table 5. PMS determination methods

Method	Substance used	Time of measurement	Limit of quantification [M]	Reference
Titration	Ce^{4+}/Fe^{2+}	<20 min	10^{-5}	(Boudeville., 1983)
Spectrophotometry	KI/HCO_3^-	5 min	1.2×10^{-5}	(Wacławek et al., 2015b)
Spectrophotometry	Co^{2+}/methyl orange	1 min	5×10^{-7}	(Zou et al., 2014)
Spectrophotometry	N,N-diethyl-p-phenylenediamine	10 min	10^{-5}	(Gokulakrishnan et al., 2016)
Ion chromatography	Mobile phase: pH 3.0; cond. 290 µS/cm; flow rate 1.5 mL/min	11 min	4.5×10^{-5}	(Ossadnik and Schwedt, 2001)
HPLC	Mobile phase: methanol/phosphoric acid buffer	-	$\sim 5 \times 10^{-7}$	(Zhang et al., 2013a)

The first methods used for the determination of PDS and PMS were most probably iodometric titrations (Kolthoff et al., 1951). Their spectrophotometric alternatives possess much higher sensitivity and do not require as much reagent and time (Liang et al., 2008; Wacławek et al., 2015b). Determination of persulfates with the use of dyes has gained popularity lately, although the method has been known for a long time (Villegas et al., 1963). Nevertheless, these methods possess very high sensitivity and short measurement time. More information on the determination of persulfates with organic dyes can be found in Ding et al. (2011) and Zhang et al. (2016c). In addition, the fast and accurate analysis of both PDS and PMS can be performed with the use of ion chromatography (Huang et al., 2014; Ossadnik and Schwedt, 2001).

2.4. Persulfate decontamination technologies

2.4.1. Direct oxidation

Although reactions of non-initiated persulfates occur at rates that are often slow, several studies reported their direct oxidation processes. Probably the best known are the Elbs and Boyland-Sims reactions, which rely on the nucleophilic displacement of peroxide oxygen from the PDS ion (Behrman, 2004). In the Elbs reaction, the nucleophile is a phenolate anion (or a tautomer) and in the Boyland-Sims reaction, it is a neutral aromatic amine. There is no radical involvement in either case, except in side reactions.

In addition, during catalysed persulfate oxidation, persulfates can react with generated radicals in several ways.

Figure 2 shows the second-order reaction rate constants of persulfate reactions with several species in an aqueous phase.

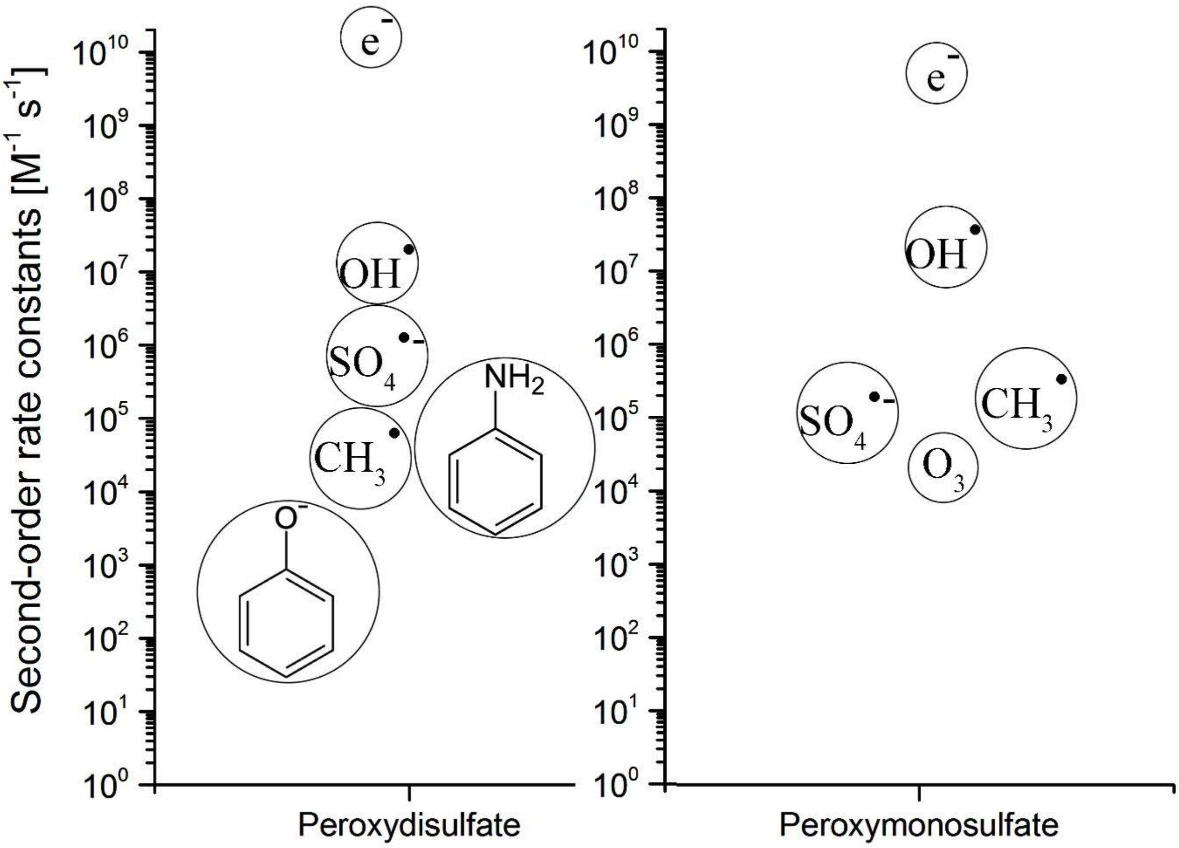

Figure 2. Comparison of the second-order reaction rate constants of persulfates with aqueous species (the middle of the circles indicates the exact rate constants). Data taken from: Yang et al. (2015); Behrman (2004); Buxton et al. (1988b); Restelli et al. (1990); Herrmann et al. (1995); Davies et al. (1984); Roebke et al. (1969); Maruthamuthu and Neta (1977); Gilbert and Stell (1990).

Another example of the direct reaction of the PDS anion with organics without radical intermediates was described by Tsitonaki et al. (2010). They reported 99% degradation of methyl tert-butyl ether (MTBE) in a system at ambient temperature without any catalytic reaction.

Lei et al. (2016) found that PMS can directly decolorize cationic pigments without activation in a broad pH range (2-12). In addition, they concluded that Cl^- anions improved the degradation efficacy of the target pollutants. Radical quenching experiments and ESR studies revealed that the degradation of cationic dyes by PMS does not rely on hydroxyl or sulfate radicals. A plausible bleaching mechanism is that cationic dyes form a complex with the PMS as a result of their electrical interaction followed by direct electron transfer from the cationic dyes to the PMS.

Zhang et al. (2014a) reported that copper oxide can work as an efficient catalyst for PDS activation under mild conditions via a nonradical process for oxidative degradation of 2,4-dichlorophenol. PDS tends to first interact with the outer sphere of CuO, which is assumed to be the rate-limiting step, and then quickly reacts with the target organic pollutants.

In addition, PMS without external activation can be used for oxidation of As(III) (Wang et al., 2014a). They stated that the addition of PMS enables As(III) to oxidize completely to As(V) within 24 h, even in the presence of high concentrations of radical scavengers (1.6 M of methanol).

2.4.2. Radical oxidation in water and wastewater treatment

As we mentioned earlier, persulfates oxidize contaminants mainly by free-radical driven processes.

2.4.2.1. Interchange of radicals

Persulfates and sulfate/hydroxyl radicals possess a common feature in the form of one or more oxygen atoms in their structure. It is because of the oxygen atoms, that these compounds have such high oxidizing power and therefore understanding oxygen chemistry is crucial when dealing with persulfates.

Oxygen in its ground state is not very reactive and its reactions mostly involve one electron transfer, which can lead later to the formation of reactive radicals (Stumm and Morgan, 1996). Also, oxygen’s role in sulfate radical systems was determined to be significant and was described carefully in a recent paper by Xu et al. (2016). The step-by-step reduction of an oxygen molecule to water followed by the formation of radicals during persulfate decomposition is shown in Figure 3.

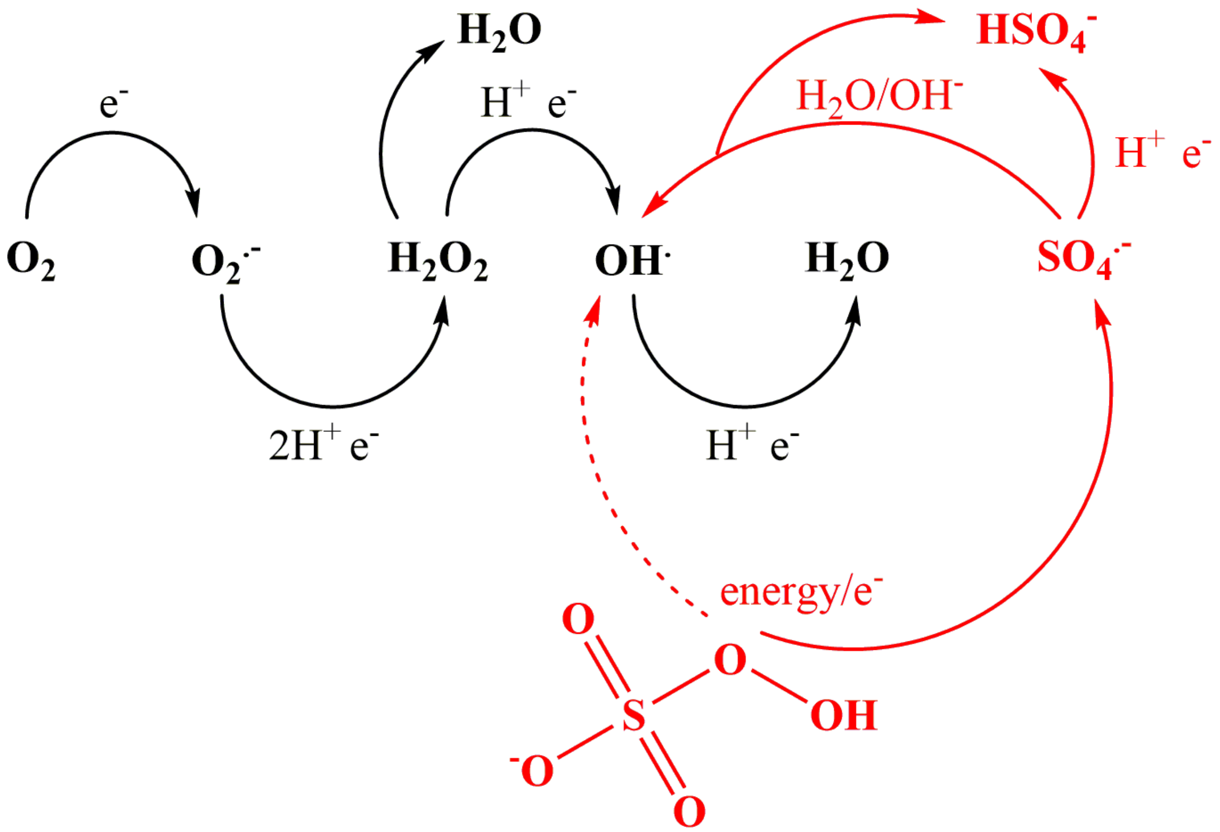

Figure 3. Black arrows - scheme of oxygen molecule reduction to water; red arrows - radical formation and behaviour in a persulfate system (dashed arrow - only valid for homolytic cleavage of the PMS O-O bond).

A hydroxyl radical can be formed by a three-electron reduction of an oxygen molecule or one electron oxidation of water. In addition, hydroxyl radicals can also be formed together with sulfate radicals after activation of PMS.

These radicals can then interchange with each other at a rate depending on the pH of the solution. Studies based on radical scavenging analyses paired with the use of the electron spin resonance (ESR) technique were performed to identify the dominant radical species involved in persulfate-based oxidation (Zhao et al., 2013; Wang et al., 2014; Wang et al., 2015). It was shown that in most cases $SO_4^{\bullet -}$ prevails in acidic media and $OH^\bullet$ preponderates in alkaline media.

$$SO_4^{\bullet -} + OH^- \rightarrow SO_4^{2-} + OH^\bullet \tag{5}$$

In general, the sulfate radical is more selective for the electron transfer reaction than the hydroxyl radical, which is more likely to participate in OH addition or hydrogen abstraction reactions (Neta et al., 1977).

For a more detailed explanation of radical identification, e.g. with the use of TBA/EtOH, see Zhang et al. (2014).

2.4.2.2. Sulfate radical interference with common anions and natural organic matter

Due to the fact that the chemicals in groundwater or sludge are always in a complex matrix the effect of its composition must be thoroughly investigated prior to implementing a persulfate system (Gu et al., 2011; Liang et al. 2006).

Table 6 shows second-order reaction rate constants of hydroxyl and sulfate radicals with common anions and natural organic matter (NOM).

Table 6. Second-order reaction rate constant of hydroxyl and sulfate radicals with common anions and NOM

Radical	Compound	Rate constants (M^{-1} s^{-1})	Reference
$OH^{\bullet}$	Cl^-	3.0-4.3 x 10^{9}	(Grigor’ev et al., 1987; Jayson et al., 1973)
$SO_4^{\bullet-}$	Cl^-	1.3-6.6 x 10^{8}	(Waldemer et al., 2007; Kim and Hamill, 1976; McElroy, 1990)
$OH^{\bullet}$	Br^-	1.9 x 10^{9}	(Zehavia and Rabani, 1972)
$SO_4^{\bullet-}$	Br^-	3.5 x 10^{9}	(Redpath and Willson, 1975)
$OH^{\bullet}$	HCO_3^-	n x 10^{7}	(Buxton et al., 1988a)
$SO_4^{\bullet-}$	HCO_3^-	2.6-9.1 x 10^{6}	(Huie and Clifton, 1990; Dogliotti and Hayon, 1967)
$OH^{\bullet}$	CO_3^{2-}	4 x 10^{8}	(Buxton et al., 1988a)
$SO_4^{\bullet-}$	CO_3^{2-}	4.1 x 10^{6}	(Padmaja et al., 1993)
$OH^{\bullet}$	Humic acid	1.4 × 10^{4}*	(Lutze et al., 2015)
$SO_4^{\bullet-}$	Humic acid	6.8 × 10^{3}*	(Lutze et al., 2015)

*(mg of C/L)$^{-1}$ s^{-1}

One of the first descriptions of bromide oxidation in a UV/PDS system was in a paper by Fang and Shang, (2012). They observed the behaviour of the bromide transformation process in a real water sample, which they attributed to the presence of NOM and its reaction with bromine atoms. Liu et al., (2015) investigated the transformation of Br^- in a cobalt-activated PMS oxidation process with the presence of phenol as an example compound imitating natural organic matter. It was determined that Br^- was efficiently converted to reactive bromine species including free bromine and bromine radicals.

These reactive bromine species were effected in the bromination of phenol and the development of brominated disinfection intermediates including bromoform and bromoacetic acids, during which brominated phenols were observed as the intermediates. Brominated disinfection by-products were also degraded by excessive $SO_4^{\bullet-}$, which played a key role in this action, and ultimately converted to bromate. Free bromine was also formed in the absence of cobalt, showing that Br^- could be directly oxidized by PMS. In another study these conclusions were confirmed and it was also found that the brominated intermediates cannot be degraded in the absence of a sulfate radical (Xie et al., 2016). Similar work was performed by Lu et al. (2015), who determined that after reacting with sulfate radicals the reactive bromine species can react with NOM to form brominated products including brominated disinfection by-products. Bromoform and bromoacetic acids were formed in the presence of humic acid.

Similarly, the sulfate radical can react with Cl^- with a very high reaction rate - 10^8 M^{-1} s^{-1} (Waldemer et al., 2007). The resulting chlorine radical can react with additional Cl, a matrix component, the contamination of concern or intermediate degradation products to create more chlorinated products (Waldemer et al., 2007). Yang et al. (2014) also investigated the conversion of $OH^\bullet$ and $SO_4^{\bullet-}$ to less reactive halogen radicals. In the presence of seawater, halogens reduced the abatement efficacy of cyclohexanecarboxylic acid and benzoic acid, which were chosen as the model pollutants. They concluded that the activated PDS was more affected by Cl^- than the activated hydrogen peroxide system because oxidation of Cl^- is more favourable by $SO_4^{\bullet-}$ than $OH^\bullet$ at pH 7. The degradation efficiency of cyclohexanecarboxylic acid was not altered by the halogens, probably due to the high reactivity of halogen radicals with alkenes. This statement was further confirmed in a study of Liu et al. (2016a) who found, using carbon isotope fractionation of trichloroethene (TCE), that in the presence of chloride there could be different degradation mechanisms rather than that of the sulfate radical.

In other work, Xie et al. (2015) focused on the formation of chlorinated by-products in a sulfate radical system, and they found that the formation of carbonaceous disinfection by-products such as chloroform and haloacetic acids only increased a little, but the development of nitrogenous disinfection intermediates i.e. haloacetonitriles and trichloronitromethane slightly decreased. On the contrary, Lu et al. (2016) found that after treatment of surface water with 0.1 μM PDS for 48 h, its potential to form chloroform, trichloroacetic acid and dichloroacetic acid increased from 197.8, 54.3, and

27.6 to 236.2, 86.6, and 57.6 μg/L, respectively. In other words, before the application of persulfates in the field, bench scale studies should be performed in detail due to the fact that the formation of dangerous by-products depends highly on the treated matrix.

Lutze et al. (2015) determined sulfate and hydroxyl radical reaction rate constants with NOM and concluded they differ considerably. For the reaction of the sulfate and hydroxyl radical with humic acids the kinetic rate constant was 6.8×10^3 L mgC^{-1} s^{-1} and 1.4×10^4 L mgC^{-1} s^{-1} (mgC = mg carbon), respectively. On the contrary, Lou et al. (2016) observed that the oxidation capacity of the hydroxyl and sulfate radical to humic acid degradation (in the presence of Cl^- and Br^-) was nearly in the same order. Both Cl^- and Br^- had a negative impact on these processes, but the inhibiting effect of Br^- was more obvious than that of Cl^-, even when the concentration of Cl^- was far above that of Br^-, which is in agreement with the study of Yang et al. (2014).

Although soil organic matter (SOM) has traditionally been considered to be a negative factor in ISCO application, a study conducted by Ahmad et al. (2010) demonstrated that SOM can promote the generation of reductants during PDS ISCO applications at high pH levels.

2.4.2.3. Decontamination of water and wastewater with free radicals generated in persulfate systems

As shown before, numerous methods of persulfate activation can be used in water and wastewater treatment technology in order to achieve the expected results. The decontamination of water and wastewater with the use of radicals generated from persulfates is described in detail below.

2.4.2.3.1. Water

Sulfate radicals are extremely reactive towards substances from which they can withdraw an electron. Even such persistent organic compounds as perfluorooctanoic acid (PFOA), that are unreactive towards $OH^•$ and possess second strongest single bond in organic chemistry (C-F), can be degraded in the sulfate radical system according to many authors (Hori et al., 2005; Lee et al., 2010; Lee et al., 2011; Lee et al., 2012; Liu et al., 2012; Lee et al., 2013). Recently, Qian et al. (2016) determined the degradation kinetics of PFOA in a UV/persulfate system and proposed its degradation mechanism, which relies on a sequential loss of CF_2 units from it and its intermediates (Qian et al., 2016; Liu et al., 2012).

It comes as no surprise that sulfate radicals can readily degrade less persistent organic compounds i.e. 2,4-dichlorophenol (Anipsitakis et al., 2005), 2-chlorobiphenyl (Wang and Hong, 1999), aniline (Hussain et al., 2014), bisphenol A (Sharma et al., 2015), calcon (Sahoo et al., 2012a), Acid Orange 7 (Yang et al., 2010), hexachlorocyclohexanes (Wacławek et al. 2015a; Wacławek et al. 2016a), Ponceau S (Sahoo et al., 2012b), 4-fluorophenol (Selvam et al., 2007), pentafluorobenzoic acid (Ravichandran, 2007), C.I. Reactive Black 5 (Yu et al., 2010), C.I. Basic Red 46 (Eskandarloo et al., 2014), endosulfan (Shah et al., 2013), antipyrine (Tan et al., 2013), dimethyl phthalate (Olmez-Hanci, 2011) or dimethylhydrazine (Zarei et al., 2015). Table 7 includes pseudo first-order reaction rate constants of various contaminants generated from persulfates radicals.

Table 7. Decontamination of common water pollutants with radicals generated in persulfate systems

Group of compounds	Model contaminant	Main oxidative specie	Comments	Pseudo first-order reaction rate constant	Reference
Chlorinated olefins	Perchloroethene	Possibly $SO_4^{\bullet -}$ (not identified)	Trace quantities of hexachloroethane as an intermediate	7.6×10^{-3} min^{-1} (activation temperature of 50 °C)	(Waldemer et al., 2007)
	Trichloroethene	Possibly $SO_4^{\bullet -}$ (not identified)	Trace quantities of hexachloroethane as an intermediate	4.7×10^{-3} min^{-1} (activation temperature of 50 °C)	(Waldemer et al., 2007)
	cis-dichloroethene	Possibly $SO_4^{\bullet -}$ (not identified)	Isomerization between trans and cis-DCE presumably after formation of a singlebonded intermediate	1.6×10^{-3} min^{-1} (activation temperature of 50 °C)	(Waldemer et al., 2007)
	trans-dichloroethene	Possibly $SO_4^{\bullet -}$ (not identified)	Isomerization between trans and cis-DCE presumably after formation of a singlebonded intermediate	3×10^{-3} min^{-1} (activation temperature of 50 °C)	(Waldemer et al., 2007)
BTEXs	Benzene	Possibly $SO_4^{\bullet -}$ (not identified)	Of all the BTEX compounds studied, benzene was most resistant to PDS oxidation	9.5×10^{2} day^{-1} (activation temperature of 20 °C; Oxidant/BTEX molar ratio 100/1)	(Kambhu et al., 2012)
	Toluene	Possibly $SO_4^{\bullet -}$ (not identified)	-	23.2×10^{2} day^{-1} (activation temperature of 20 °C; Oxidant/BTEX molar ratio 100/1)	(Kambhu et al., 2012)
	Ethylbenzene	Possibly $SO_4^{\bullet -}$ (not identified)	-	14.5×10^{2} day^{-1} (activation temperature of 20 °C; Oxidant/BTEX molar ratio 100/1)	(Kambhu et al., 2012)
	Xylene	Possibly $SO_4^{\bullet -}$ (not identified)	-	21.9×10^{2} day^{-1} (activation temperature of 20 °C; Oxidant/BTEX molar ratio 100/1)	(Kambhu et al., 2012)
Phenols	Phenol	Possibly $SO_4^{\bullet -}$ /$OH^{\bullet}$ (not identified)	Greater total organic carbon (TOC) removal was observed at pH 11, possibly due to the fact that the sulfate radical interchanges to the hydroxyl radical, which is the responsible oxidizing species, although this was not confirmed experimentally	0.14–0.16 min^{-1} (UV activation parameters: $\lambda = 254$ nm; Oxidant/ Phenol molar ratio 84/0.5)	(Lin et al., 2010)
	Bisphenol A	$SO_4^{\bullet -}$ (Scavenging tests were performed)	The Bisphenol A degradation with sulfate radicals was found to proceed via one electron transfer reaction mechanism	0.025 min^{-1} (UV activation parameters: $\lambda = 254$ nm; 40 W power; Io = 1.26 $\mu E\ s^{-1}$; Oxidant/Bisphenol A molar ratio 3/1)	(Sharma et al., 2015)
Pharmaceuticals	Diclofenac	$SO_4^{\bullet -}$ (scavenging tests were performed)	Degradation involved one electron transfer decarboxylation, hydroxylation, and bond cleavage reactions to mineralization	0.032 h^{-1} (Activation temperature of 50 °C; Oxidant/ Diclofenac molar ratio 10/1)	(Chen et al., 2016)
	Carbamazepine	$SO_4^{\bullet -}$ (scavenging tests were performed)	Electron-transfer between sulfate radicals and carbamazepine was found to be the major mechanism.	0.087 min^{-1} (UV activation parameters: $\lambda = 254$ nm; 9 W power; Oxidant/ Carbamazepine molar ratio 10/1)	(Zhang et al. 2015a)
Pesticides	Lindane	Possibly $SO_4^{\bullet -}$ /$OH^{\bullet}$ (not identified)	Approx. 96.4% of chloride ion was released after the optimised treatment, which was consistent with the TOC analysis.	10^{-3} sec^{-1} (UV activation parameters: $\lambda = 254$ nm; 10 μM = Fe^{2+}; Oxidant/ Lindane molar ratio 73/1)	(Khan et al., 2016)
	Atrazine	$SO_4^{\bullet -}$ (scavenging tests were performed)		1.7×10^{-3} sec^{-1} (UV activation parameters: $\lambda = 254$ nm; Oxidant/ Atrazine molar ratio 50/1)	(Luo et al., 2015)
	Endosulfan	$SO_4^{\bullet -}$ /$OH^{\bullet}$ (identified)	The destruction of endosulfan was initiated at the endosulfans S=O group	4.14×10^{-4} sec^{-1} (UV activation parameters: $\lambda =$ 254 nm; Oxidant/ Endosulfan molar ratio 10/1)	(Shah et al., 2013)
Other	Acid orange 7	Possibly $SO_4^{\bullet -}$ (not identified)	Reaction rates differed between UV/PMS and UV/PDS, possibly due to the production of the hydroxyl radical during the photolysis of PMS	0.175 min^{-1} (UV activation parameters: $\lambda = 254$ nm; Oxidant/Acid orange 7 molar ratio 10/1)	(Yang et al., 2010)
	PFOA	$SO_4^{\bullet -}$ and $S_2O_8^{\bullet -}$	$SO_4^{\bullet -}$ draws an electron from the carboxylate group to generate the carboxylate radical	0.18 h^{-1} (UV activation parameters: $\lambda = 254$ nm; Oxidant/PFOA molar ratio 33/1)	(Qian et al., 2016)

Moreover, Neppolian et al. (2008) proved that these radicals can also be used for the treatment of inorganic pollution in water. They investigated the photochemical oxidation of As(III) to the less harmful As(V) using PDS as the oxidizing agent under UV light irradiation. It was established that humic acid had no consequence on the reaction rate, even at a concentration of 20 ppm. Yet, the continual purging of nitrogen considerably minimized the reaction rate (20%), confirming that the dissolved oxygen plays a role in this reaction (at high PDS concentrations this situation was overcome). Surprisingly, according to Diao et al. (2016a, 2016b) sulfate radicals coupled with bentonite-supported nanoscale zero-valent iron (used as a radical initiator), can be effective for the simultaneous abatement of Cr(VI) and phenol from water. The proposed mechanism involved the removal of Cr(VI) mainly by reduction with bentonite-supported nanoscale zero-valent iron and phenol removal mainly by the sulfate radical generated from the decomposition of PDS.

Contamination with chlorinated olefins is ubiquitous, and although they can be degraded with many biological (Gerritse et al., 1995) and less invasive chemical treatments (i.e. H_2O_2) (Hirovonen et al., 1996), persulfates are often used for their degradation *in situ*. Recently, Yan et al. (2015) combined siderite-catalysed H_2O_2 with PDS and effectively used it for the remediation of trichloroethene contamination from groundwater. In the absence of PDS (only catalysed peroxide), most of the hydrogen peroxide was reduced within the first hour of the test, resulting in non-efficient use of hydroxyl radicals. After the addition of PDS, the decomposition rate of H_2O_2 was mitigated due to a more sustainable release of hydroxyl radicals. Furthermore, the heat released by the decomposition of hydrogen peroxide activated the PDS, and the generated $SO_4^{\bullet-}$ was the main oxidative agent during the first two hours of the reaction. Dichloroacetic acid was detected as an intermediate. Xu et al. (2014) also studied the degradation of trichloroethene (TCE) but in a thermally activated persulfate system. Their results showed that TCE can be completely degraded within 9 minutes at 50 ^{o}C with an initial trichloroethene concentration of 0.15 mM and a dose of 0.3 M PDS, as a result of the presence of active oxygen species ($SO_4^{\bullet-}$, $OH^{\bullet}$, and $O_2^{\bullet-}$). Moreover, Zhao et al. (2014) studied the simultaneous decontamination of 1,4-dioxane, the inherent associate of TCE (frequently used as a solvent stabilizer for TCE), with heat- and Fe^{2+} PDS activation.

Carbon balance analysis showed that 96 and 93% of the carbon as removed from the 1,4-dioxane degradation as intermediates with and without the addition of Fe^{2+}, respectively. Another commonly found and very toxic group of contaminants is pesticides, which contribute to nine out of the twelve most hazardous and assiduous organic compounds defined by the Stockholm Convention on Persistent Organic Pollutants (POPs) (Sharma et al., 2014). A very recent study by Qin et al. (2016) presented 1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane (DDT) degradation with Co^{2+} catalysed PMS. It was found that DDT was efficiently decomposed within several hours, proportionally to PMS and Co(II) concentrations. The degradation kinetics of DDT were well characterized with pseudo-first-order equations over a range of temperatures (10-40 °C), and the activation energy calculated using the Arrhenius equation was 72 kJ/mol. Dichlorobenzophenone, 4-chlorobenzoic acid and benzylalcohol were the dominant intermediates for DDT degradation, and the possible degradation pathway of DDT was suggested on the foundation of these identified products. Zhu et al. (2016) also found that DDT and its dechlorination products were degraded efficiently by PDS activated by nano zero-valent iron. GC/MS results showed that benzoic acid, benzyl alcohol, dichlorobenzophenone (DBP) and 1-chloro-2,2-bis (p-chlorophenyl)-ethane (DDNS) were the dominant products of DDT degradation. In addition, ESR results showed that both sulfate and hydroxyl radicals were involved in the degradation process. Luo et al. (2015) investigated atrazine degradation by irradiation at a wavelength of 254 nm in the presence of three oxidants - hydrogen peroxide, PMS and PDS at various initial atrazine concentrations and oxidant doses. The effects of the water matrix, such as carbonate/bicarbonate, Cl^-, and NOM, were evaluated on these three AOPs. Modelling results showed that the steady-state concentrations of $OH^\bullet$ and $SO_4^{\bullet-}$ decreased with an increase in CO_3^{2-}/HCO_3^- concentrations, and the relative contribution of $OH^\bullet$ to atrazine degradation significantly decreased in UV/H_2O_2 and UV/HSO_5^- systems. It should also be noted that some of the determined transformation products (e.g., di-isopropyl-atrazine, diethylatrazine) are as toxic as the parent compound. Cao et al. (2008) and Khan et al. (2016a) focused on the oxidation of lindane (γ-hexachlorocyclohexane) by Fe^{2+} activated PDS and PMS, respectively. Their experimental results indicated that the application of persulfate treatment is very beneficial not only for the complete elimination of the parent compound but also for the achievement of full mineralization. In addition, in a further study, Khan et al. (2016b) determined the second-order rate constant of lindane with sulfate radicals for the first time using a competition kinetics approach (1.3×10^9 M^{-1} s^{-1}). Kuśmierek et al. (2015) investigated the degradation of 2,4-dichlorophenol and 2,4-dichlorophenoxyacetic acid by ammonium PDS under different activation conditions. The results showed that the initial PDS concentration had a significant influence on the degradation effectiveness of both contaminants. The reaction rates increased with an increase in oxidant dose. 2,4-dichlorophenol degraded faster and more efficiently in an alkaline environment (pH = 9.0), whereas 2,4-dichlorophenoxyacetic degraded better in an acidic environment (pH = 3.0). They also examined the synergistic activation of PDS with heat and ferrous iron to enhance the oxidation of 2,4-dichlorophenol and 2,4-dichlorophenoxyacetic acid. Under optimal experimental conditions, where the PDS/Fe^{2+} molar ratio was 1:2 at 50 °C, complete oxidation of 2,4-dichlorophenol and 2,4-dichlorophenoxyacetic acid was achieved after approximately 45 and 60 minutes, respectively. In all circumstances, 2,4-dichlorophenol degraded faster and more efficiently than 2,4-dichlorophenoxyacetic acid, which indicates that the pesticide molecule is more stable and less susceptible to degradation by PDS.

As was mentioned in the introduction, the rapid emergence of resistant bacteria worldwide is probably due to the overuse of medications that can later become a contamination of concern. Several authors have focussed on the remediation of pharmaceuticals and since persulfates are one of the newest ISCO reagents to be used, there are also several new studies describing the use in the oxidation of pharmaceuticals. Monteagudo et al. (2015) investigated ISCO of a carbamazepine solution by PDS simultaneously activated by heat energy, UV-C light, Fe^{2+} ions and hydrogen peroxide. Zhang et al. (2015a) determined the main intermediates formed during the oxidation process, including 10,11-epoxy-carbamazepine, acridine-9-carbaldehyde, acridine and other low molecular compounds.

Trimethoprim and sulfamethoxazole in expired sulfamethoxazole tablets were the subject of research conducted by Liu et al. (2016), who studied their degradation by catalysed PDS treatment. Zero valent-iron showed much better catalytic properties than alkaline activation, which was completed after 0.5 hours, while full mineralization was achieved after 2 hours.

Chen et al. (2016) examined the performance of thermally activated PDS on the degradation of diclofenac in both water and polluted groundwater. The results implied that the oxidation of diclofenac was well fitted to a pseudo-first-order kinetic model, and the rate constants increased with temperature. The rate constants from 50-70 °C also fitted to the Arrhenius equation, yielding an activation energy of 158 kJ/mol. The presence of a small dose of Cl^- (0-10 mM) boosted the degradation of diclofenac, whereas high Cl^- addition (>10 mM) inhibited its degradation. HCO_3^- demonstrated an insignificant effect on diclofenac elimination, while NOM, e.g., humic acids, delicately inhibited diclofenac degradation. The fast degradation of diclofenac was further confirmed in the real groundwater sample. In addition, radical quenching tests revealed that sulfate radicals were the leading reactive species for diclofenac oxidation.

Sulfate radical treatment also proved to be effective for highly contaminated mature landfill leachate. Li et al. (2016b) used ferrous iron loaded granular activated carbon as a heterogeneous PDS catalyst for its pretreatment. The effects of the iron dose, PDS concentration and initial pH on the abatement of the organic pollution in the landfill leachate were determined. In single factor experiments, the maximum chemical oxygen demand (COD) removal rate reached 66.8, 66.2 and 76.3% at an iron dose of 127 mg L^{-1} (ferrous iron/PDS = 254 mg/mol), a PDS concentration of 0.5 M and an initial pH of 3, respectively. It was shown that the COD removal rate exceeded 87.8% when simultaneous conditions were applied i.e. Fe^{2+} dose of 127 mg L^{-1}, PDS concentration of 0.5 M and initial pH of 3.0. Asha et al. (2016) also found these pH conditions (3-4) to be very efficient for the removal of organic pollutants from stabilized leachate and observed a 78% reduction of the COD value.

2.4.2.3.2. Wastewater and sludge

Several studies can be found in the literature that describe the use of persulfates in wastewater treatment technologies. Their use is focused on exploiting their oxidative potential (removal of contaminants) and improving the properties of sludge i.e. dewaterability. Kronholm et al. (1999) tried to answer the question whether potassium persulfate is a feasible choice for wastewater oxidation below the critical temperature of water. The efficiency of phenol, 2,3-dichlorophenol, and 1-naphthol oxidation in high-temperature pressurized wastewater was investigated in an aqueous environment at 75-340 °C and pressure adjusted to 25-45 MPa. The removal percentages of phenol were good even at 115 °C. The concentration of the oxidant, temperature and reaction time proved to be very important parameters.

The removal of COD from petrochemical wastewater and from real high-strength industrial effluent was studied by Babaei and Ghanbari (2016) and Kattel et al. (2016), respectively. In both studies, the persulfates proved to be a viable alternative to the conventionally used oxidants (i.e. percarbonate, hydrogen peroxide).

Fagier et al. (2016) presented the efficiency of coagulation-flocculation pretreatment coupled with a sulfate radical oxidation process in the removal and mineralization of organic matter of sugarcane vinasse. Ferric chloride (15 g/l), a standard coagulation agent in wastewater treatment plants (WWTP), was used and achieved 70 % TOC removal. The pretreated vinasse subjected to a PDS/PMS oxidation process (activated by Fe^{2+}) showed the highest TOC removal efficiency at pH 7. Under the selected optimum conditions, approximately 70 and 49 % TOC removal was achieved for PMS/Fe(II) and PDS/Fe(II), respectively. Also, Rodríguez-Chueca et al. (2016) investigated winery wastewater treatment using PMS coupled with a transition metal and UV light. High COD and TOC removal efficacy (79 % and 64 %, respectively) was observed under optimal conditions after three hours of treatment.

In another study, cytarabine containing wastewater was successfully treated with UV/PDS (Ocampo-Pérez et al., 2010). Shu et al. (2016) investigated the UV/PMS degradation of Acid Blue 113 containing wastewater. They observed that the initial pH showed no significant effect on dye removal efficiency but UV light intensity significantly affected the efficiency of TOC mineralization.

Heterogeneous activation of PMS could also be used for the remediation of organic contaminants in wastewater according to Yao et al. (2015). They concluded that a $CoMn_2O_4$ catalyst was efficient and environmentally benign for the heterogeneous activation of PMS, although it showed almost no catalytic activity to PDS and H_2O_2. They observed that Rhodamine B degradation in wastewater was enhanced with an increase in reaction temperature (15-55 °C) and inhibited with an increase in fulvic acid concentration (0-0.08 g/L).

To date, a very limited number of papers have been published concerning the use of persulfates for sludge disintegration. There are many investigations in the matter of sludge disintegration by PDS and only a few focusing on the disintegration of activated sludge by PMS. The methods often used for determining the degree of waste activated sludge (WAS) disintegration include the measurement of soluble chemical oxygen demand (SCOD) and the sludge volume index (SVI). Determining the SCOD can unveil the degree of polymer transfer from the solid phase to the liquid phase, whereas the SVI is a measurement of the settleability of the sludge, which can be measured in a 1000 mL measuring cylinder after 30 minutes of sedimentation and expressed for a known initial sludge concentration. one of the first references to persulfates being used for sludge disintegration can be found in a study by Zhen et al. (2012a), who observed that ferrous iron activated PDS has a positive effect on enhancing sludge dewaterability with an 88.8 % capillary suction time (CST) reduction within 1 minute. In addition, similar results were obtained by Shi et al. (2015), whereby the highest specific resistance to filtration and CST reduction efficiencies of 88.5 and 91.5 %, respectively were obtained under the synergetic conditioning of Fe^{2+} activated PDS. Electro-activated PDS, was has also been applied for sludge treatment (Chen et al., 2014) and it was concluded that the process can be potentially applied to deal with wastewater from toluene nitration processes. In addition, it was determined that 2,4-dinitrotoluene in wastewater under electro-activated PDS oxidation can mainly be treated by virtue of sulfate radicals descended from the reduction of PDS anions. Also, Zhen et al. (2013b) performed electrolysis integrated with PDS/Fe(II) oxidation to effectively disrupt the protective barrier and crack the entrapped cells, releasing the water inside extracellular polymeric substances and cells, hence improving the dewaterability. Zhen et al. (2012b) found that a combined thermal oxidation process (at a mild temperature) is efficient in enhancing the dewaterability of sludge. They concluded that when the temperature is increased to 80 ^{o}C, the flocs of waste activated sludge were drastically changed and that this pretreatment resulted in the disruption of sludge flocs by degrading extracellular polymeric substances. These results were confirmed in our recent study focusing on the disintegration of sludge with heat activated PDS (Wacławek et al., 2015d). It was observed that organic matter and polymer transfer from the solid phase to the liquid phase occurred. An increase in SCOD, (almost a 15-fold increase over the WAS value) and a decrease in the SVI from 89.8 $cm^3\ g^{-1}$ to 30.6 $cm^3\ g^{-1}$ were also observed. A large issue for introduction of the presented method in WWTP, concerns heat activation of persulfates. However, the mild temperature threshold sufficient for PDS initiation (50-90 ^{o}C) can be reached using e.g. the heat generated in the fermentation process, steam or hot air injection.

Probably the first reference to the use of PMS for chemical disintegration of waste activated sludge was made in our recent papers (Wacławek et al., 2015c; Wacławek et al., 2016b). Similarly to an earlier study (Wacławek et al., 2015d), it was concluded that heat application (50, 70 and 90 °C) as a catalyst method for PMS activation causes an increase in the soluble COD value and protein concentration in the supernatant and positively influences the SVI, which decreased from 89.8 to 17.2 mL/g. Also, Niu et al. 2016 observed positive effects of WAS oxidation with PMS. Sludge disintegration was characterised by a change in disintegration degree (DD), sludge particle size and the properties of extracellular polymeric substances.

Although thermally activated persulfates are efficacious for the disintegration and improvement of sludge sedimentation properties (Wacławek et al., 2015c), Zhen et al. (2013a) observed a possible inhibitory effect on anaerobic digestion. On the contrary, Sun et al. (2012b) found that PDS disintegration had a positive influence on the biogas yield. Therefore, the composition of the sludge and the type of fermentation could be crucial for assessing the usefulness of persulfates for WAS disintegration.

Sludge treatment with persulfates can also be focused on anaerobically digested sludge as reported in our recent study (Waclawek et al. 2016c) and in a recent article published in Nature: Scientific Reports (Song et al., 2016). In addition to the enhancement of dewaterability, good efficiency of toluene removal from anaerobically digested sludge could be observed after the treatment with persulfates initiated with elevated temperatures from meso- or thermophilic digestion (Waclawek et al. 2016c).

2.4.3. Post-treatment toxicity assessment

Although persulfate treatment has many benefits, there are also several downsides that have to be taken into consideration i.e. contamination with sulfate salts or even worse newly created hazardous compounds due to e.g. additional chlorination and/or bromination (as discussed before). In our recent study concerning the decontamination of groundwater polluted with various chlorinated olefins (Wacławek et al., unpublished data), many new substances (with a molecular mass larger than 250 g/mol) were observed after UV/persulfate treatment that were unnoticed after e.g. UV/hydrogen peroxide treatment. Therefore, during bench-scale testing performed before field application, toxicity tests should be performed in order to avoid any environmental damage.

Zhang et al. (2015a) conducted acute toxicity tests with Vibrio qinghaiensis sp. Q67 photobacteria after the PDS treatment of carbamazepine and concluded that acute toxicity significantly decreased along with the degradation of the pharmaceutical, with the inhibitory effect of the carbamazepine solution decreasing from 100% to 65% within 60 minutes.

Olmez-Hanci et al. (2015) went even further and used three different toxicity tests (*Daphnia magna, Vibrio fischeri* and *Pseudokirchneriella subcapitata*) as well as the Yeast Estrogen Screen bioassay to assess the possible toxic and estrogenic properties of nonionic surfactant octylphenol ethoxylate and its oxidation products. In the case of *Daphnia magna* and *Vibrio fischeri* the inhibitory effect of nonionic surfactant octylphenol ethoxylate dropped considerably during the PMS treatment. On the other hand, PMS/UV-C oxidation products exhibited a high toxic effect towards *Pseudokirchneriella subcapitata* (approximately 60%).

Temiz et al. (2016) conducted acute toxicity tests using two different bioassays to examine the toxicological safety of the zero-valent iron/PDS oxidation of Triton X-45. Acute toxicity profiles significantly decreased from an original value of 66% relative inhibition to 21% and from 16% relative inhibition to non-toxic values according to *Vibrio fischeri* and *Pseudokirchneriella subcapitata* bioassays, respectively. The photobacterium *V. fischeri* appeared to be more sensitive to TX-45 and its degradation products than the microalgae *P. subcapitata*.

3. Remediation of hexachlorocyclohexanes by electrochemically activated persulfates

Abstract: Hexachlorocyclohexane (HCH) isomers represent a family of formerly widely utilized pesticides that are persistent, capable of undergoing long-range transport and tend to bioaccumulate in human and animal tissue. Their widespread global utilization coupled with a propensity to adversely impact human health and the environment translates into an urgent need to develop feasible methodologies by which to treat HCH-impacted groundwater and soil. The present study was conducted to evaluate the efficacy of two persulfate-based oxidants: peroxydisulfate ($S_2O_8^{2-}$, PDS) and peroxymonosulfate (HSO_5^-, PMS) activated by electrochemical processes (EC) to treat HCH-impacted environmental media. This research demonstrated that the optimal experimental conditions (oxidant dose and electrical current) were 2 mM PDS and 20 mA for an aqueous solution of 4 μM of summed HCHs (ΣHCH). GC/MS full scan analysis revealed the presence of 2,4,6–trichlorophenol as the only detectable intermediate formed during electro-activated PDS treatment of ΣHCH. The investigated method was tested on leachate from a known HCHs-impacted site in Hajek, Czech Republic which contained 106 μg/L of ΣHCH and 129 μg/L of chlorobenzenes. Results from batch treatment showed positive results for electro-activated PDS but only negligible effectiveness for electro-activated PMS. In addition to explaining the efficacy of the electro-activated PDS, this research also explored the basis for the differing reactivities of these two persulfates.

Citation: Wacławek, S., Antoš, V., Hrabák, P., Černík, M., and Elliott, D. (2016). Remediation of hexachlorocyclohexanes by electrochemically activated persulfates. *Environ. Sci. Pollut. Res.* 23, 765–773.

4. Remediation of hexachlorocyclohexanes by cobalt-mediated activation of peroxymonosulfate

Abstract: Hexachlorocyclohexane isomers (HCHs) are one of the most ubiquitous and most easily detected organochlorine pesticides in environmental samples. This global distribution is enabled by HCH persistence. Moreover, HCH tend to bioaccumulate in human and animal adipose tissue. Since certain HCHs cause central nervous system, reproductive, and other endocrine damage there is necessity of a suitable remediation method to remove HCH from contaminated groundwater and soil. The present study was conducted to evaluate the potential of peroxymonosulfate (Oxone) induced by cobalt salt ($Co(NO_3)_2$; Co(II)) to degrade HCHs. Cobalt (II) nitrate has been chosen instead of Cobalt (II) chloride (which presents better activation properties for Oxone) in order to avoid an excess of chloride interference and more additional chlorination by-products. The optimal conditions (oxidant dose as well as cobalt dose) were determined for spiked water with HCH (0.85 µM of summed HCH isomers). Optimal oxidant dose was established by running a test with three different Oxone concentrations (molar ratio of Oxone:$Co(NO_3)_2$ - 1:0.1): 0.06, 0.6 and 6 mM. Degradation curves of summed HCH isomers were fitted into the pseudo first-order kinetic model and reaction rates shown to be: 0.03, 0.31 and 0.55 min^{-1} for doses: 0.06, 0.6 and 6 mM respectively. Further experiments were carried out to determine the optimal Oxone:$Co(NO_3)_2$ molar ratio. Effectiveness of HCHs decontamination by Oxone:$Co(NO_3)_2$ in various molar ratios was in order: 1:0.1 > 1:1 > 1:0.01 > 1:0.001. It was observed that surplus of $Co(NO_3)_2$ can slow down degradation rate constants. A reaction between sulfate radicals and $Co(NO_3)_2$ could be responsible for this phenomenon, which can lead to formation of sulfate ions without HCHs oxidation. In addition, tests with higher HCH dose (close to the solubility limit) were carried out to determine by-products of decontamination. In these tests 2,4,6-trichlorophenol (2,4,6—TCP) was found to be the major intermediate of HCH isomers degradation. Trace levels of the trichlorobenzene (TCB), tetrachlorophenol (TeCP) and pentachlorophenol (PCP) were detected as well. The study revealed that Oxone induced by Co(II) shows a high degradation rate with HCH isomers, which can make it an attractive method for HCHs decontamination in the future.

Citation: Wacławek, S., Antoš, V., Hrabák, P., and Černík, M. (2015). Remediation of hexachlorocyclohexanes by cobalt-mediated activation of peroxymonosulfate. *Desalination Water. Treat.* 1-6.

5. Simple spectrophotometric determination of monopersulfate

Abstract: A simple, sensitive and accurate spectrophotometric method has been developed and validated for the determination of monopersulfate (MPS) which is an active part of potassium monopersulfate triple salt that has the commercial name - Oxone. This work proposes a spectrophotometric determination of monopersulfate based on modification of the iodometric titration method. The analysis of absorption spectra was made for the concentration range from 1.35 to 13.01 ppm of MPS (with a detection and quantification limit of 0.41 ppm and 1.35 ppm, respectively) and different pH values. The influence of several anions on the measurement was also investigated. Furthermore, the absorbance of iron and cobalt (often used as free radical initiators) proved to have no effect on the measurement of MPS concentrations. On the basis of the conducted studies, we propose 395 nm as an optimal wavelength for the determination of MPS concentrations.

Citation: Wacławek, S., Grübel, K., and Černík, M. (2015). Simple spectrophotometric determination of monopersulfate. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 149, 928–933.

6. A novel approach for simultaneous improvement of dewaterability, post-digestion liquor properties and toluene removal from anaerobically digested sludge

Abstract: Anaerobically digested sludge (ADS) is a major product of anaerobic digestion a widely used and economically viable microbial process used in wastewater treatment plants (WWTP) to break down biodegradable material in the absence of oxygen. Although anaerobic digestion is considered environmentally safe, the sludge often possesses undesirable properties including resistance to dewatering and high concentrations of harmful or deleterious compounds. Toluene is one of the hazardous products of anaerobic digestion that can be harmful to humans and the environment. In previous studies, it was demonstrated that persulfates: peroxydisulfate (PDS, $S_2O_8^{2-}$) and peroxymonosulfate (PMS, HSO_5^-) could be successfully used in the sludge treatment process. In this study, it was demonstrated that elevated temperatures from meso- or thermophilic digestion could activate persulfate creating highly reactive sulfate and hydroxyl radicals. These radicals can oxidize toluene and other organic matter in ADS thereby improving its dewaterability. Furthermore, supernatant obtained after oxidation treatment was conditioned by struvite precipitation in order to remove ammonium nitrogen and phosphates. The results of this study indicate large improvements in ADS properties after PDS treatment in comparison to PMS or temperature conditioning alone.

Citation: Wacławek, S., Grübel, K., Dennis, P., Padil V.T., V., and Černík, M. (2016). A novel approach for simultaneous improvement of dewaterability, post-digestion liquor properties and toluene removal from anaerobically digested sludge. *Chem. Eng. J* 291, 192–198.

7. Conclusions

Applied study unveiled that PDS electrochemically activated and PMS activated by cobalt are suitable for HCH isomers degradation. In addition, heat-activated persulfates had shown excellent efficacy in the improvement of anaerobically digested sludge properties. Data on decontamination kinetics using activated persulfates were determined to be extremely fast in comparison to biological or chemical reductive treatment. In our studies, the pseudo-first order kinetic model (experiments conducted with an excess of oxidant) was used. It is worthy to note that summed HCH isomers can be almost completely oxidised by persulfates under the optimal conditions. Furthermore, in the thesis many determination methods for persulfates were presented and assessed and developed herein simple spectrophotometric determination of peroxymonosulfate was successfully implement in the determination of it in water and sludge, which allowed to calculate its decomposition rate constants and the optimal dose. Moreover, in our recent study, tests concerning persulfates oxidation of sludge reviled ability of persulfates to simultaneously improve dewaterability, post-digestion liquor properties and remove toluene from anaerobically digested sludge.

List of authors articles

Concerning persulfates:

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