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VYUŽITÍ PERSULFÁTU PRO ODBOURÁVÁNÍ ORGANICKÝCH LÁTEK

USE OF PERSULFATES FOR DEGRADATION OF ORGANIC POLLUTANTS

Disertační práce

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Podpis: Stanisław Wacławek

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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

Attachments

- 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.
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1. ABBREVIATIONS

2,4,6-TCP - 2,4,6-trichlorophenol

ADS - anaerobically digested sludge

BTEX - benzene, toluene, ethylbenzene and xylenes

C-DBP - carbonaceous disinfection by-products

COD - chemical oxygen demand

CST - capillary suction time

DBP - dichlorobenzophenone

DD - disintegration degree

DDNS - 1-chloro-2,2-bis (p-chlorophenyl)-ethane

DDT - 1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane

DMP - dimethyl phthalate

DNT - dinitrotoluene

EC - electrochemical

EK - electrokinetics

ESR - electron spin resonance

HCH - hexachlorocyclohexane

HDI - human development index

ISCO - in situ chemical oxidation

MPS - peroxymonosulfate (monopersulfate)

MTBE - methyl tert-butyl ether

N-DBP - nitrogenous disinfection by-products

NMR - nuclear magnetic resonance

NOM - natural organic matter

PCP - pentachlorophenol

PDS - peroxydisulfate

PFOA - perfluorooctanoic acid

PMS - peroxymonosulfate (monopersulfate)

POPs - persistent organic pollutants

SCOD - soluble chemical oxygen demand

SOM - soil organic matter

SVI - sludge volume index

TCB - trichlorobenzene

TCE - trichloroethene

TeCP - tetrachlorophenol

TOC - total organic carbon

TS - total solids

UV-C - Ultraviolet C

WAS - waste activated sludge

WWTP - wastewater treatment plants

2. 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.

Oxidants used for environmental purposes can generally be divided into ones that possess a peroxide bond and ones that do not (Fig. 1).

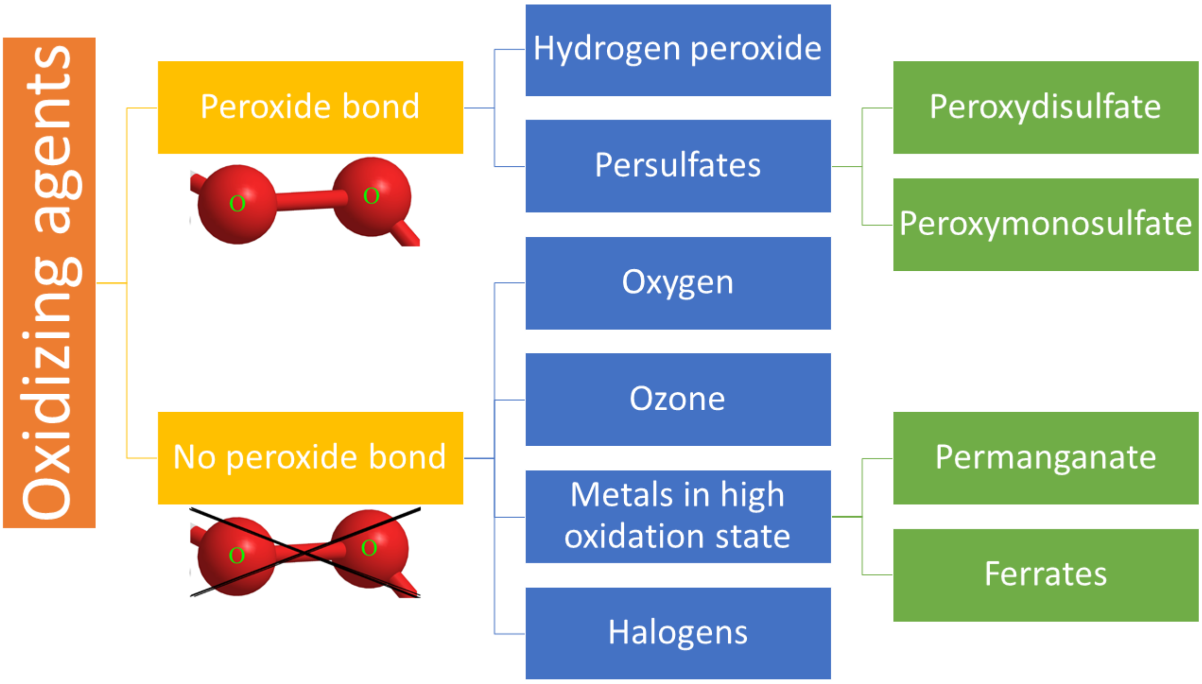

Figure. 1 Oxidizing agents used in water and wastewater treatment

Oxidizing agents like ozone and halogens have long been employed for water and wastewater treatment (Sonntag and von Gunten, 2012; Spellman, 1999). The second group of oxidants are those that oxidize via direct electron transfer. Oxidants possessing the O-O bond (known as peroxide or the peroxo group), are not only capable of direct oxidation but can also form free radicals. Unlike oxygen in the molecular form of O_2, the oxygen atoms in the peroxo group have an oxidation state of -1 (IUPAC, 1997). Compounds containing these bonds are known as peroxides.

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).

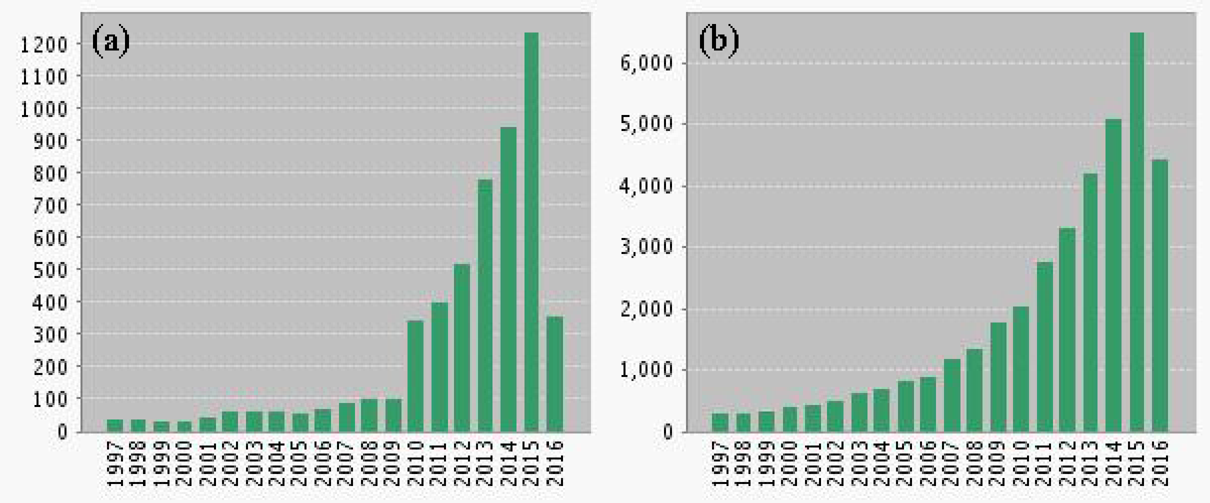

Figure 2. Annual number of a) publications concerning PDS and PMS and b) citations. Source: Web of knowledge (data as of August 2016)

As it can be observed in Fig. 2a, the number of articles concerning PDS and PMS almost doubled after 2013. Similarly, the number of citations has grown significantly within the last 3 years (Fig. 2b). Therefore, assuming that recently persulfates are popular in environmental sciences, we strongly believe that it would be beneficial to focus on their chemistry in water and wastewater treatment.

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. From these papers, four the most relevant were selected for this thesis. The other papers are included in the attachment for information. These papers concern on different contaminant in water, namely persistent organic pollutants and sludge treatment.

Persistent organic pollutants (POPs) are toxic for human health and for wildlife, persist in the environment for a long time, are widely distributed in the environment and bioaccumulate in fatty tissues of humans and animals. Several isomers of hexachlorocyclohexanes were added to the POPs list in 2009. It was determined in present work that electrochemical processes can effectively induce peroxydisulfate to form free radicals and in this manner degrade HCH. The investigated method was tested on leachate from a site Hajek, Czech Republic, which contained HCH and chlorobenzenes. Results from batch treatment showed positive results for electro-activated PDS but only insignificant effectiveness for electro-activated PMS.

In contrary, peroxymonosulfate activated with a cobalt salt was found to be effective for degradation of HCH as well. 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 degradation. Trace levels of the trichlorobenzene (TCB), tetrachlorophenol (TeCP) and pentachlorophenol (PCP) were detected as well.

Moreover, developed herein simple spectrophotometric determination method for peroxymonosulfate allowed to accurately determine the decomposition kinetics of PMS and therefore to understand better the degradation mechanisms. The accuracy of the method was validated and the detection and quantification limit was found to be 0.41 ppm and 1.35 ppm, respectively. The influence of several anions on the measurement was also investigated in the developed method.

In addition, improvement of anaerobically digested sludge properties with heat activated persulfates was done. Anaerobically digested sludge is the main end-product of anaerobic digestion that causes a chain of complications in post-treatment processing and disposal. In presented study, thermally activated peroxydisulfate and peroxymonosulfate were used for toluene oxidation and dewaterability improvement of anaerobically digested sludge.

3. THEORETICAL PART

3.1. 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. 3b). 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.

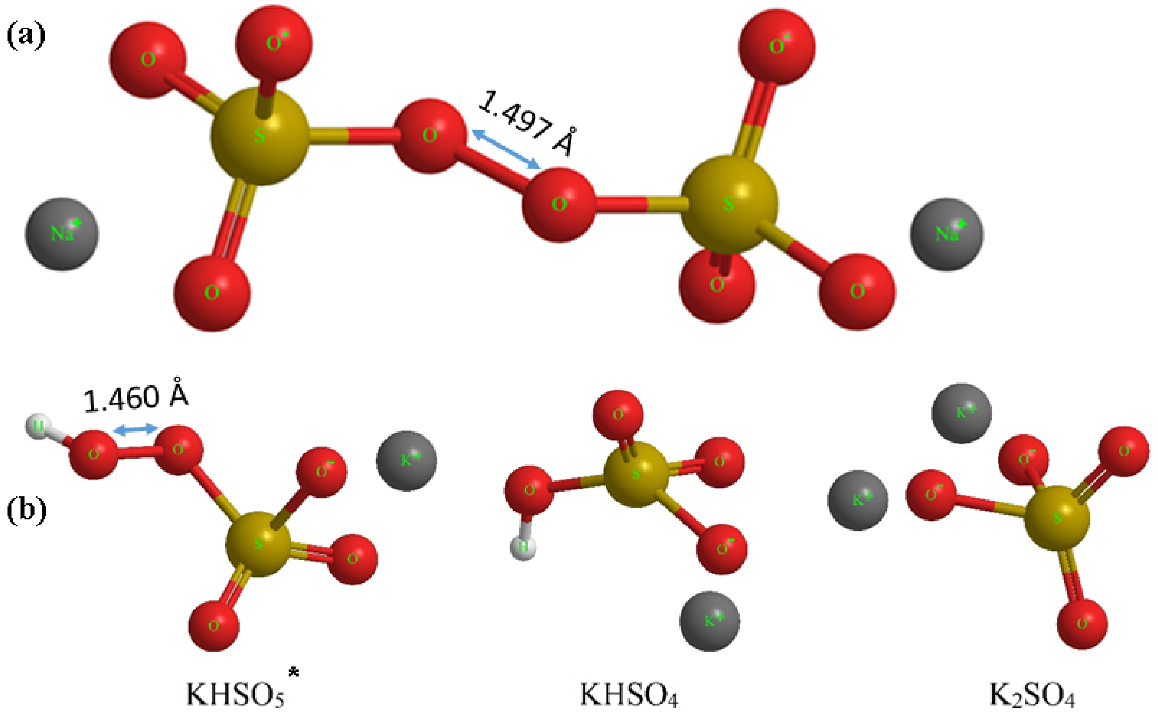

Figure 3. (a) Sodium PDS and (b) Oxone triple salt molecular structure (*potassium PMS ($KHSO_5$) - active part of Oxone). (Spivey et al., 2015).

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.

3.2. 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.

3.2.1. 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.

3.2.2. 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.

3.2.3. 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.

3.2.4. 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.

3.2.5. 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).

3.2.6. 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 $OH^{\bullet}$.

3.3. 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 x 10^{-2}	(Liang et al., 2008)
Spectrophotometry	H_2SO_4/NH_4SCN	~40 min	2.1 x 10^{-4}	(Huang et al., 2002)
Spectrophotometry	Methylene blue under microwave radiation	1 min	3 x 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 x 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 x 10^{-5}	(Oliveira et al., 2000)
Ion chromatography	Mobile phase: 50 mM KOH; flow rate: 1 mL/min	18 min	5.2 x 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 x 10^{-5}	(Wacławek et al., 2015b)
Spectrophotometry	Co^{2+}/methyl orange	1 min	5 x 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 x 10^{-5}	(Ossadnik and Schwedt, 2001)
HPLC	Mobile phase: methanol/phosphoric acid buffer	-	~5 x 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).

3.4. Persulfate decontamination technologies

3.4.1. 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 4 shows the second-order reaction rate constants of persulfate reactions with several species in an aqueous phase.

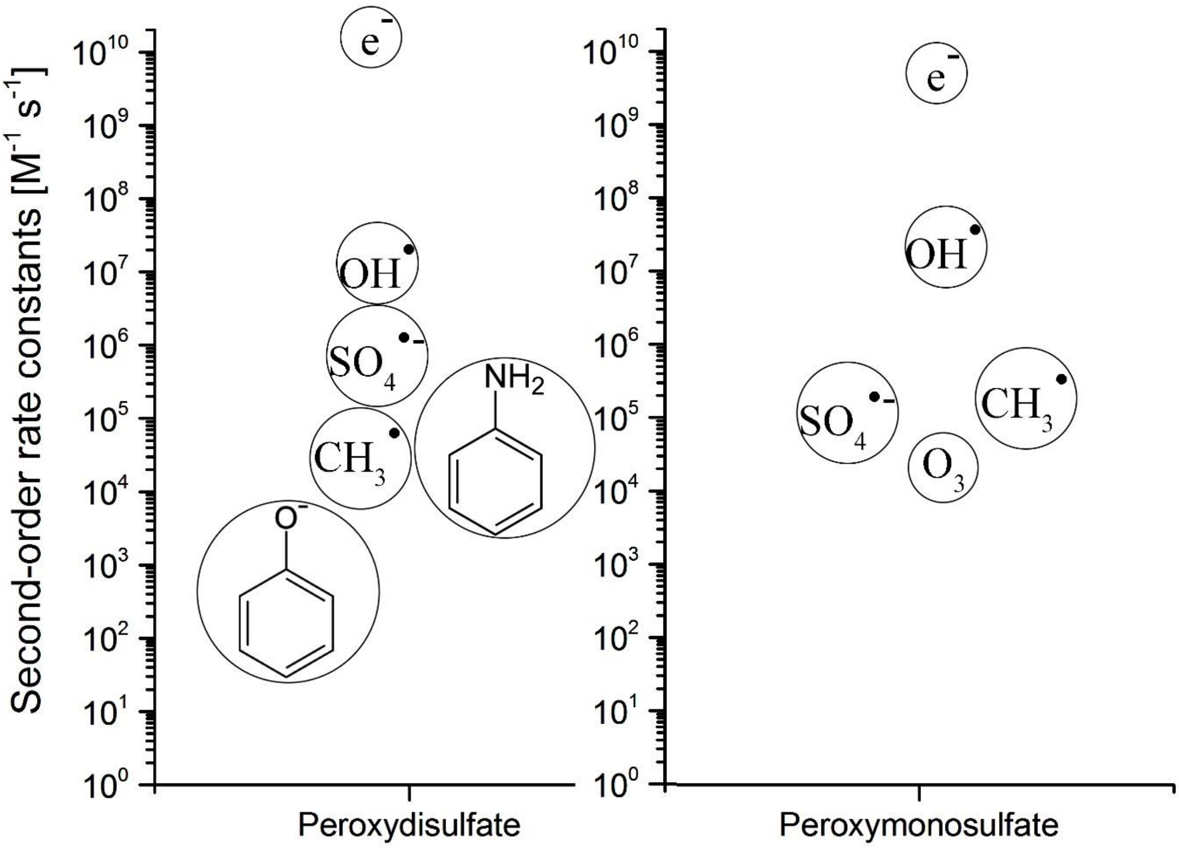

Figure 4. Comparison of the second-order reaction rate constants of persulfates with aqueous species (the middle of the circles indicates the exact rate constants). Data taken from: Yang et al. (2015); Behrman (2004); Buxton et al. (1988b); Restelli et al. (1990); Herrmann et al. (1995); Davies et al. (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).

3.4.2. Radical oxidation in water and wastewater treatment

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

3.4.2.1. 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 5.

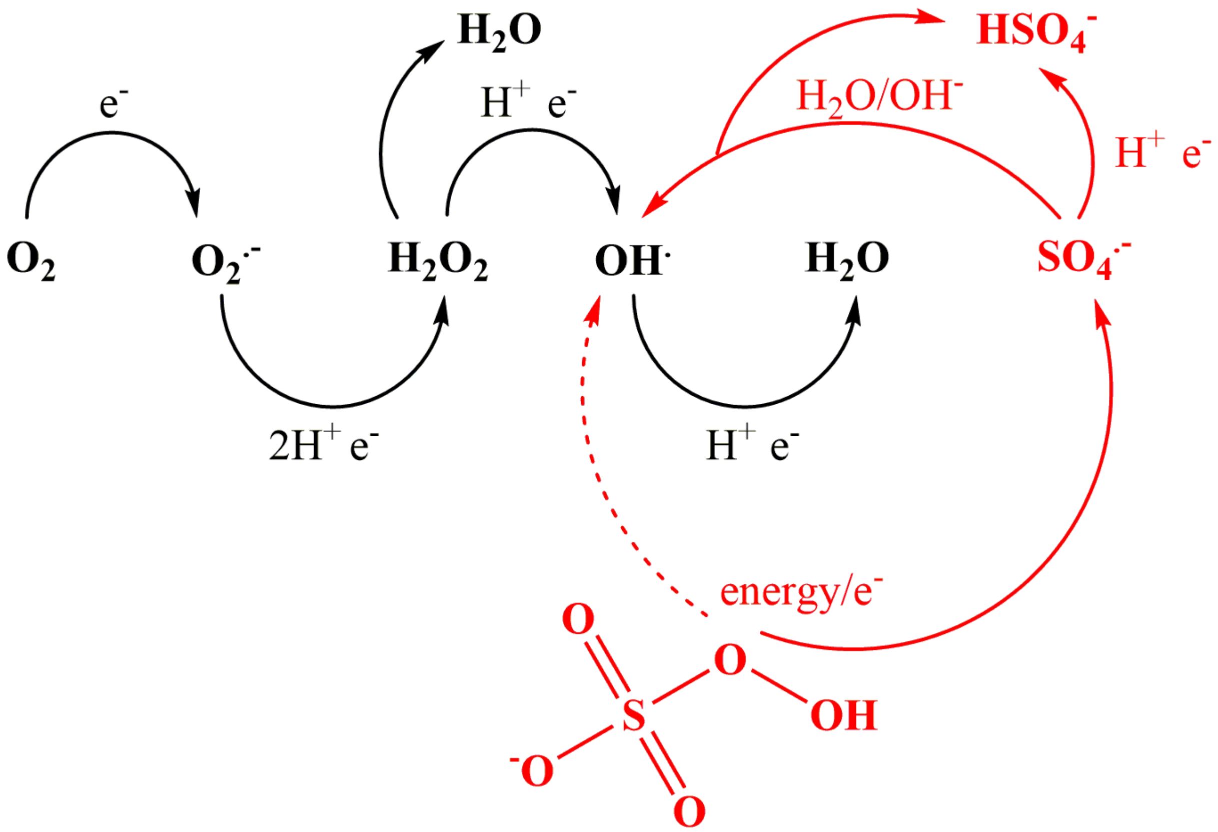

Figure 5. Black arrows - scheme of oxygen molecule reduction to water; red arrows - radical formation and behaviour in a persulfate system (dashed arrow - only valid for homolytic cleavage of the PMS O-O bond).

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.

$$SO_4^{\bullet -} + OH^- \rightarrow SO_4^{2-} + OH^{\bullet} \quad (5)$$

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).

3.4.2.2. 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**
$OH^•$	Cl^-	$3.0\text{-}4.3 \times 10^9$	(Grigor'ev et al., 1987; Jayson et al., 1973)
$SO_4^{•-}$	Cl^-	$1.3\text{-}6.6 \times 10^8$	(Waldemer et al., 2007; Kim and Hamill, 1976; McElroy, 1990)
$OH^•$	Br^-	1.9×10^9	(Zehavia and Rabani, 1972)
$SO_4^{•-}$	Br^-	3.5×10^9	(Redpath and Willson, 1975)
$OH^•$	HCO_3^-	$n \times 10^7$	(Buxton et al., 1988a)
$SO_4^{•-}$	HCO_3^-	$2.6\text{-}9.1 \times 10^6$	(Huie and Clifton, 1990; Dogliotti and Hayon, 1967)
$OH^•$	CO_3^{2-}	4×10^8	(Buxton et al., 1988a)
$SO_4^{•-}$	CO_3^{2-}	4.1×10^6	(Padmaja et al., 1993)
$OH^•$	Humic acid	1.4×10^{4}*	(Lutze et al., 2015)
$SO_4^{•-}$	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.

3.4.2.3. 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.

3.4.2.3.1. 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 $OH^{\bullet}$ 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 x 10^{-3} min^{-1} (activation temperature of 50 ºC)	(Waldemer et al., 2007)
	Trichloroethene	Possibly $SO_4^{\bullet-}$ (not identified)	Trace quantities of hexachloroethane as an intermediate	4.7 x 10^{-3} min^{-1} (activation temperature of 50 ºC)	(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 x 10^{-3} min^{-1} (activation temperature of 50 ºC)	(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 x 10^{-3} min^{-1} (activation temperature of 50 ºC)	(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 x 10^2 day^{-1} (activation temperature of 20 ºC; Oxidant/BTEX molar ratio 100/1)	(Kambhu et al., 2012)
	Toluene	Possibly $SO_4^{\bullet-}$ (not identified)	-	23.2 x 10^2 day^{-1} (activation temperature of 20 ºC; Oxidant/BTEX molar ratio 100/1)	(Kambhu et al., 2012)
	Ethylbenzene	Possibly $SO_4^{\bullet-}$ (not identified)	-	14.5 x 10^2 day^{-1} (activation temperature of 20 ºC; Oxidant/BTEX molar ratio 100/1)	(Kambhu et al., 2012)
	Xylene	Possibly $SO_4^{\bullet-}$ (not identified)	-	21.9 x 10^2 day^{-1} (activation temperature of 20 ºC; 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: λ = 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: λ = 254 nm; 40 W power; Io = 1.26 μE 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 ºC; 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: λ = 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: λ = 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 x 10^{-3} sec^{-1} (UV activation parameters: λ = 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 x 10^{-4} sec^{-1} (UV activation parameters: λ = 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: λ = 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: λ = 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.

3.4.2.3.2. 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 ^oC) 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).

3.4.3. 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*.

4. RESULTS AND DISCUSSION

During my PhD studies, I have already published 8 articles (and additional 3 are under preparation/review) in impact factored journals concerning the use of persulfates for the treatment of organic pollution from which 4 was chosen to be presented below.

4.1. 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.

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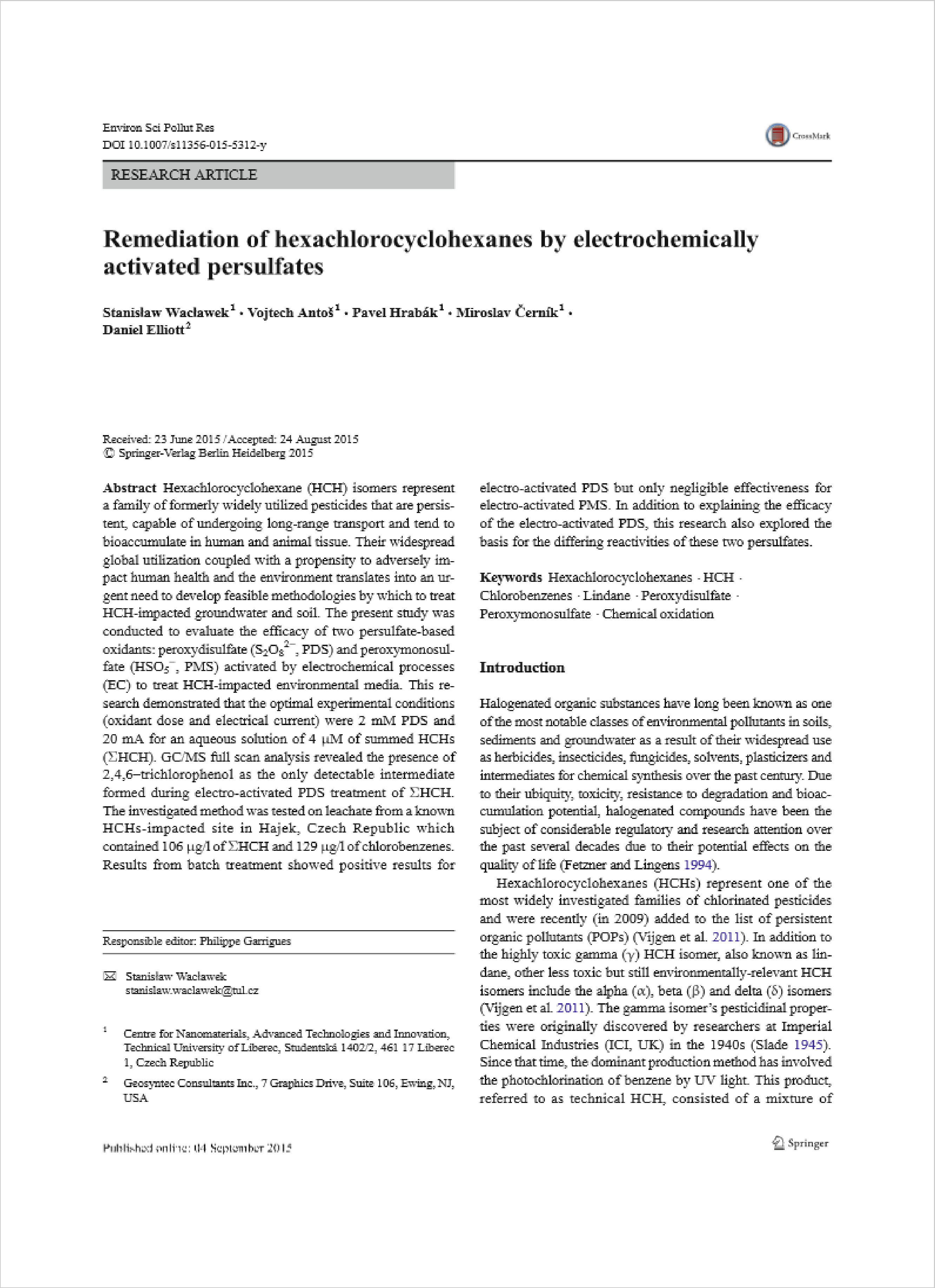

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RESEARCH ARTICLE

Remediation of hexachlorocyclohexanes by electrochemically activated persulfates

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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.

Keywords Hexachlorocyclohexanes · HCH · Chlorobenzenes · Lindane · Peroxydisulfate · Peroxymonosulfate · Chemical oxidation

Introduction

Halogenated organic substances have long been known as one of the most notable classes of environmental pollutants in soils, sediments and groundwater as a result of their widespread use as herbicides, insecticides, fungicides, solvents, plasticizers and intermediates for chemical synthesis over the past century. Due to their ubiquity, toxicity, resistance to degradation and bioaccumulation potential, halogenated compounds have been the subject of considerable regulatory and research attention over the past several decades due to their potential effects on the quality of life (Fetzner and Lingens 1994).

Hexachlorocyclohexanes (HCHs) represent one of the most widely investigated families of chlorinated pesticides and were recently (in 2009) added to the list of persistent organic pollutants (POPs) (Vijgen et al. 2011). In addition to the highly toxic gamma (γ) HCH isomer, also known as lindane, other less toxic but still environmentally-relevant HCH isomers include the alpha (α), beta (β) and delta (δ) isomers (Vijgen et al. 2011). The gamma isomer's pesticidinal properties were originally discovered by researchers at Imperial Chemical Industries (ICI, UK) in the 1940s (Slade 1945). Since that time, the dominant production method has involved the photochlorination of benzene by UV light. This product, referred to as technical HCH, consisted of a mixture of

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isomers and, because of its lower cost, was favoured in developing economies. A typical composition for technical HCH is as follows: 60–70 % α-HCH, 10–12 % γ-HCH, 5–12 % β-HCH, 6–10 % δ-HCH and 3–4 % ε-HCH (Iwata et al. 1993). The highly toxic isomer γ-HCH, a pesticide used worldwide for controlling agricultural pests, in seed treatments and in medical applications could be obtained by multiple recrystallizations from technical HCH (Voldner and Li 1995; Willett et al. 1998). The use of high purity lindane treatments tended to be preferred in the developed economies of Western Europe, the USA, and Canada (Ramos et al. 2011).

Considering that approximately 10 million tons of HCHs were utilized globally during the timeframe of 1948–1997, it is reasonable to assume that a significant number of impacted sites require cleanup (Willett et al. 1998). Although the threat is obvious, HCHs are still being used as pesticides in developing as well as developed countries (Li 1999). For example, a mixture of technical HCHs and lindane has been used in India in both pharmaceutical products and agriculture (Central Insecticide Board and Registration Committee 2005) and lindane has been used for seed treatment in Canada and USA (Sang et al. 1999).

It is therefore important to develop cost-effective remedial technologies to treat soil, water and waste sites contaminated by HCH isomers and to help speed up the disposal of HCH products. Degradation of HCH can be achieved by various remedial techniques using both biological and chemical reduction methods (Phillips et al. 2005; Boyle et al. 1999; Elliott et al. 2009; Singh et al. 2012; Zinovyev et al. 2004), but according to our knowledge, there have been relatively few investigations on the use of chemical oxidation to degrade HCHs in the literature. Previous studies employing H_2O_2 for assisted UV photo-degradation of synthetic lindane solutions (Nienow et al. 2008; Nitoi et al. 2013) and various oxidants including H_2O_2, PDS and permanganate (Usman et al. 2014; Cao et al. 2008) are known. Usman et al. (2014) reported the oxidative treatment of HCH isomers in soil by PDS both activated by Fe^{2+} and non-activated. Application of soluble Fe^{2+} showed a negative impact on the reactivity of PDS after 24 h of reaction. The utilization of PDS alone resulted in relatively high degradation of HCH isomers, which decreased in the order γ-HCH (95 %), δ-HCH (92 %), α-HCH (79 %) and β-HCH (43 %) (Usman et al. 2014).

PDS and PMS are among the strongest oxidants used in environmental remediation applications. The standard ORP for the reaction (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) (Block et al. 2004; Bajpai 2012).

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

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

Furthermore, PDS and PMS can form free radicals analogous to the hydroxyl radical pathways generated by Fenton's chemistry (Eqs. 3, 4) (Block et al. 2004; Wang and Chu 2012). Yuan et al. (2014) claimed that $OH^\bullet$ can be produced from $SO_4^{\bullet-}$ (Eq. 5) and can play a more important role than $SO_4^{\bullet-}$ for degradation of certain contaminants, e.g. VOC.

$$S_2O_8^{2-} \rightarrow SO_4^{\bullet-} + \left(SO_4^{\bullet-}\ \mathit{or}\ SO_4^{2-}\right) \qquad (3)$$

$$HSO_5^- \rightarrow OH^\bullet + SO_4^{\bullet-} \qquad (4)$$

$$H_2O + SO_4^{\bullet-} \rightarrow OH^\bullet + SO_4^{2-} + H^+ \qquad (5)$$

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 are usually generated during the activation of PDS under heat-, photo-, metal-, chelated metal-, quinone-, phenols-, hydrogen peroxide- or alkaline-catalysed conditions (Huang et al. 2002; Block et al. 2004; Fang et al. 2013; Siegrist et al. 2011; Ahmad et al. 2013). Wang and Chu (2012) reported that PMS can be easily activated into highly reactive radicals through homolytic cleavage of the peroxide bond of HSO_5^- by photolysis or thermolysis (Eq. 4). However, the activation of PDS and PMS under electrochemical conditions is still not widely known (Yuan et al. 2014; Govindan et al. 2014; Lin et al. 2014). The mechanisms in which iron oxidation plays an important role in the anodic and cathodic reactions can be described by (Eqs. 6 to 9) (Govindan et al. 2014).

Anodic reactions:

$$4Fe_{(s)} \rightarrow 4Fe^{2+}{}_{(aq)} + 8e \qquad (6)$$

$$4Fe^{2+}{}_{(aq)} + 10H_2O_{(aq)} + O_{2(aq)} \rightarrow 4Fe(OH)_{3(s)} + 8H^+{}_{(aq)} \qquad (7)$$

Cathodic reaction:

$$8H^+{}_{(aq)} + 8e^- \rightarrow 4H_{2(g)} \qquad (8)$$

Overall reaction:

$$4Fe_{(s)} + 10H_2O_{(aq)} + O_{2(aq)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)} \qquad (9)$$

The reactions taking place on anodes and cathodes contribute to the activation of oxidants. Fe^{2+} produced from the iron anode activates oxidants to generate strongly oxidizing $SO_4^{\bullet-}$ and $OH^\bullet$ species (Eqs. 10, 5) and the Fe^{2+} is regenerated from the reduction of Fe^{3+} on the cathode (Eq. 11) (Lin et al. 2014).

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{\bullet-} + SO_4^{2-} \qquad (10)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (11)$$

Iron electrodes can be easily introduced into the contaminated zone to control the in situ activation of PDS, thus minimizing potential losses during its injection and transportation in the subsurface (Yuan et al. 2014). For this and many other reasons, the oxidation efficiency of organic and inorganic pollutants can be significantly enhanced by coupling electrochemical processes with PDS and PMS injection (Lin et al. 2014; Govindan et al. 2014).

On the other hand, according to literature, the electrochemically produced Fe^{2+} can also act as a sulfate radical scavenger at high concentrations as expressed by Eq. (12) (Usman et al. 2014; Cao et al. 2008; Xu and Li 2010). Thus, ferrous iron represents a double-edged sword—it can both catalyse the formation of sulfate radicals and quench them depending upon its concentration.

$$Fe^{2+} + SO_4^{\bullet -} \rightarrow Fe^{3+} + SO_4^{2-} \quad (12)$$

This study was conducted to evaluate the efficacy of two persulfate-based oxidants, PDS and PMS, activated by electrochemical processes (EC) to degrade HCH isomers in contaminated water. To our knowledge, this represents the first published research concerning the degradation of HCHs by electro-activated persulfates. Following controlled bench-scale experiments, the optimized methodology was demonstrated on groundwater from an HCH-impacted site in the Czech Republic.

Methodology

Reagents and solutions

All of the chemicals used in the experiments were analytical reagent grade. PMS (Oxone®, 99.0 %) and sodium bicarbonate (99.7 %) were purchased from Sigma–Aldrich, sodium thiosulfate pentahydrate (99.0 %), PDS (sodium persulfate, 99.0 %), potassium iodide (99.5 %) and sodium sulfate were purchased from Lach-Ner. A saturated stock solution of HCH was prepared by dissolving standard mix of HCH isomers (purity >99.3 %; Fluka, Sigma–Aldrich Co.) in deionized water. This was filtered through a 0.45-μm filter after vigorous stirring for 3 days. The stock solution (summed HCH concentration, ΣHCH: 40 μM; pH~6.8; α-HCH (13.6 %), β-HCH (12.4 %), γ-HCH (45.6 %) and δ-HCH (28.4 %)) was then stored in a refrigerator at 5 °C. Deionized water (18.2 MΩ cm^{-1}) was prepared by an ELGA Purelab flex system (ELGA, Veolia Water, Marlow, UK).

A representative sample of contaminated groundwater was taken from the Hajek dump site (Czech Republic). The site is an uncontrolled dump associated with a former uranium and kaoline mine which, in the 1960s, was used for disposal of waste product from lindane and chlorobenzene production by the Spolana, a.s., a chemicals manufacturer in Neratovice, Czech Republic. Approximately 3000 tons of chemicals were disposed in steel barrels, paper bags or loosely at the dump site (Hešnaur and Jech 2001). Seepage water is collected by drainage pipes which flow into an open channel discharging into a nearby lake, where HCH concentrations exceed the appropriate limit (0.02 μg/l). The water from the pipe was collected by a 10-l glass vessel, transferred to the laboratory and stored at 4 °C. The contaminant content was determined prior to the experiments. The water contains a mixture of HCHs (ΣHCH=106.51 μg/l) and CB at 129.90 μg/l (Table 1).

Analytical

HCH and CB isomers were quantified by a gas chromatograph (Thermo Trace 1310 combined with an MS detector TSQ 8000 triple quadrupole). Headspace solid-phase microextraction (HS-SPME) was utilized for sample preparation and injection (PDMS SPME fibres, Supelco). A TR-Pesticide chromatographic column, 30 m in length, 0.25 mm in diameter was used for gas chromatography. For detection of the polar chlorophenols, as by-products of the oxidation reactions, sample aliquots were derivatized with acetic anhydride. For calibration, standard mixtures of HCH and CB (Neochema, Pesticides Mix 5 and Chlorobenzenes Mix 12) were employed along with deuterated γ-HCH (Ehrenstorfer, GmBH) as an internal standard.

In addition, potential volatile reaction intermediates and products (other than chlorophenols) were qualitatively searched for in the full scan mode of a GC/ion trap MS instrument (Varian Saturn 3800), equipped with a DB-624 column, 60 m in length and 0.25 mm in diameter.

A ultraviolet-visible spectrophotometer HACH DR 6000 (HACH LANGE s.r.o., Czech Republic) with matched 1-cm quartz cells (cuvettes) was used for the determination of PDS and PMS concentration according to the method developed by (Liang et al. 2008) and (Wacławek et al. 2015), respectively. At selected time points, 0.2-ml samples were taken from the reactors, mixed with a 5-ml potassium iodide solution and the resulting mixtures were then measured using the spectrophotometer (characteristic wavelengths of 400 and 395 nm). A calibration curve was established using PDS and PMS solutions ranging from 4 to 40 and 1.35 to 13 mg/l, respectively.

The pH and ORP measurements were determined by a WTW pH-meter equipped with SenTix pH electrodes (MultiLine® Multi 3430 IDS). ORP values are presented as values against a saturated calomel electrode (SCE) and were not corrected to the standard hydrogen electrode (SHE). TOC was analysed by a Multi N/C 3100 analyser (Jena Corporation, Germany).

Table 1 Composition of contaminated groundwater from the Hajek site

HCH isomer	Concentration (μg/l)	CB congener	Concentration (μg/l)
α	9.22	1,3,5-TCB	6.78
δ	4.55	1,2,4-TCB	107.82
γ	11.96	1,2,3-TCB	13.24
δ	71.17	1,2,3,4-TeCB	1.05
ε	9.60	1,2,4,5+1,2,3,5-TeCB	0.88
pH	~8.0	pentachlorobenzene	0.11
ORP	200 mV	Hexachlorobenzene	0.00

EC experiment setup

EC tests were performed at room temperature in a non-tightened undivided batch electrolytic cell (1.5 l) containing 1 l of electrolyte solution as shown in Fig. 1. Two iron electrodes were employed and were connected in parallel through a DC regulated power supply (HQ POWER PS3010) at an inter-electrode distance of 8 cm in the electrolytic cell. Sodium sulfate at 0.7 mM was used as a background electrolyte. Sample aliquots of 10 ml were taken from the reactor and mixed with sodium thiosulfate to quench the oxidant and stop the reaction. Unless otherwise specified, the reaction conditions were based on a 4-μM ΣHCH mixture, containing 0.5 μM (α-HCH), 0.5 μM (β-HCH), 1.9 μM (γ-HCH) and 1.1 μM (δ-HCH), 2 mM PDS or 6 mM PMS initial concentrations and 20 mA applied current (6 V). The experiment with two separated compartments was conducted in two 2 l reactors separated by an anion-exchange membrane (MemBrain s.r.o., Czech Republic) that transmits anions and blocks the cations and hydrodynamic flow of the solvent. All of the experiments were carried out in duplicate at least.

Results and discussion

Applied electric current significantly changed the concentrations of contaminants and other parameters as well as the solution pH and ORP during the tests. Fe^{2+} produced from the iron electrode activated the oxidants in solution to generate strongly oxidizing $SO_4^{\bullet -}$ and $OH^{\bullet}$ radicals which subsequently degraded the HCHs. Both $SO_4^{\bullet -}$ and $OH^{\bullet}$ are possibly responsible for the destruction of HCH and either radical may predominate over the other depending on solution pH. The kinetics of pH and ORP changes in the EC, EC+PDS and EC+PMS experimental sets were observed (Fig. 2). According to Liang and Huang (2012), $SO_4^{\bullet -}$ was the predominant radical at acidic solution pH. Both PDS and PMS have the potential to dramatically lower pH and increase ORP in groundwater. Figure 2 shows that after the addition of 2 mM of PDS, the solution pH and ORP changed to about 2.5 standard units and 450 mV, respectively, within 30 min of treatment. By comparison, following the addition of 6 mM of PMS, the solution pH dropped to 2.5 standard units and the ORP increased to 550 mV. Based on these results, PDS and PMS generate similar pH and ORP profiles when combined with EC. According to Anipsitakis and Dionysiou (2004), $SO_4^{\bullet -}$ and $OH^{\bullet}$ exhibit similar reduction potentials under acidic conditions. These radicals are highly reactive to C–H bonds (Lee and von Gunten 2010) located in HCH.

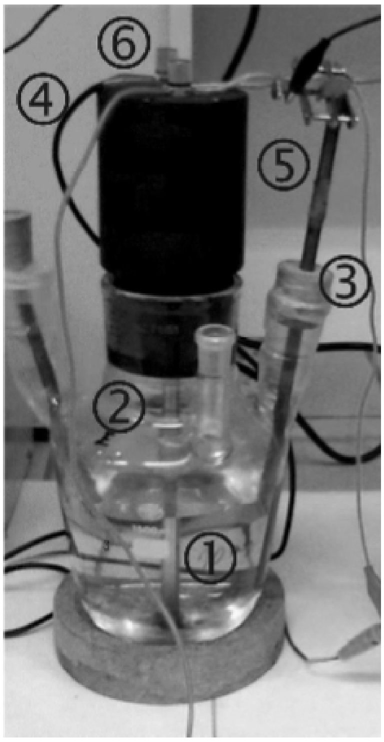

Fig. 1 Experimental apparatus: (*1*) HCH-spiked deionized water, (*2*) glass reactor, (3) rubber caps, (4) power lines to supply, (*5*) iron electrodes, (*6*) stirrer

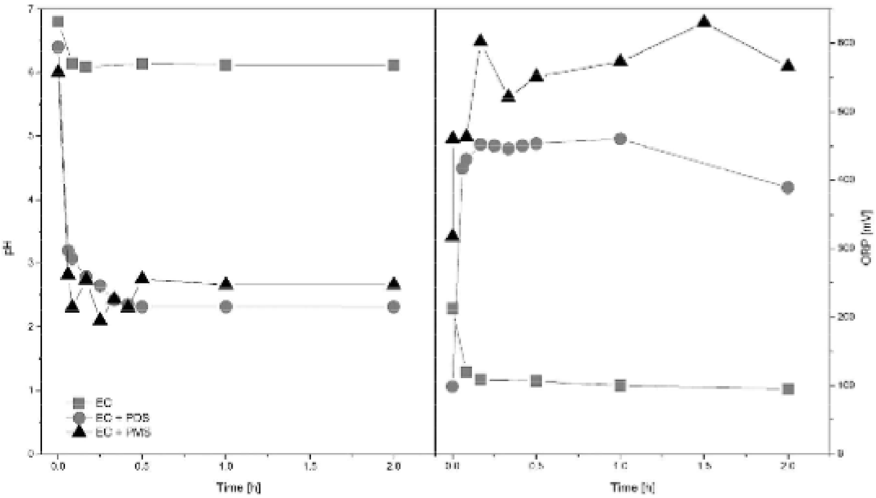

Fig. 2 Changes in pH and ORP values during the experiment. PDS concentration=2 mM, PMS concentration=6 mM, HCH=4 μM

Effect of various oxidant doses on summed HCH isomers degradation

In this study, a pseudo first-order kinetic model (Eq. 13) was applied to evaluate the kinetics of HCHs degradation.

$$\ln\left(\frac{C}{C_0}\right) = -kt \tag{13}$$

where C and C_0 are the summed HCH isomers concentrations at time (t) and $t-0$, respectively, and k is the reaction rate constant.

The effect of PDS and PMS doses on the degradation of summed HCH isomers is shown in Figs. 3, 4 and 5. As the source of radicals, the PDS quantity played an important role in the HCH degradation process with the oxidant dose being directly correlated to the extent of observed HCH degradation. In the presence of electrolysis alone, no significant HCH removal was observed during the 2 h timeframe of the experiment. As increasing PDS concentrations were added into the solution, the degradation of summed HCH isomers appeared. The reaction rate constants for 2 mM PDS concentration equals to 0.045 min^{-1} and is c.a. 15 times higher than the rate constant for the 0.5 mM dose (0.003 min^{-1}). The variation of PDS dosage from 0.5 to 4 mM resulted in an increased efficiency of HCH loss from 23 to 95 % within 2 h. Because there is no improvement in HCHs degradation between the dosages of 2 and 4 mM (k−0.045 and 0.032 min^{-1} respectively), the dosage of 2 mM was taken as being optimal.

In contrast, the degradation rate of HCH isomers by EC coupled with PMS (up to 9 mM) is negligible during the 2 h of the experiment. This result differs from the data presented by Govindan et al. (2014) in which PMS was shown to be the best electro-activated oxidant for pentachlorophenol removal from groundwater. This phenomenon could be explained by a much lesser reactivity of PMS with Fe^{2+} in comparison to other transition metals, i.e. Co^{2+} (Anipsitakis and Dionysiou 2004; Do et al. 2009). Since the effect of PMS on HCH isomer degradation was found to be negligible, no further tests with it were conducted.

Figure 4 shows the kinetics of the degradation of individual isomers by electro-activated PDS. There were no significant differences between the degradation rate constants of the individual isomers 0.026 min^{-1} (α-HCH), 0.037 min^{-1} (β-HCH), 0.040 min^{-1} (γ-HCH) and 0.049 min^{-1} (δ-HCH).

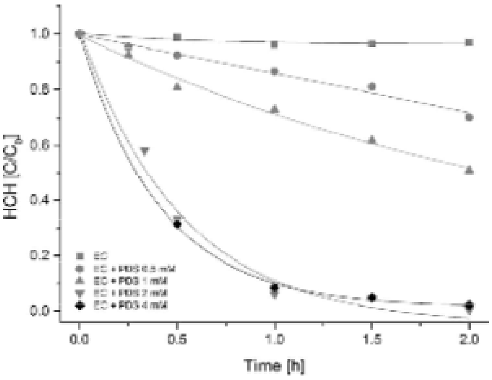

Fig. 3 Kinetics of total HCH degradation by various PDS doses coupled with electro-activation

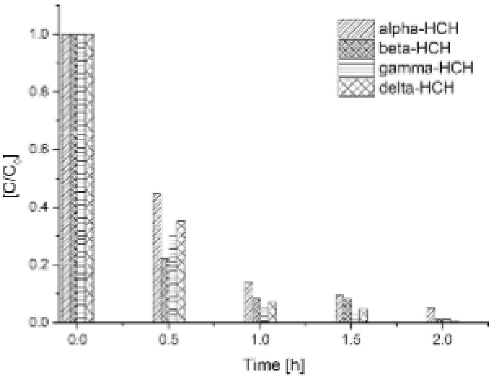

Fig. 4 Kinetics of HCH isomer degradation by electro-activated PDS

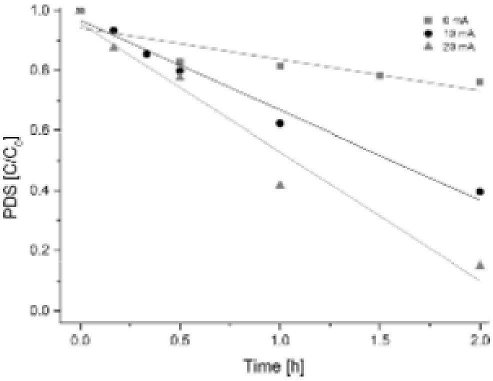

Fig. 6 Decomposition of PDS induced by various current levels

Although α-HCH is known as one of the most reactive isomers, it shows the lowest degradation rate, much smaller compare to β-HCH, considered the most persistent HCH isomer. After 30 min, the β-HCH concentration was approximately a half of the concentration of α-HCH. The final concentration of α-HCH was about 5 % of its initial concentration compared to a maximum of 1 % for the others. In general, compared to the results obtained by Usman et al. 2014, our method shows much higher and faster degradation.

Effect of variable current on HCH degradation and oxidant decomposition

Whereas Fig. 3 shows the effect of increasing PDS concentrations, Fig. 5 shows the effect of variable current with a fixed PDS dose. With increasing applied current, there is a progressive increase of the HCH degradation up to 20 mA. According to (Eq. 10), Fe^{2+} produced from corroded anode activates PDS to generate strongly oxidizing SO$_4^{\bullet-}$ and OH$^{\bullet}$ radicals. As the current level increases, the production of Fe^{2+} also increases (Yuan et al. 2014; Govindan et al. 2014) and more oxidizing species are formed from PDS. This is confirmed by measurement of the kinetics of PDS decomposition induced by various currents (Fig. 6). Specifically, the PDS decomposition is faster by higher current density.

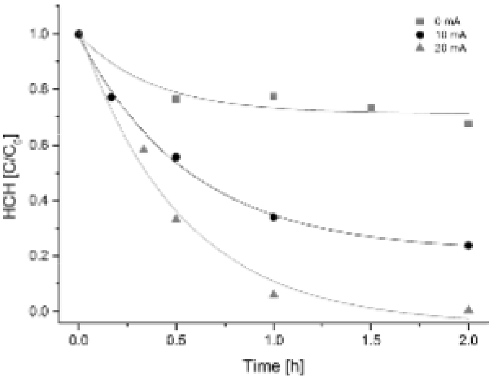

Fig. 5 Kinetics of total HCH degradation by electro-activated PDS with various currents

Based on the results of the above study, a PDS dose of 2 mM and a current of 20 mA were found to be optimal for our experimental set-up. It has been found that applying higher current can slower reaction kinetics of HCH degradation. One possible reason is that electrochemically produced Fe^{2+} can act also as a radical scavenger at its elevated concentration.

Membrane separation processes

In the system, the electron donors included not only Fe^{2+} produced from the electrochemical corrosion but also Fe^{2+} regenerated from Fe^{3+} reduction on the cathode (Eq. 11) and the electrons donated by the cathode. To estimate the contributions of these effects, experiments in a split electrolytic system (with two separated compartments) were carried out. Figure 7 depicts the results of the degradation of summed HCHs at the anode and cathode, both with 2 mM of PDS and without added PDS.

When EC tests were performed without the addition of PDS, a significant decrease in HCH concentrations was observed only in the cathodic compartment. This effect is believed to be attributable to the increase of pH from an initial value of 6.6 to 11.4 by water electrolysis. According to literature, when the level of pH rises significantly above 9, the HCH isomers are transformed into chlorobenzenes by base-catalysed hydrolysis (Ren et al. 2006; Li et al. 2011; Homolková et al. 2014). After the introduction of PDS, the degradation of HCH isomers was significant in both the anodic and cathodic compartments and at a far faster rate than

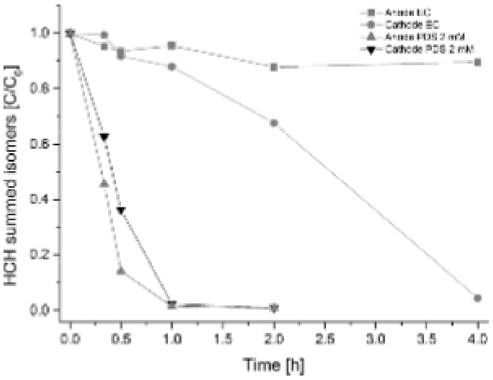

Fig. 7 Decrease of HCH and PDS in anodic and cathodic compartments

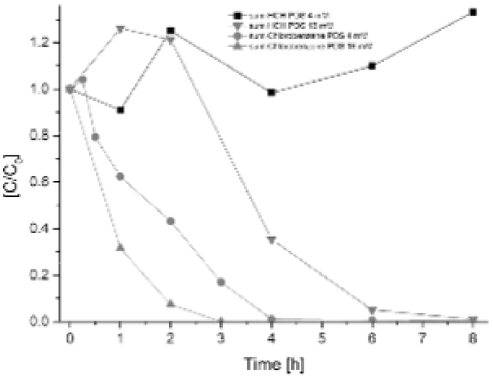

Fig. 8 Effect of electro-activated PDS on HCH and CB degradation in contaminated groundwater

was observed for EC alone. These results validate the contribution of Fe^{2+} produced from the electrochemical corrosion of iron around anode (Eq. 6) and also the impact of the cathodic reactions mentioned above. Degradation in the cathodic compartment reflects the contribution of Fe^{2+} regenerated from the reduction of Fe^{3+} on the cathode (Eq. 11) and PDS direct decomposition by electron capture (Lin et al. 2014). These two processes cannot be separated and therefore assessed their contribution.

TOC removal

The products of HCH degradation were investigated using gas chromatography. Derivatization and SPME injection of sample (PDS concentration—2 mM, contact time—30 min) in the GC/MS and its full scan analysis revealed the presence of 2,4,6–trichlorophenol as the only detectable intermediate formed during electro-activated PDS treatment of HCH. The other expected intermediates or final products such as chlorophenols, chlorobenzenes and chlorinated cyclohexanes reported in literature (Cao et al. 2008) were not observed. TOC analysis was performed in order to confirm the complete transformation of HCH to CO_2 and H_2O. In the case of EC alone, a negligible TOC change was observed during the 5 h of the experiment. However, electro-activated PDS oxidation (20 mA and 2 mM) clearly indicated that the removal efficiency of TOC via PDS oxidation was about 60 % in 1 h, which is in agreement with observed HCH removal (Fig. 3) and PDS decomposition (Fig. 6). The final TOC removal was 92 % after 5 h.

Environmental sample

Contaminated leachate from the Hajek dump site contaminated with HCH isomers was selected in order to test the efficiency of the proposed method on a real-world sample from an HCH-impacted site. Since the degree of the HCH contamination is higher than in previous spiked experiments, higher doses of PDS were applied (Fig. 8).

As shown in Fig. 8, the rapid degradation of CB can be observed by both PDS doses coupled with electro-activation. This can be explained by the high reaction rate between both sulfate and hydroxyl radicals and the aromatic double bonds located in the chlorobenzenes CB (Rickman and Mezyk 2010; Wojnárovits and Takács 2014). In contrast, the HCHs proved to be significantly more recalcitrant. In the test conducted with the lower dose of PDS (4 mM), HCH degradation was negligible even after 8 h of contact, indicating that PDS was probably preferentially consumed by CB oxidation. However, in the experiment with the higher PDS dose (16 mM), both CB and HCH were almost completely eliminated after 6 to 8 h. Even in this case, HCH degradation is slower compared to CB, probably because of the lack of aromatic double bonds. Stated in another way, the prevalence of C–Cl single bonds in the HCHs proved to be more recalcitrant to the studied remedial approach than did the aromatic C–Cl bonds of the chlorobenzenes.

With respect to the results for the individual HCH isomers, interesting trends were observed. In consensus with the literature and contrary to our findings with the spiked HCH samples, β-HCH degradation in the field sample was observed to be significantly slower to the other isomers. While the other isomer concentrations dropped (16 mM PDS) below 1 % of their initial values after 8 h, β-HCH remained at 16 %. Concerning the CBs, no significant difference was observed between individual congener removal rates.

Conclusions

This study confirmed that the Fe^{2+} ions produced and regenerated in the process of electrolysis can be a suitable reactant for the transformation of PDS into sulfate and hydroxyl radicals for the rapid degradation of HCH isomers. Surprisingly, PMS coupled with EC is ineffective for the removal of HCH isomers (which could be explained by a lesser reactivity of PMS with Fe^{2+}) and therefore was not detailed investigated. The concentration of PDS and the applied current are essential parameters influencing the rate of HCH degradation. Furthermore, it is noteworthy that HCH isomers can be almost completely degraded using an applied current of 20 mA and a PDS concentration of 2 mM. In addition, GC/MS analysis found no hazardous by-products or intermediates after electro-activated PDS treatment. The method was successfully tested on contaminated groundwater containing HCHs and CBs from a former pesticides manufacturing site in the Czech Republic. Although these results are promising, further investigations are needed to thoroughly assess the cost-effectiveness of the remedial approach for removing HCH and CB from groundwater and wastewater.

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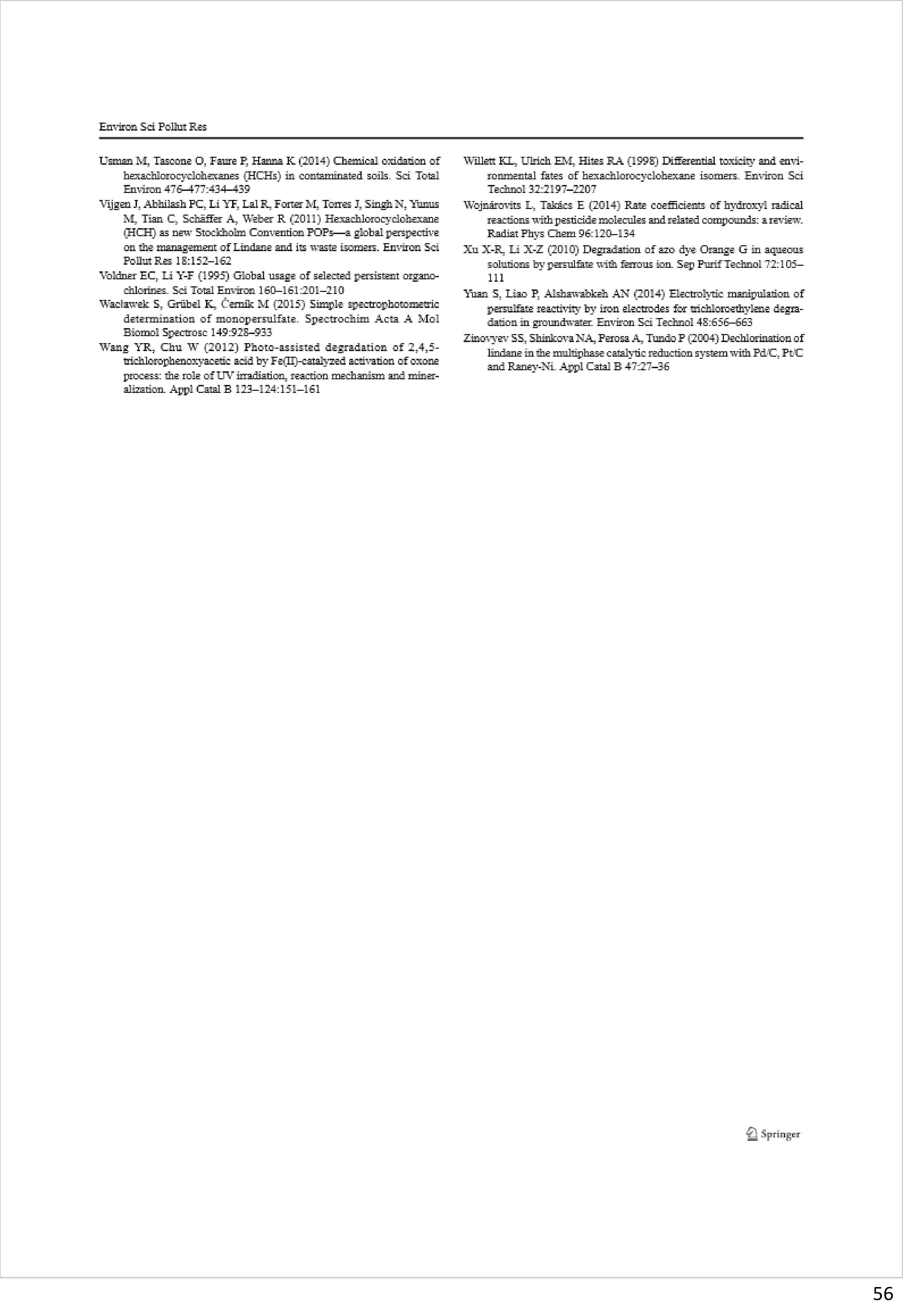

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4.2. Remediation of hexachlorocyclohexanes by cobalt-mediated activation of peroxymonosulfate

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.

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Remediation of hexachlorocyclohexanes by cobalt-mediated activation of peroxymonosulfate

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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 tends to bioaccumulate in human and animal adipose tissue. Since certain HCHs cause central nervous system, reproductive, and other endocrine damages, there is a necessity of a suitable remediation method to remove HCH from contaminated groundwater and soil. This 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 are 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 the 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 the degradation rate constants. A reaction between sulfate radicals and $Co(NO_3)_2$ could be responsible for this phenomenon, which can lead to the 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.

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Keywords: Hexachlorocyclohexanes; HCH; Chlorobenzenes; Lindane; Peroxymonosulfate; Monopersulfate; AOP; Oxone

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1. Introduction

Hexachlorocyclohexanes (HCHs) represent one of the dominant and extensively researched kinds of chlorinated pesticides that have recently been included in the list of persistent organic pollutants (POPs) [1]. Hence, it is crucial to establish cost-effective remedial technologies to treat water, soil and waste contaminated by HCH isomers.

Degradation of HCH can be achieved by various remedial techniques using both biological and chemical methods. Phillips et al. provided an overview of early studies of lindane-contaminated soil treatment in which they suggest that degradation of HCH isomers is faster under anoxic conditions and that microbial degradation is the primary route of HCH removal from soil. In addition, biodegradation of HCH isomers in an aerobic/anaerobic environment is enabled by the fungal metabolism of *Sphingomonas paucimobilis* [2]. Boyle et al. reported the dehalogenation of lindane under sulfate-reducing conditions by anaerobic bacteria from marine sediments, *Desulfovibrio africanus* and *Desulfococcus multivorans,* yielding benzene and monochlorobenzene [3]. Elliott et al. studied the degradation of lindane by zero-valent iron nanoparticles (nZVI). They identified γ-3,4,5,6-tetrachlorocyclohexene as a key reaction intermediate of lindane dechlorination. Trace levels of additional products including benzene and biphenyl were detected but only in experiments with high lindane concentrations conducted in 50% ethanol. Following nZVI treatment, up to 80% of the chlorine from the lindane molecules ended as chloride in water in comparison with only 38% of the expected chloride concentration was observed from the microscale iron experiment [4]. Singh et al. performed the degradation of lindane-spiked soil using stabilized Pd/Fe^0 bimetallic nanoparticles. Pentachlorocyclohexene, tri- and dichlorobenzene were identified as intermediate products while benzene was formed as the most stable end product. In addition, carboxymethyl cellulose (CMC) stabilized bimetallic Pd/Fe^0 nanoparticles displayed up to 7-fold greater efficiency for lindane degradation in comparison with plain nZVI [5]. Zinovyev et al. conducted dehalogenation of lindane in a multiphase catalytic reduction system with Pd/C, Pt/C, and Raney-Ni, in which at the temperature of 50°C and atmospheric pressure full conversion of lindane to 1,2,4-tricholorobenzene (1,2,4-TCB) was achieved in 5–10 min via base assisted dehydrochlorination, followed by metal-catalyzed hydrodechlorination with hydrogen to benzene [6].

Although reductive dehalogenation of HCHs was reported many times, there have been relatively few investigations on the use of chemical oxidation to degrade HCHs in the literature.

One of the oxidizing reagents which could be beneficially applicable for this purpose is peroxymonosulfate (Oxone) (Fig. 1).

Oxone is a source of a powerful oxidant peroxymonosulfate (HSO_5^-) which can be further induced to form sulfate radicals (Eq. (1)).

It is this formation of sulfate radicals that makes Oxone applicable in many industries and can be introduced for removing contaminants and environmental remediation. Sulfate radical-advanced oxidation process (SR-AOPs) can be used for simultaneous removal of refractory organic contaminants [7,8] and has a high efficiency removal of halogenated pollutants [9]. Compared to $OH^{\bullet}$, $SO_4^{-\bullet}$ has higher reduction potential at neutral pH and is more selective for direct electron transfer [10]. Anipsitakis and Dionysiou reported that Co-catalyzed activation (Co(II)) of Oxone served as a highly efficient route for achieving complete oxidation of organic pollutants. Anipsitakis et al. [8] reported that HSO_5^- has a high oxidation potential and the production of $SO_4^{-\bullet}$ and the mineralization of organic compounds can be expressed as follows (Eqs. (1) and (2)):

$$CoOH^{+} + HSO_5^{-} \rightarrow CoO^{+} + SO_4^{-\bullet} + H_2O \qquad (1)$$

$$SO_4^{-\bullet} + \text{organics} \rightarrow \langle \text{manysteps} \rangle \rightarrow CO_2 + H_2O \qquad (2)$$

The main aim of this article was to describe the effects of cobalt-mediated activation of peroxymonosulfate

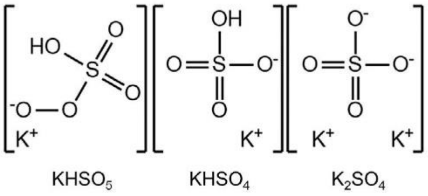

Fig. 1. Model of Oxone compounds.

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(an active Oxone compound) on HCH isomers degradation. According to our knowledge, there is no report describing the degradation of HCH isomers using Oxone.

2. Materials and methods

2.1. Reagents and solutions

All of the chemicals used in the experiments were of analytical reagent grade. Oxone (OXONE, 99.0%) and cobalt(II) nitrate hexahydrate (99.999%) were purchased from Sigma-Aldrich; sodium thiosulfate pentahydrate (used for quenching reactions) (99.0%) was purchased from Lach-Ner. A saturated stock solution of HCH was prepared by dissolving standard HCH (isomer mixture $\alpha:\beta:\gamma:\delta = 1:1:1:1$; 99.3%; Sigma-Aldrich Co.; 8.5 μM) in deionised water. Deionised water (18.2 $M\Omega\ cm^{-1}$) was prepared by an ELGA purelab flex system (ELGA, Veolia Water, Marlow, UK).

2.2. Analytical

HCH isomers were quantified by a gas chromatography (Thermo Trace 1310 combined with an MS detector TSQ 8000 triple quadrupole). Headspace solid-phase microextraction (HS-SPME) was utilized for sample preparation and injection (PDMS SPME fibers, Supelco). A TR-Pesticide chromatographic column, 30 m in length, 0.25 mm in diameter, was used for gas chromatography. For detection of the polar chlorophenols, as by-products of the oxidation reactions, sample aliquots were derivatized with acetic anhydride [11]. For calibration, standard mixtures of HCH (Neochema, Pesticides Mix 5) were employed along with deuterated γ-HCH (Ehrenstorfer GmBH) as an internal standard.

A ultraviolet-visible spectrophotometer (HACH LANGE s.r.o., Czech Republic) with matched 1-cm quartz cells was used for the determination of peroxymonosulfate (an active part of Oxone) concentration according to the method developed by Wacławek et al. [12]. At selected time points, 0.2 cm^3 samples were taken from the reactors, mixed with a 5 cm^3 potassium iodide solution, and the resulting mixtures were then measured using the spectrophotometer (characteristic wavelength of 395 nm).

2.3. Experiment setup and calculations

Experiments were performed at room temperature in 200-ml glass bottle containing 200 ml solution. Solution was stirred magnetically at the constant rate of 350 rpm.

Tests were performed with three different Oxone concentrations (6, 0.6, and 0.06 mM). In addition, after establishing the optimal Oxone concentration for HCHs decontamination, experiments with various molar ratios between Oxone (6 mM) and cobalt(II) nitrate (6, 0.6, 0.06, and 0.006 mM) were done.

Experiments were performed at least twice using freshly prepared samples. The mean of the data was calculated from these tests.

Pseudo-first-order kinetic model (Eq. (3)) was applied for the evaluation of the kinetics of HCHs degradation:

$$\ln\left(\frac{C}{C_0}\right) = -kt \tag{3}$$

where C and C_0 are the summed HCH isomers concentrations at time (t) and $t = 0$, respectively, and k is the reaction rate constant.

3. Results and discussion

3.1. Effect of various Oxone doses on HCH degradation

In the presence of $Co(NO_3)_2$ alone, no significant HCH removal was observed during the 30 min of the experiment. As increasing Oxone concentrations were added into the solution, the degradation of summed HCH isomers appeared. The variation in Oxone dosage and increased efficiency of HCH decontamination are presented in Fig. 2.

Degradation curves of summed HCH isomers can be fitted well with the pseudo-first-order kinetic

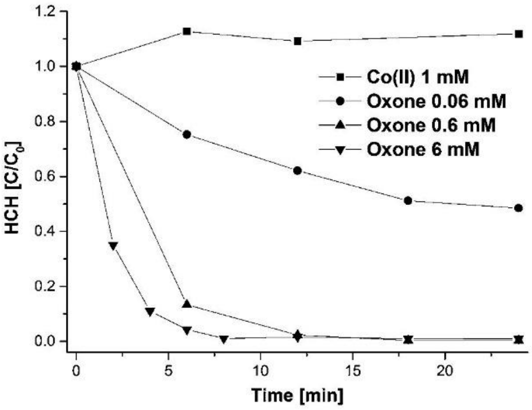

Fig. 2. Kinetics of summed HCH isomers degradation by various Oxone doses ($C_{HCHs} = 0.85$ μM, molar ratio$_{Oxone:Co(II)} = 1:0.1$).

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Table 1
Oxone dose dependence on HCHs removal

Sample name	Oxone concentration (mM)	Oxone/Co(II) molar ratio	Pseudo-first-order rate constant (min^{-1})	R^2
Oxone 0.06 mM	0.06	1:0.1	0.03	0.990
Oxone 0.6 mM	0.60	1:0.1	0.31	0.999
Oxone 6 mM	6.00	1:0.1	0.55	0.997

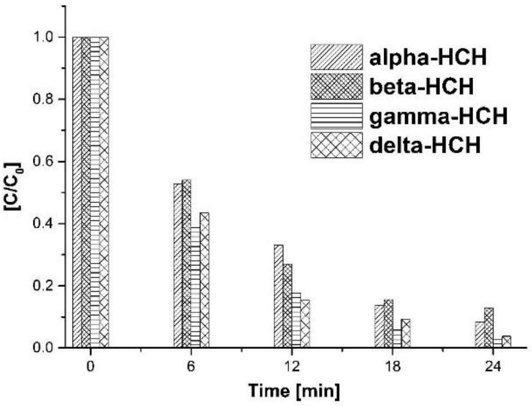

Fig. 3. Kinetics of HCH isomer degradation by Oxone activated by Co(II) (C_{HCHs} = 0.85 μM, C_{Oxone} = 6 mM, molar ratio$_{Oxone:Co(II)}$ = 1:0.01).

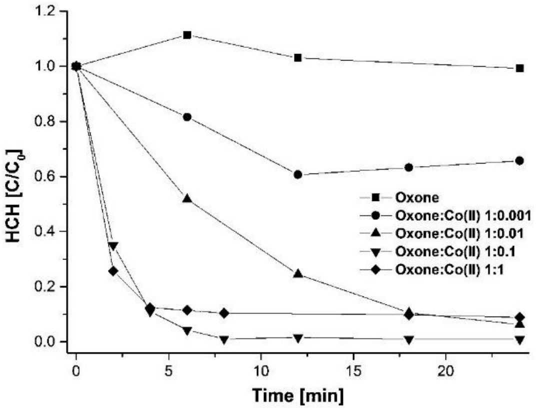

Fig. 4. Kinetics of summed HCH isomers degradation by various Oxone/Co(II) molar ratios (C_{HCHs} = 0.85 μM, C_{Oxone} = 6 mM).

model and the calculated rate constants can be found in Table 1.

Fig. 3 shows the kinetics of the degradation of individual isomers by Oxone induced by Co(II). Although differences between the degradation rate constants of the individual isomers were not significant, *α*-HCH and *β*-HCH show the lowest degradation rate, smaller in comparison with *γ*-HCH and *δ*-HCH. After 12 min, *γ*-HCH and *δ*-HCH concentrations were approximately a half of the concentrations of *α*-HCH and *β*-HCH. These results are in agreement with our previous study concerning HCH oxidation with electro-activated persulfate, which revealed *α*- and *β*-isomers as the most persistent ones from all HCH isomers [13].

3.2. Effect of various Co(II) doses on HCH degradation

In Fig. 4, the effect of various Oxone/Co(NO_3)$_2$ molar ratios with a fixed Oxone dose (6 mM) on HCHs degradation can be seen.

In the absence of Co(II) or Oxone, the HCHs degradation is negligible. But after mixing this compounds in certain concentrations, HCHs are continuously degraded to the point when Oxone and Co(II) were coupled in the molar ratio of 1:1. Degradation efficiency caused by Oxone induced by Co(II) in molar ratio of 1:0.1 is higher than in 1:1.

The kinetics of peroxymonosulfate decomposition induced by Co(II) were studied to explain this change

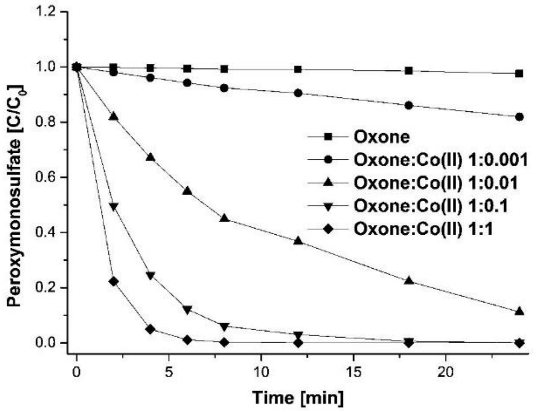

Fig. 5. PMS decomposition during the experiment with various cobalt concentrations (C_{HCHs} = 0.85 μM, C_{Oxone} = 6 mM).

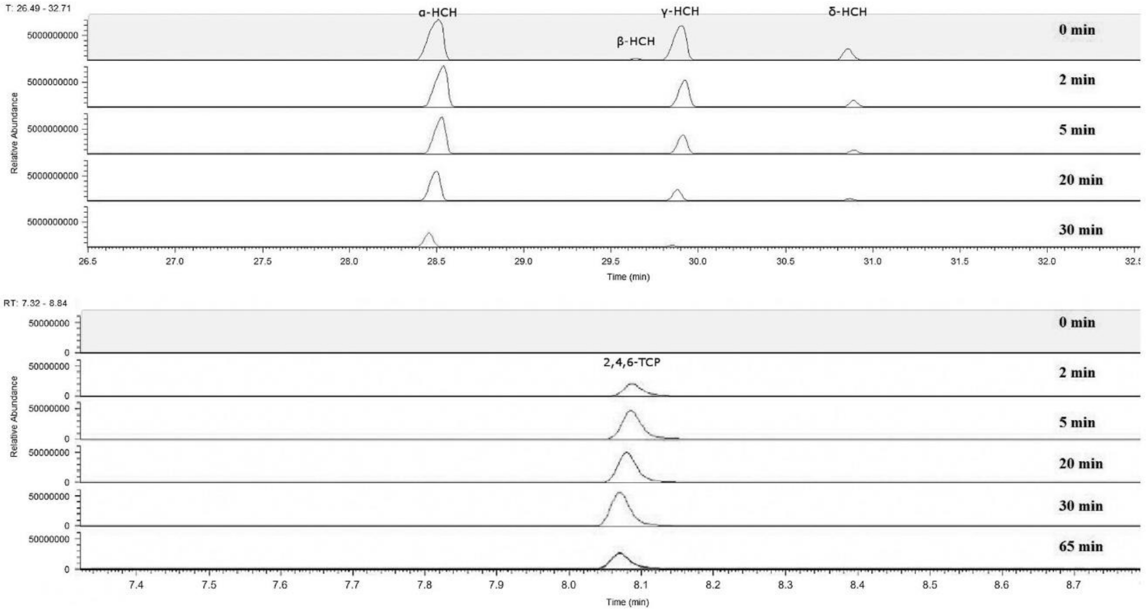

Fig. 6. Production of 2,4,6-TCP during oxidation of HCHs (C_{HCHs} ~ 40 μM, C_{Oxone} = 6 mM, molar ratio$_{\mathrm{Oxone:Co(II)}}$ = 1:0.1).

in the rate of HCH degradation (Fig. 5). Similarly to HCH removal, the rate of peroxymonosulfate decomposition is not significant without cobalt salt dose but is enabled as the Co(II) dose increases. The trend is consistent with HCH degradation up to molar ratio of Oxone:Co(II)—1:0.1. The maximal peroxymonosulfate decomposition for a Oxone:Co(II) molar ratio of 1:1 and the simultaneous decrease in HCH degradation (Fig. 4) indicate that the excess of Co(II) can also act as a sulfate radical scavenger at high concentrations as expressed by Eq. (4) [14]:

$$\mathrm{Co(II)} + \mathrm{SO}_4^{-\bullet} \rightarrow \mathrm{Co(II)} + \mathrm{SO}_4^{2-} \qquad (4)$$

3.3. Intermediates

GC/MS full scan analysis after derivatization and SPME injection revealed the formation of 2,4,6–trichlorophenol (2,4,6-TCP) during cobalt-mediated Oxone treatment of HCHs (Fig. 6).

Based on the results presented above, it can be concluded that chlorine and hydrogen atoms were abstracted from the Cl–C–H groups (constituting HCHs), which could be the cause of penta- and tetrachlorocyclohexene formation. These by-products after further oxidation could be transformed to trichloro-cyclohexadiene-ol and ultimately 2,4,6-TCP.

Experiments on rats have shown that 2,4,6-TCP have moderate acute toxicity [15].

Degradation of 2,4,6-TCP by sulfate radicals was well described in a recent study [16]. It was determined therein, that after ring cleavage, there is formation of ring-opening products (e.g. 2,4-dichloro-5-oxo-2-hexenedioic acid and 1,1,3,3-tetrachloro-2-propanone) which are further oxidized to low-molecular weight organic compounds and finally transformed to CO_2 and H_2O.

In our study, trace levels of the trichlorobenzene (TCB), tetrachlorophenol (TeCP), and pentachlorophenol (PCP) were detected as well. TeCP and PCP could be formed in the chlorination process of 2,4,6-TCP. This phenomenon was described by Anipsitakis and Dionysiou [9]. Future research has to be done to quantify these intermediates and to determine the exact degradation pathway of HCHs oxidized by $\mathrm{SO}_4^{-\bullet}$.

4. Conclusions

Applied study unveiled that cobalt-mediated Oxone activation is a suitable method to degrade HCH isomers. It is worthy to note that summed HCH isomers (0.85 μM) can be almost entirely degraded under the optimal conditions of Co(II) dose (0.6 mM) and Oxone concentration (6 mM). Furthermore, it was observed that surplus of $Co(NO_3)_2$ negatively influences the degradation of HCHs. Responsible for this phenomenon could be a reaction between sulfate

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radicals and excess of Co(II). Experiments in very concentrated HCH solution had shown 2,4,6-TCP as a major intermediate. Performed research revealed that Oxone coupled with Co(II) has a high reaction rate with HCH isomers, and future study has to be performed in order to establish exact degradation pathways for HCHs and to confirm effectiveness of proposed method in the field.

Acknowledgments

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4.3. 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.

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Simple spectrophotometric determination of monopersulfate

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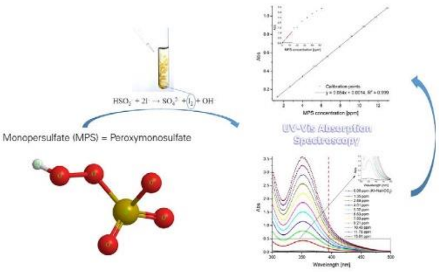
HIGHLIGHTS

- Simple, sensitive and accurate method for monopersulfate (MPS) determination was described.
- Spectrophotometric UV/VIS technique was used.
- Accuracy of the method was confirmed.
- The implementation of the present method is easy and cheap.

GRAPHICAL ABSTRACT



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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 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.

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Introduction

In recent years, advanced oxidation processes (AOPs) have stimulated a great deal of interest due to their effectiveness in the degradation and removal of various pollutants and chemicals i.e. pharmaceuticals like antibiotics [1,2].

The generation of hydroxyl radicals ($OH^{\cdot}$) or sulfate radicals ($SO_4^{\cdot-}$), can lead to the complete mineralization of organic compounds [3–5]. Specifically, the sulfate radical is one of the strongest oxidants with a redox potential estimated to be 2.6 V (2.5–3.1 V) [6], which possesses several advantages over $OH^{\cdot}$ (redox potential of 1.8–2.7 V) [7] with regards to a faster oxidation rate and greater stability in the aquatic environment [8].

Oxone, the commercial name of potassium monopersulfate ($2KHSO_5{\cdot}KHSO_4{\cdot}K_2SO_4$, its molecular model is presented in Fig. 1), is dissociated in water to a strong oxidant monopersulfate (MPS) (HSO_5^-) which can be transformed to the sulfate radical ($SO_4^{\cdot-}$) (Eq. (1)).

The generation of sulfate radicals allows Oxone to be used in many industries [1,2,9–12] as well as being introduced for the

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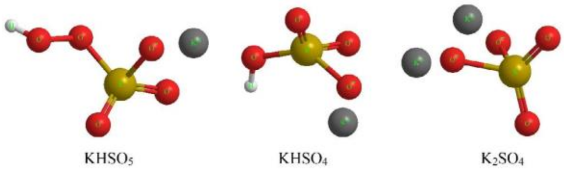

Fig. 1. Molecular model of Oxone compounds.

removal of contaminants in environmental remediation. The sulfate radical based process can be used e.g. for simultaneous removal of refractory organic contaminants and ammonia in landfill leachateble compounds [13–17] and is highly effective in the removal of halogen-substituted pollutants [15,18]. The rapid destruction of organic contaminants by $SO_4^{-\cdot}$ at a near diffusion-controlled rate ($10^9\ M^{-1}\ s^{-1}$) has attracted great interest among practitioners as a potential method for on-site hazardous waste remediation [19]. Compared to $OH^\cdot$, $SO_4^{-\cdot}$ demonstrates a higher oxidation–reduction potential at neutral pH and is more selective for electron transfer which may result in a higher selectivity to electron rich moieties compared with the hydroxyl radical [20].

Wang and Chu [21] reported that MPS can be easily activated into highly reactive radicals through homolytic cleavage of the peroxide bond of HSO_5^- by photolysis or thermolysis (Eq. (1)) [21] or into sulfate radicals via a single electron transfer (Eq. (2)) [22] by a transition metal (e.g. Co^{2+} and Fe^{2+}).

$$HSO_5^- \xrightarrow{h\nu/\Delta} SO_4^{-\cdot} + OH^\cdot \quad (1)$$

$$HSO_5^- + Fe^{2+} \rightarrow SO_4^{-\cdot} + Fe^{3+} + OH^- \quad (2)$$

Anipsitakis and Dionysiou [17] reported that Co-catalysed activation (Co(II)) of Oxone served as a highly efficient route for achieving complete oxidation of organic pollutants. Anipsitakis et al. [23] reported that HSO_5^- has a high oxidation potential and the production of $SO_4^{-\cdot}$ and the mineralization of organic compounds can be expressed as follows (Eqs. (3) and (4)) [23,24]:

$$CoOH^+ + HSO_5^- \rightarrow CoO^+ + SO_4^{\cdot} + H_2O \quad (3)$$

$$SO_4^{\cdot} + \text{organics} \rightarrow \langle \text{many steps} \rangle \rightarrow CO_2 + H_2O \quad (4)$$

Pi et al. [25] reported that Oxone can be used successfully as a source of the $SO_4^{-\cdot}$ radical to drive oxidative degradation of ofloxacin (OFX). The initial transformation of OFX proceeded through the formation of 13 intermediates, identified using UPLC–MS and MS fragmentation analysis. They concluded that Oxone has more facile transformation mechanisms compared with the reported reaction pathways of OFX degradation involving $OH^\cdot/H^+$ as the oxidant. It was confirmed that MPS can be a suitable oxidant for the decomposition of dyes and organic compounds [9–12].

Vogel [26] determined using iodometric titration that 1 g of Oxone contained 2.75 mmol of $KHSO_5$. A solution of 10.1 mg of Oxone and 10 cm^3 of water had a pH of 2.93. The solution contained 4.2 mg (2.77 mmol) of $KHSO_5$ and 5.9 mg of $[KHSO_4 + K_2SO_4]$. From the p*Ka* of $KHSO_4 = 1.92$, the equilibrium calculation showed that the above solution contained 2.2 mg (1.60 mmol) of $KHSO_4$ and 3.7 mg (2.14 mmol) of K_2SO_4. Thus, the analyzed molar ratio of $KHSO_5/KHSO_4/K_2SO_4$ in Oxone was 1.73:1.0:1.34.

Since Oxone is still not widely used due to, inter alia, the complicated procedure of monopersulfate anion (HSO_5^-) determination from triple salt, there is a need to create a rapid and simple method for its precise determination. This method may be helpful for determining the dosage, strength and speed of MPS oxidation (kinetics). This work describes a spectrophotometric determination of MPS based on modification of the iodometric titration method [27].

On the basis of iodometric titration [27] a correlation between the amount of monopersulfate and the obtained absorbance is possible. The result of the study is a procedure that allows the active part of Oxone to be determined without conducting time-consuming iodometric titration. The absorption spectra were analyzed for the concentration range from 1.35 to 13.01 ppm of monopersulfate and different pH values. In our study, we compared the spectra of cobalt and iron with what we consider to be the best wavelength for MPS determination. In addition, the impact of SO_4^{2-}, Cl^- and CO_3^{2-} anions were investigated.

Methodology

Apparatus

An ultraviolet–visible/visible spectrophotometers (Hach Lange DR 6000, Hach Lange DR 3900, Hach Lange DR 2800 and XION 500 DR Lange) with matched 1 cm quartz cells (cuvettes) were used for recording the absorption spectra. The calibration linear dependency was checked on mentioned spectrophotometers. The pH was determined using a WTW pH-meter (xylem brand) equipped with SenTix pH electrodes (TMultiLine® Multi 3430 IDS).

Reagents and solutions

All of the chemicals used in the experiments were analytical reagent grade. Oxone (99.0%, *228036 SIGMA–ALDRICH*), potassium iodide (99.5%), sulfuric acid (98.0%), sodium hydroxide (99.0%), starch (ACS grade), sodium bicarbonate (99.7%), potassium carbonate (99.0%), sodium sulfate (99.0%), acetic acid (99.0%), sodium acetate (99.0%), cobalt(II) nitrate hexahydrate (99.9%), iron(II) sulfate heptahydrate (99.0%) and sodium chloride (99.0%) were purchased from Sigma–Aldrich. Deionised water was used in all of the experiments.

The results were repeated 10 times and presented as mean values $n = 10$ and standard deviation. The estimator of the highest credibility was used for determination of the standard deviation (STATISTICA 6.0).

Characteristic of waste activated sludge sample

The applicability of the proposed method for the determination of MPS has been tested in the waste activated sludge (WAS). WAS was taken from the bioreactor of a municipal wastewater treatment facility located in south of Poland. The facility works according to the Enhanced Biological Nutrient Removal (EBNR) processes. The amount of treated wastewater is in range of $10^5\ m^3/d$. Solid retention time (SRT) is about 14 days and the concentration of mixed liquor suspended solids (MLSS) fluctuates between 4.3–4.7 g/dm^3. Characteristic of WAS sample is presented in Table 1.

MPS was measured in WAS at the same time with two methods. For the determination of MPS in sludge with the iodometric method, samples were centrifuged for 3 min at 6000 RPM, filtrated through a 0.45 μm syringe filter, withdrawn by pipet (5 cm^3), quenched in 30 cm^3 of acetate buffer (pH = 3) containing KI and titrated with 0.1 N sodium thiosulfate using starch indicator.

General recommended procedure

Potassium iodide solution

To a 1 dm^3 volumetric flask, add 100 g of potassium iodide (KI) and 5 g of sodium bicarbonate ($NaHCO_3$ – added to avoid oxygen-oxidation of iodide) and dilute to the mark.

Table 1
Characteristic of WAS sample (mean values and ± standard deviations of concentration/value in supernatant or in dry mass (d.m.) were calculated from 5 repeated measurements).

Indicator	Unit	Mean value ± standard deviation
pH	–	6.8 ± 0.4
Temperature [temp.]	°C	16.8 ± 1.7
Oxidation/reduction potential [ORP]	mV	82.4 ± 9.3
Conductivity	mS/cm	1.0 ± 0.2
Total solids [TS]	g/dm^3	5.2 ± 0.3
Volatile solids [VS]	g/dm^3	3.5 ± 0.3
Total nitrogen [TN]	% d.m.	5.0 ± 0.4
NH_4^+	mg/dm^3	15.8 ± 3.2
PO_4^{3-}	mg/dm^3	34.4 ± 2.8
Soluble chemical oxygen demand [SCOD]	$mg\ O_2/dm^3$	118 ± 12
Cd	$mg/kg_{d.m.}$	0.10 ± 0.05
Cr	$mg/kg_{d.m.}$	44.2 ± 3.1
Cu	$mg/kg_{d.m.}$	289 ± 23
Hg	$mg/kg_{d.m.}$	0.14 ± 0.07
Ni	$mg/kg_{d.m.}$	24.7 ± 5.2
Pb	$mg/kg_{d.m.}$	93.8 ± 3.5
Zn	$mg/kg_{d.m.}$	889 ± 31

Sample preparation for the determination

To a 5 cm^3 potassium iodide solution, earlier dosed to vials, add a volume of sample possessing MPS that will correspond to the concentration obtained in the vial from 1.35 to 13.01 ppm.

Absorbance reading

Mix the obtained sample with a vortex and measure absorbance at a wavelength of 395 nm.

Definition of the concentration of MPS

The concentration of MPS can be calculated based on the following Eq. (5):

$$C_{MPS} = \frac{\mathrm{Abs} - B}{A} \frac{5 + V_{added}}{V_{added}} \quad (5)$$

where: C_{MPS} – concentration of MPS in ppm; Abs – obtained absorbance of measured sample; V_{added} – volume of sample containing MPS [cm^3] added to 5 cm^3 of potassium iodide solution; A, B – slope and y-intercept of the linear calibration curve, which can be determined for particular set-up of measurement ($A = 0.084$ and $B = 0.0014$ were determined constant on four different spectrophotometers).

Results

Selection of analytical wavelength

Addition of monopersulfate to an iodide solution causes the appearance of a yellow color after the iodide transforms to iodine (Eq. (6)) which further reacts with iodide to form a complex with a strong absorption in the ultraviolet–visible range (I_3^-).

$$HSO_5^- + 2I^- \rightarrow SO_4^{2-} + I_2 + OH^- \quad (6)$$

The analysis, in terms of absorbance spectra wavelengths of 300–500 nm, was conducted for various MPS concentrations (1.35–13.01 ppm) (Fig. 2).

The linear relation between the concentration and absorbance of MPS can be observed in Fig. 2. The main absorbance forms a single peak in wavelengths from 320 to 500 (Fig. 2). Although the maximum absorbance peaks are around 350 nm, the wavelength of 395 nm was selected for the determination because of anion, pH and transition metal interference (shown below). A slight peak of potassium iodide and sodium bicarbonate solution in this region was also observed (see 0.00 ppm in Fig. 2).

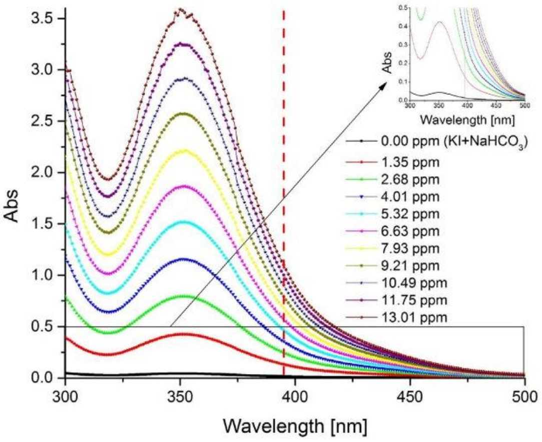

Fig. 2. Changes in absorbance with various MPS concentrations ($C_{(MPS)} = 0.00$–13.01 ppm, optical path length = 10 mm, reaction time = 15 min, $pH_{(MPS)} = 3$, temp. = 21 ± 2 °C; dashed line represents wavelength of 395 nm which was selected for the determination).

In order to select the best wavelength for measurements we took into account the spectra of the two most common initiators of MPS, which are cobalt(II) and iron(II), in quantities of 355 and 200 ppm, respectively (Fig. 3).

As we can see from the figure, neither of the metals most commonly used for sulfate radical generation in Oxone chemistry interfere with the measurements conducted at a wavelength of 395 nm. Hence, we can conclude that the absence of interference from these metals can be a suitability factor for the precise determination of monopersulfate activated by the above-mentioned transition metals.

In addition, we determined that the ratio of the absorbance of potassium iodide used for the determination of MPS to the sum of the absorbance of the two metals confirmed the high sensitivity of the investigated method at a wavelength of 395 nm (Fig. 4).

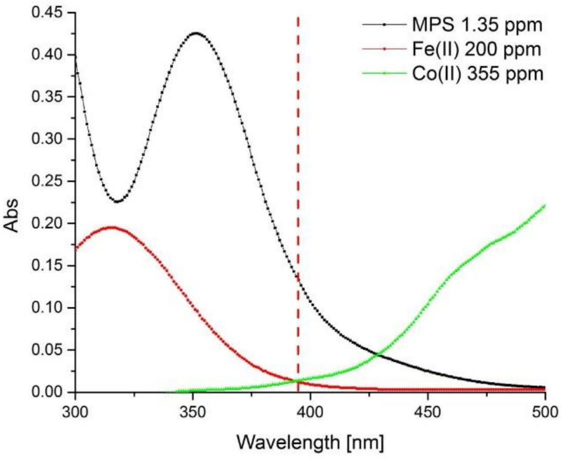

Fig. 3. Interference of Co(II) and Fe(II) in MPS determination at wavelengths 300–500 nm ($C_{(MPS)} = 1.35$ ppm, optical path length = 10 mm, reaction time = 15 min, $pH_{(MPS)} = 3$, temp. = 21 ± 2 °C; dashed line represents wavelength of 395 nm which was selected for the determination).

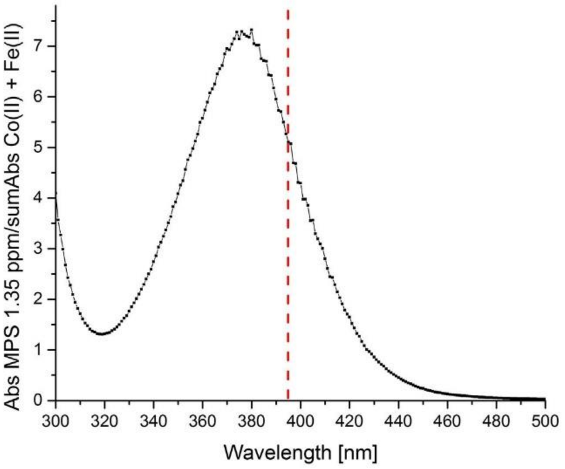

Fig. 4. Ratio of MPS absorption towards the absorption of the sum of Co(II) and Fe(II) (dashed line represents wavelength of 395 nm which was selected for the determination).

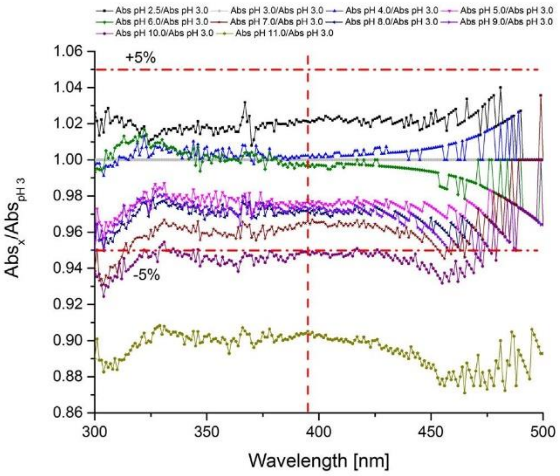

Fig. 5. Influence of pH values on absorbance, pH = 3 taken as a standard (C_{MPS} = 13.01 ppm, optical path length = 10 mm, reaction time = 15 min, temp. = 21 ± 2 °C; vertical dashed line represents wavelength of 395 nm which was selected for the determination, horizontal dashed lines determines +5% and −5% difference from absorbance obtained by MPS without pH adjustment).

Despite the fact that the peak does not have its maximum at a wavelength of 395 nm, further analysis showed that this is the optimal wavelength.

Method validation

According to the recommendations of ISO 8466:1990 [28], a calibration curve was established based on the analyses of ten Oxone concentrations (1.35–13.01 ppm). Each calibration point was replicated ten times. Linearity of tested method was determined within this range (Table 2):

The limit of detection (LOD) and the limit of quantification (LOQ) were established based on Konieczka and Namiesnik [29] and the values were 0.41 and 1.35 ppm for LOD and LOQ, respectively. Boudeville [30] proposed MPS determination method using titration with higher LOD (1.1 ppm) than presented here.

The repeatability was calculated using the relative standard deviation (RSD) from ten MPS analyses series of ten concentration levels (1.35–13.01 ppm). RSD values have no trend and are randomly distributed between 0.3% and 2.7%, with a mean value of 1.1%, which therefore is considered as RSD of MPS determination by the tested method.

For the method robustness, the reaction time is an important experimental variable. Therefore, analysis was performed after a reaction time of 1, 15 and 75 min by taking three different concentrations of MPS (1.35 ppm, 5.32 ppm and 13.01 ppm). We found values and RSD unaffected by time as shown by mean concentrations (1.33 ppm, 5.30 ppm and 12.94 ppm) and RSD values in the range of 0.6–2.9%.

Table 2
Concentration of MPS in each calibration point and standard deviation calculated from 10 repeated measurements (reaction time = 15 min, $pH_{(MPS)}$ = 3, temp. = 21 ± 2 °C).

Sample No.	Concentration of MPS [ppm]
1	1.35 ± 0.03
2	2.68 ± 0.01
3	4.01 ± 0.01
4	5.32 ± 0.13
5	6.63 ± 0.07
6	7.93 ± 0.02
7	9.21 ± 0.05
8	10.49 ± 0.11
9	11.75 ± 0.09
10	13.01 ± 0.06

Method ruggedness was expressed as the RSD of the same procedure applied by three different analysts at similar environmental conditions as well as using four different spectrophotometers. The % RSD values were found to be less than 3%. The low % RSD values indicated that the method has a good accuracy and specificity.

Influence of pH

Due to the high oxidizing properties of MPS and the possibility of its use in different environments the possible changes and impact of pH must also be taken into account in determining its concentration. Therefore, analysis was performed on the influence of pH values (adjusted by sulfuric acid and sodium hydroxide) on absorbance at selected wavelengths (Fig. 5).

Changes in pH values from 2.5 to 10 caused no significant color or spectral change under identical conditions at the wavelength proposed for the MPS determination (±5%). However, high pH (around 11) is not suitable for determining monopersulfate. Problems with the determination of MPS in pH > 10 can be explained by adversely affected stability of MPS in higher pH range (according to Yan [31] in particular above pH 9).

Influence of anions

We investigated the influence of several anions on MPS determination. This was evaluated through testing the response of the assay to various environmentally relevant anions including CO_3^{2-}, SO_4^{2-}, Cl^- at a concentration of 500 ppm, which is often an upper limit of EPA water quality standards (Fig. 6) [32].

The absorption spectra of a MPS concentration of 13.01 ppm in a KI/NaHCO$_3$ solution before and after the addition of CO_3^{2-}, SO_4^{2-}, and Cl^- were almost unaffected. From this we can conclude that the proposed method is insensitive to the addition of anions at the described doses.

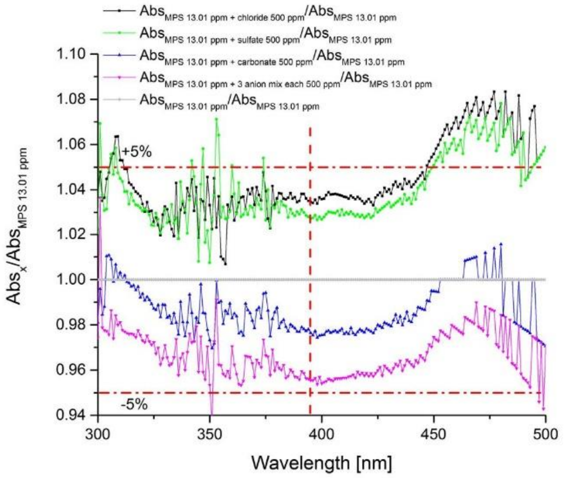

Fig. 6. Impact of anions – carbonate (CO_3^{2-}), sulfate (SO_4^{2-}), chloride (Cl^-) and a mixture of them on absorption ($C_{(MPS)}$ = 13.01 ppm, optical path length = 10 mm, reaction time = 15 min, $pH_{(MPS)}$ = 3, temp. = 21 ± 2 °C; vertical dashed line represents wavelength of 395 nm which was selected for the determination, horizontal dashed lines determines +5% and −5% difference from absorbance obtained by MPS alone).

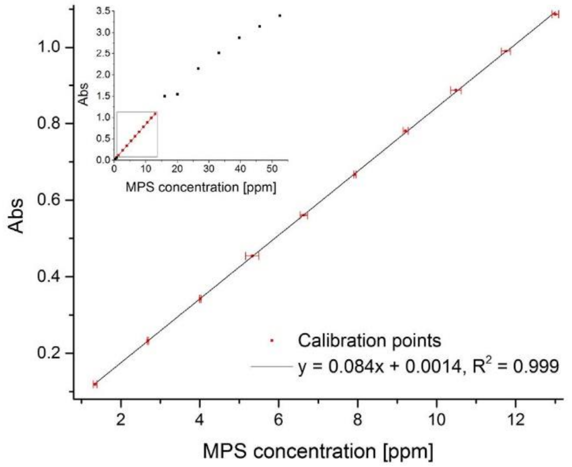

Fig. 7. Relationship of calibration at a wavelength of 395 nm. Error bars represent 95% confidence intervals (n = 10) (reaction time = 15 min, optical path length = 10 mm, $pH_{(MPS)}$ = 3, temp. = 21 ± 2 °C).

Calibration

In our research work we made a calibration curve for MPS concentrations from 1.35 to 13.01 ppm (Fig. 7).

Fig. 7 suggests a linear relationship ($y = 0.084x + 0.0014$, $R^2 = 0.999$) between the absorbance intensity of the iodine and the concentration of MPS in the range from 1.35 to 13.01 ppm at an absorption wavelength of 395 nm.

Estimation of MPS in real samples

The applicability of the proposed method for the determination of MPS has been successfully tested in the waste activated sludge (WAS).

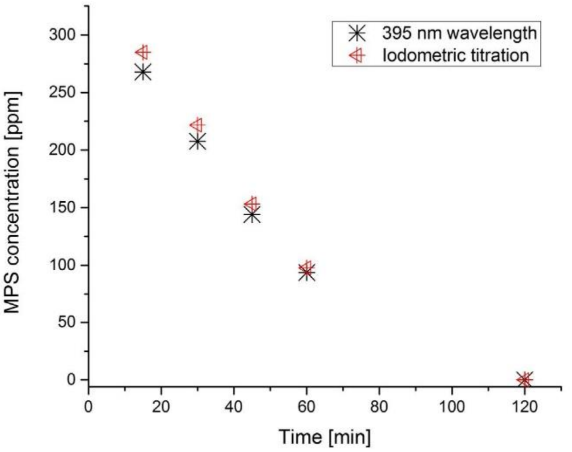

Fig. 8. Comparison of the investigated method with the iodometric titration method performed in waste activated sludge supernatant ($C_{(MPS)}$ = 300 ppm, temp. = 16.8 ± 1.7 °C).

The proposed method was validated by the iodometric titration method. Also, analysis of MPS in the liquid of WAS samples confirmed a good correlation with measurements by the titration method (Fig. 8).

Instability of MPS in sludge matrix can be attributed to the direct oxidation of various organic components present in the waste activated sludge. In addition WAS contains large amounts of transition metals that can rapidly react with MPS. Furthermore, in a recent study conducted by Yang et al. [33], it was suggested that MPS can be activated by various anions (e.g. PO_4^{3-}) which can contribute to MPS decomposition.

Conclusions

The developed spectrophotometric method of MPS determination is a sensitive, selective, and rapid method which is also superior to the previously reported iodometric methods in terms of its simplicity and rapidity. We have found that the wavelength of 395 nm is the best for the determination of MPS in the presence of Co^{2+} and Fe^{2+}. In addition, no interference by pH (in range 2.5–10) or anions (CO_3^{2-}, SO_4^{2-}, Cl^-) was observed at this wavelength. The limit of detection and the limit of quantification were established at 0.41 and 1.35 ppm, respectively. Furthermore, all of the analytical reagents are inexpensive and available in any analytical laboratory. It is a practical and valuable method for routine application in quality control laboratories for the analysis of MPS. It has also been tested on waste activated sludge and the results were comparable with the standard iodometric titration method.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2015.05.029.

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4.4. 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.

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

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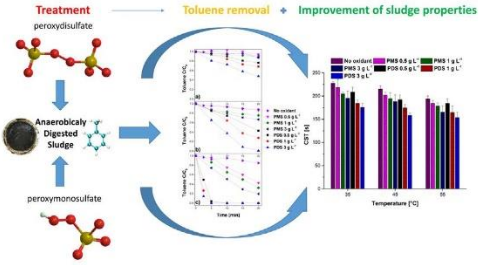
HIGHLIGHTS

- Heat activated persulfates can oxidize toluene in anaerobically digested sludge.
- Dewaterability of digested sludge greatly improved after persulfates treatment.
- NH_4^+ and PO_4^{3-} in separated supernatant were recovered in the form of struvite.

GRAPHICAL ABSTRACT



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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.

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1. Introduction

One of the major and essential part of many modern wastewater treatment plants (WWTP) is anaerobic digestion (AD) process. Four phases: hydrolysis, acidogenesis, acetogenesis and methanogenesis cause reduction of the amount of sludge for disposal and convert biodegradable substances of the sludge to biogas [1–3]. Therefore, anaerobic digestion is economical, energy efficient and competitive [4–6].

Anaerobic digestion process can be conducted in two conventional operational temperature levels: mesophilic process (MAD, optimally around 30–38 °C) and thermophilic process (TAD, which takes place optimally around 49–57 °C) [7–9].

Currently, most anaerobic digesters are operated under MAD conditions, in the temperature range of 25–40 °C. MAD is well understood and requires less heat to sustain, furthermore, the process is very robust and stable – due to the large diversity of bacteria involved. The main product is biogas, where the predominant component is methane (60–70% of volume, [CH_4]). The nutrient-rich digestate, that is also produced can be used as a fertilizer [10].

Even with its innumerable advantages, the main end-product of AD – anaerobically digested sludge (ADS) commonly possesses undesirable characteristics such as high dry mass content and viscosity, which causes a chain of complications in post-treatment processing and disposal [11,12].

Mrowiec et al. [13] found that toluene is produced in the supernatant as other product of AD in relatively large concentrations in many cases. This phenomenon was also recently observed in Liberec's Municipal WWTP.

Toluene is a typical volatile organic compound (VOC) in that it is emitted in high levels and difficult to abate [14]. VOCs, as the chief atmospheric pollution precursors, are destructive to humans and the environment [15].

Digested sludge requires proper treatment including dewatering and removal of hazardous substances in order to be suitable for further processing i.e. landfarming, incineration etc. Both of these goals can be achieved by chemical oxidation with reagents such as persulfate [16,17].

Long et al. [17] focused on toluene oxidation, but we are not aware of another study that evaluated of the efficiency of peroxydisulfate (PDS) and peroxymonosulfate (PMS) oxidation of toluene in the ADS.

In the process of PDS and PMS activation, sulfate and hydroxyl radicals can be generated. This occurs by persulfate activation, via cleavage of the oxygen bond under elevated temperature, alkaline conditions, UV radiation or single electron transfer with transition metals [17–19].

Yang et al. [18] performed oxidation of azo dye Acid Orange 7 using peroxydisulfate and peroxymonosulfate activated by heat, UV and anions and concluded that temperatures above 50 °C, can efficiently induce PDS. Zhao et al. [20] determined that a temperature of 40 °C effectively activated PDS to degrade 1,4-dioxane in water.

In addition to hazardous organics removal, persulfates can improve the dewatering and sedimentation properties of sludge [16]. Sludge dewatering is the separation of a liquid and solid phase to, ideally, achieve the least possible residual moisture in the solid phase and the lowest possible solid particle residues are required in the separated liquid phase ("the centrate").

Post-digestion liquors contain a higher concentration of organic compounds and nutrients, which may negatively impact wastewater treatment processes (unfavorable C/N ratio), if directed back to the biological treatment facility [21,22]. Moreover, individual unit processes (e.g. coagulation, ammonia desorption, advanced oxidation, biological methods, immobilized bioprocesses, membrane techniques) do not ensure complete contaminant removal, mostly due to a high of ammonium–nitrogen and organic matter content [23–27].

Different treatment technologies are commonly applied in WWTP in order to abolish phosphates and ammonium nitrogen [28]. Most nutrient elimination processes create wastes, which consequently desire landfilling or incineration [29]. Another alternative, is the recovery of nitrogen and phosphates as a by-product, by means of crystallization processes where minerals with use in agriculture as fertilizer, can be produced, specifically struvite ($NH_4MgPO_4 \cdot 6H_2O$). Struvite is an excellent slow-release fertiliser that does not "burn" roots when over applied, an usual difficulty with conventional ammonium-phosphate fertilisers [30–32].

The novel concept described in this paper is based on the process of toluene oxidation and dewaterability improvement of anaerobically digested sludge by thermally activated peroxydisulfate and peroxymonosulfate. In the recent literature, there can be found a lot of information about the use of this substances for oxidation of waste activated sludge. However, to our knowledge, this represents the first published research on their impact on digested sludge. The activation temperatures used were similar to those required in meso- and thermophilic digestions. Our study was conducted for chemical treatment of ADS by PDS and PMS in doses of 0.5, 1 and 3 $g\ L^{-1}$ activated at temperatures of 35, 45 and 55 °C. The efficiency of this method was evaluated in terms of toluene degradation and dewaterability improvement – expressed as changes in capillary suction time (CST). In addition to the successful separation of supernatant, which contained high concentrations of ammonium nitrogen and phosphates, we attempted to remove these compounds in the form of struvite.

2. Experimental methodology

2.1. Materials

All of the chemicals used in the experiments were analytical reagent grade. PMS (OXONE, 99.0%), NaOH (sodium hydroxide, ACS reagent, ⩾97.0%), tert-butyl alcohol (⩾99.0%), ethanol (⩾99.5%) and sodium bicarbonate (99.7%) were purchased from Sigma–Aldrich. Sodium thiosulfate pentahydrate (99.0%) and PDS (sodium persulfate, 99.0%) were purchased from Lach-Ner. Deionised water (18.2 $M\Omega\ cm^{-1}$) was prepared by an ELGA purelab flex system (ELGA, Veolia Water, Marlow, UK).

For struvite precipitation it was necessary to provide magnesium and phosphate ions as concentrations were lower in the sludge than required for struvite precipitation according to the stoichiometric ratio of the reagents. Magnesium and phosphate ions were supplemented by the addition of magnesium oxide (Magnesium Oxide for Agricultural Applications, AniMag BLX 30 by Martin Marietta, USA) and sodium phosphate (96%, Sigma–Aldrich), respectively.

Anaerobically digested sludge was taken from the Liberec Waste Water Treatment Plant, the largest WWTP in both the Liberecky and the Ústecky regions of the Czech Republic. The treatment plant was designed for nutrient removal. For purposes of phosphate and nitrogen compounds removal, anaerobic, anoxic and aerobic sectors are maintained. The plant was designed for a flow of 103,882 $m^3\ d^{-1}$. At present, the amount of treated wastewater is approximately 54,806 $m^3\ d^{-1}$ (Table 1).

2.2. Analytical methods

An ultraviolet–visible spectrophotometer HACH DR 6000 UV/VIS (HACH LANGE s.r.o., Czech Republic) was used with a 1 cm quartz cuvette for recording the absorption spectra. The pH and

Table 1
Characteristics of anaerobic digested sludge (ADS) (mean values ± standard deviations of concentration/value in supernatant calculated from 3 repeated measurements).

Indicator	Unit	Mean value ± standard deviation
pH	–	7.6 ± 0.3
Temperature	°C	25 ± 2
Total Solids [TS]	$g\ L^{-1}$	29.3 ± 1.8
CST	s	230 ± 15
NH_4^+	$mg\ L^{-1}$	1449.6 ± 2.8
PO_4^{3-}	$mg\ L^{-1}$	358 ± 36
Mg^{2+}	$mg\ L^{-1}$	18.8 ± 2.3
Soluble chemical oxygen demand [SCOD]	$mg\ L^{-1}$	1786 ± 270
Toluene	$\mu g\ L^{-1}$	300 ± 20

oxidation–reduction potential (ORP) was determined by a WTW pH-meter equipped with SenTix pH electrodes (TMultiLine® Multi 3430 IDS, Germany). ORP values are presented as values against a saturated calomel electrode (SCE) and were not corrected to the standard hydrogen electrode (SHE). Soluble chemical oxygen demand (SCOD) was determined following the standard methods for examination of water and wastewater, procedure 5220D [33]. To analyse the soluble phase, the particulate sludge matter was removed by centrifugation (10 min at 5000 rpm) and the resulting centrate was filtrated through 0.45 μm pore size membrane filters. The content of Total Solids (TS) (procedure 2540 solids) and the concentration of ammonium nitrogen and phosphates was determined according to Rice et al. [33] (procedures 4500-NH_3 and 4500-P, respectively).

Concentration of magnesium ions was determined by atomic absorption analysis AAnalyst 100 (Perkin Elmer, USA). Toluene and intermediates were searched for in the full scan mode of a GC/ion trap MS instrument (Varian Saturn 3800, USA), equipped with a DB-624 column (60 m in length, 0.25 mm in diameter). For toluene quantification, 7 ml samples were taken from the reactor and mixed with sodium thiosulfate to quench the oxidant and stop the reaction. For the determination of capillary suction time (CST) device Type 304 M CST (Triton Electronics Limited, England) equipped with a Whatman™ 17 Chr Chromatography Paper as the base was used. For the microscope struvite analysis, a microscope coupled with a camera (Nikon Alphaphot-2YS – with camera MOTICAM PRO-252A) and a scanning electron microscope (SEM) Vega XMU (TESCAN s.r.o., Czech Republic) was used. Struvite crystal size measurements were determined automatically using Advanced 3.2. software series (Motic Images, Germany).

2.3. Experimental set-up

In the experiments sodium peroxydisulfate (PDS, $S_2O_8^{2-}$) and Oxone (PMS, $KHSO_5$, sodium peroxymonosulfate) in doses of 0.5, 1 and 3 $g\ L^{-1}$, activated at temperatures of 35, 45 and 55 °C were used. Reactors were mixed continuously using standard hot plate stirrers.

Struvite precipitation was performed in a 5 L tank, in batch mode at a constant temperature of 20 °C and pH of 9.5 [34–36]. The pH value of post-digestion liquors was adjusted using 1 M NaOH. Retention time of post-treated liquors in a crystallizer was as high as 24 h. The process was conducted using a stoichiometric ratio of Mg^{2+}, NH_4^+ and PO_4^{3-} as well as 20% excess amounts of magnesium and phosphate ions ($Mg^{2+}:NH_4^+:PO_4^{3-} = 1.2:1:1.2$). Due to the high ammonium concentration in the supernatant, it was

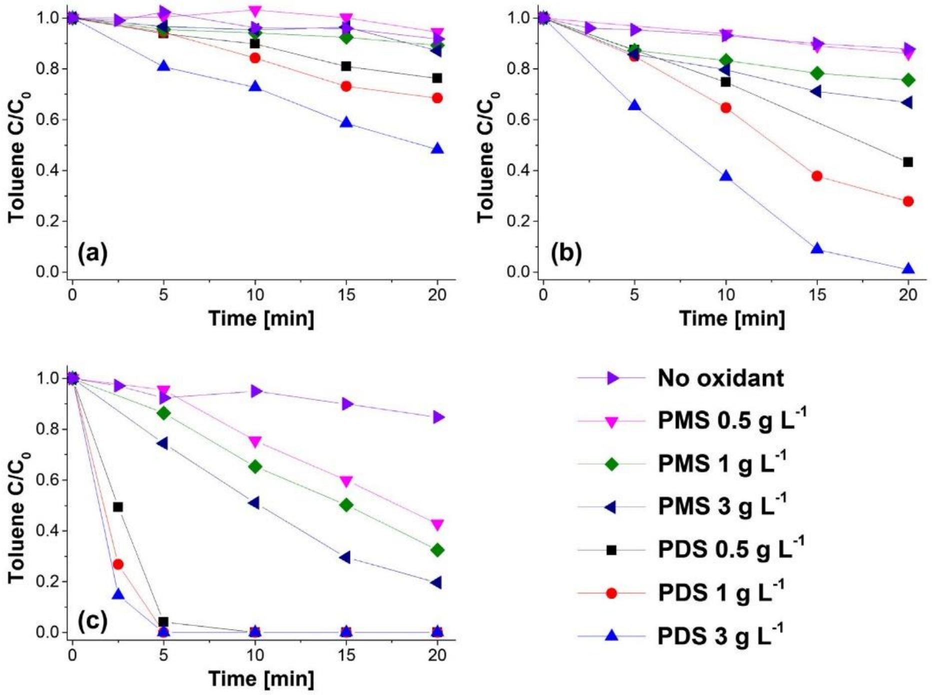

Fig. 1. Toluene removal using activation temperatures of (a) 35 °C, (b) 45 °C and (c) 55 °C.

necessary to supplement magnesium (in the form of MgO) and phosphate (in the form of Na_3PO_4).

3. Results and discussion

3.1. Impact of oxidants and temperature on toluene removal

Elevated temperature coupled with PDS significantly altered the concentrations of toluene and other parameters, during the tests. Heat causes the cleavage of the weakest O—O bond in persulfates, thereby activating them in solution generating strongly oxidizing free radicals [37], which subsequently degrade toluene.

In our previous studies conducted on waste activated sludge, it was also confirmed that these free radicals can contribute to the change in sludge dewaterability [16].

Fig. 1 shows rapid degradation of toluene which can be attributed to the high reaction rate between the radicals and the aromatic double bonds located in the toluene [38,39].

It is clear that raising the temperature of sludge did not influence the concentration of toluene in an airtight reactor. Furthermore, oxidants alone did not cause significant degradation of toluene in the presented timeframe (data not shown), therefore possible reaction of persulfates with transition metals [40,41] present in sludge was considered negligible.

The PDS and PMS concentrations were positively correlated with the oxidation rate, and as the persulfates concentration increased from 0.5 g L^{-1} to 3 g L^{-1}, the reaction rates increased proportionally.

Activation at 35 °C did not cause observable degradation of toluene by PMS, these results are in agreement with the data presented by Yang et al. [18], indicating that PMS requires more heat energy for activation. In contrast, the degradation kinetics of toluene oxidized by PDS are faster with increasing dose and the highest dose of PDS activated at the temperature of 35 °C abated almost half of the initial toluene concentration.

As the temperature increased to 45 and 55 °C, complete oxidation of toluene by PDS was observed after 20 and 5 min, respectively, for the highest dose of PDS. In contrast, toluene degradation kinetics by PMS were slower. At temperatures from 35 to 55 °C, increased efficiency of toluene decontamination from 13% to 33% within 20 min, for the highest dose was observed.

In order to determine the main radical species in the peroxydisulfate and peroxymonosulfate system, scavenging tests with the use of tert-butyl alcohol (TBA) and ethanol (EtOH) were carried out (Fig. S3) (Detailed explanation of the process can be found in the supporting information section of the article and [42]). TBA ($k_{\text{hydroxyl radical}} = 6.0 \times 10^8\ M^{-1}\ s^{-1}$, $k_{\text{sulfate radical}} = 4.0 \times 10^5\ M^{-1}\ s^{-1}$) and ethanol ($k_{\text{hydroxyl radical}} = 1.2 \times 10^9\ M^{-1}\ s^{-1}$, $k_{\text{sulfate radical}} = 1.6 \times 10^7\ M^{-1}\ s^{-1}$) were used to evaluate the relative contribution of $SO_4^{\bullet-}$ and $OH^{\bullet}$ because of their different reaction rates [42,43].

In this tests, degradation of toluene by PDS (3 g L^{-1} and the activation temperature of 55 °C) was not significantly affected by the presence of TBA but after addition of ethanol the oxidation rate of the substrate decreased, indicating that the major species formed from PDS and responsible for the transformation of toluene are the sulfate radicals. On the other hand, the effect of TBA and EtOH on the abatement of toluene with PMS (3 g L^{-1} and the activation temperature of 55 °C) suggests that sulfate radicals as well as hydroxyl radicals are being generated. Based on this results, it can be concluded that a faster depletion of toluene by PDS, may be also linked to higher reaction rates of (generated in the PDS system in a greater quantity) sulfate radicals with aromatic ring of toluene [17].

3.2. Impact of oxidants and temperature on dewaterability

Sludge is generally conditioned before thickening and dewatering, in order to increase the volume of recovered water. Sludge dewatering is defined as "the removal of enough of the liquid portion of the sludge so that it behaves as a solid" [44]. Digested sludges are often difficult to dewater by mechanical processes alone. The difficulty is two-fold: the extremely slow rate at which water can be removed from digested sludge and the low total proportion of water to solid sludge that can be removed. Use of the proper sludge conditioning process is critical for the sludge management due to a high unit cost and the large volume of conditioning agents required [45].

The capillary suction time (CST) test is a commonly used as a tool to determine the dewaterability/filterability of the sludge [46–48]. This is a type of static filtration test for water-base drilling fluid that determines the filtration rate (time for free water to pass between two electrodes) using filter paper (chromatography paper) as the medium [49].

In Fig. 2 the relationship between oxidant dose, activation temperature and CST is shown.

A positive correlation between the decrease in CST and increase in the temperature, can be observed in the data presented in Fig. 2. CST decreased from 230 s at temperatures of 35 °C to 215 and 194 s at temperatures of 45 and 55 °C, respectively. Addition of oxidants, caused further decreases in the CST value, which confirms destructive impact of the free radicals formed by these oxidants.

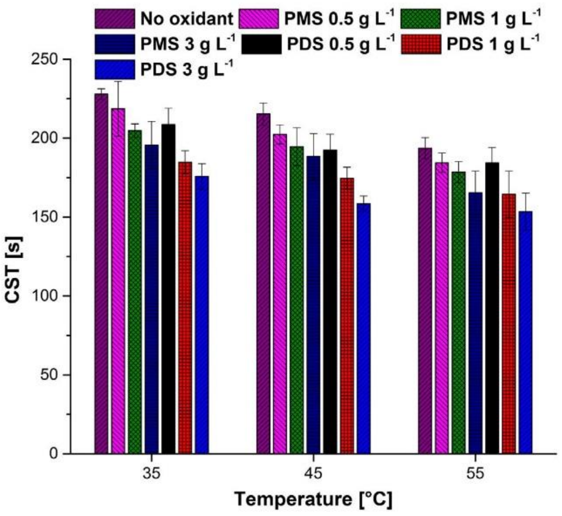

Fig. 2. Impact of various oxidant doses and activation temperatures on CST ($n = 3$).

Table 2
Characteristics of post-treated liquor* and liquor after struvite precipitation (mean values ± standard deviation of concentration in supernatant calculated from 3 repeated measurements).

	SCOD [mg L^{-1}]	N-NH_4^+ [mg L^{-1}]	PO_4^{3-} [mg L^{-1}]
	Post-treated liquor*		
	1792 ± 191	1617 ± 12	392.4 ± 8.2
Molar ratio Mg^{2+}:NH_4^+:PO_4^{3-}	Post-treated liquor after precipitation of struvite		
1.0:1.0:1.0	1123 ± 59	120.7 ± 8.4	74.8 ± 5.8
1.2:1.0:1.2	978 ± 75	64.8 ± 4.2	52.4 ± 4.6

* Post-treated liquor was taken after PDS treatment ($C_{PDS} = 3\ g\ L^{-1}$, temp. = 55 °C).

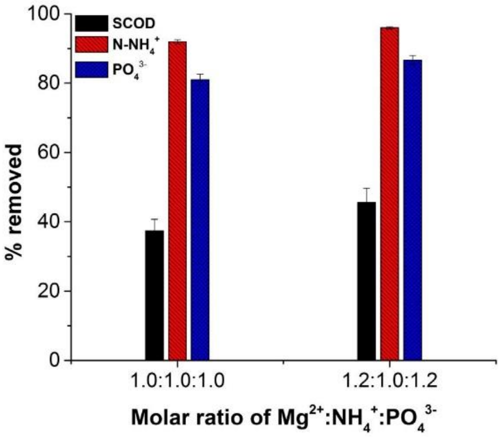

Fig. 3. Influence of struvite precipitation conditions on the SCOD, N-NH_4^+ and PO_4^{3-} removal efficiency ($n = 3$).

Compared to PMS, PDS was superior at improving sludge dewaterability, which is in agreement with observed toluene removal by this compound (Fig. 2).

With the highest dose of reagents and the highest activation temperature, CST decreased significantly in comparison to increased temperature alone by 20.8% and 14.6% for PDS and PMS, respectively.

Although the use of persulfates to enhance the dewaterability of sludges was reported extensively, most of these reports concern dewaterability of waste activated sludge which possesses different properties than investigated herein digested sludge. Nevertheless, Zhen et al. [50] observed that Fe(II)-activated persulfate oxidation has a positive effect on enhancing sludge dewaterability with 88.8% CST reduction within 1 min. In addition, similar results were obtained by Shi et al. [51] in which 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 peroxydisulfate.

Zhen et al. [52] in their study investigated the same process but under elevated temperatures and demonstrated good efficiency in enhancing the dewaterability of sludge.

One of the reasons why persulfates were used herein on the digested sludge, is possible inhibitory effect of persulfates on the anaerobic digestion as was presented in [53].

3.3. Ammonium nitrogen, phosphorus and SCOD removal by struvite precipitation

In addition to better separation of supernatant rich in ammonium nitrogen, there was observed a slight increase in concentration of NH_4^+ and PO_4^{3-} in the liquid phase of ADS after the thermally activated PDS treatment (Fig. S4 and Table 2). Hence, the released substances can be recovered in the form of struvite with simultaneous removal of them from the supernatant. In Table 2, characteristics of post-treated supernatant and supernatant after struvite precipitation was shown.

Struvite precipitation is an effective treatment method for the co-digestion of effluents. However, in order to achieve sufficient liquid quality to allow direct release to a natural receiver, it was necessary to apply an increased molar ratio of reagents (Mg^{2+}:NH_4^+:PO_4^{3-} = 1.2:1:1.2) during struvite precipitation.

As indicated in the methodology, magnesium and phosphates were supplemented into the supernatant, taking into account that ammonium nitrogen can precipitate in the form of struvite.

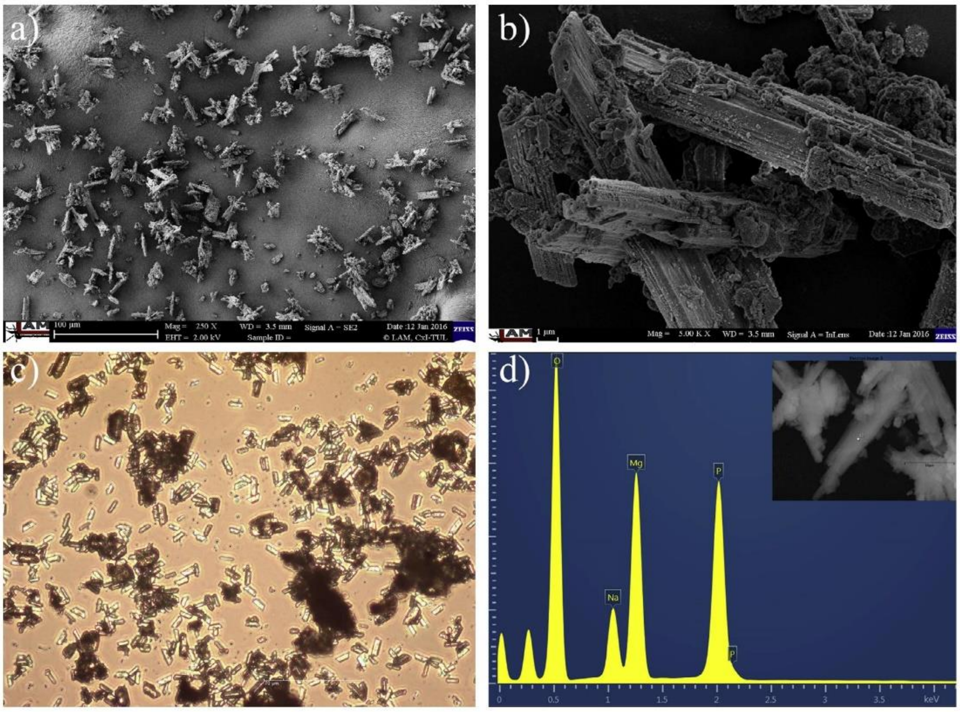

Fig. 4. (a)–(c) Struvite crystals under various magnification; (d) EDX analysis of struvite crystal (molar ratio of Mg^{2+}:NH_4^+:PO_4^{3-} = 1.0:1.0:1.0; post-treated liquor for struvite precipitation was taken after PDS treatment (C_{PDS} = 3 g L^{-1}, temp. = 55 °C)).

After addition of reagents and a reaction time of 24 h, concentrations of ammonium nitrogen and phosphates decreased using a reagent molar ratio of 1:1:1 by 92.6% and 81%, respectively and for the reagent molar ratio of 1.2:1:1.2 by 96% and 86.7%, respectively (Table 2 and Fig. 3). Similar results were observed by Kuglarz et al. [54].

In addition to ammonia and phosphate removal, SCOD decreases were also observed (Table 2). The effect was ascribed to the coagulative properties of MgO. It is hypothesized that a portion of organic substances were adsorbed by $Mg(OH)_2$ and co-precipitated with struvite [55,56].

The precipitated struvite crystals are demonstrated in Fig. 4a–c. In addition, SEM/EDX analysis of struvite is presented in Fig. 4d. Furthermore, the impact of precipitation conditions, including the initial NH_4^+ concentration and reagent dose during precipitation, on the structure of struvite crystals is demonstrated in Fig. S5.

4. Conclusions

Removal of toluene and improvements in dewaterability of ADS by chemical treatment using peroxydisulfate and peroxymonosulfate were investigated. We conclude that toluene can be efficiently removed from ADS by optimization of key parameters in the persulfate oxidation processes. Temperatures of 45 and 55 °C, were capable of complete oxidation of toluene by PDS after 20 and 5 min, respectively, when a sufficient dose of PDS was used. PMS at the highest dose, of $3\ g\ L^{-1}$ and activated at temperatures of 35–55 °C, for 20 min resulted in an increased efficiency of toluene decontamination from 13% to 33%.

In addition, sludge dewaterability improved significantly at the highest doses of reagents ($3\ g\ L^{-1}$) at the highest activation temperature (55 °C), in comparison to the temperature treatment alone increased dewaterability by 20.8% and 14.6% for PDS and PMS, respectively. Furthermore, SCOD, ammonium nitrogen and phosphates were successfully removed from the supernatant using the struvite precipitation method. After reagent addition and the reaction time (24 h), concentrations of NH_4^+ and PO_4^{3-} were decreased using a reagent molar ratio (Mg^{2+}, NH_4^+ and PO_4^{3-}) of 1:1:1 by 92.6% and 81%, respectively and for the reagent molar ratio of 1.2:1:1.2 by 96% and 86.7%, respectively while producing struvite an excellent slow release fertilizer.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2016.01.103.

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5. 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.

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