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APPLICATION OF PERSULFATE FOR WATER AND WASTEWATER TREATMENT

Master's thesis

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Abbreviations

1,4-D - 1,4 – dioxane

2-MIB - 2-methylisoborneol

AB113 - azo dye Acid Blue 113

AMP - penicillins

AP – antipyrine

AOP - advanced oxidation processes

AOS 7 - acid orange 7

ATZ - atrazine

BIS – bisoprolol

BPA - bisphenol A

CAP - chloramphenicol

CBZ – carbamazepine

CEP – cephalosporin

CIP – ciprofloxacin

DCP - 2,4-dichlorophenol

DMP - dimethyl phthalate

EtOH - ethanol

HBA - p-hydroxybenzoic acid

IBU - ibuprofen

ISCO – in situ chemical oxidation

LVX – levofloxacin

MCB - monochlorobenzene

MTBE - methyl tert-butyl ether

NAP – naproxen

OG - azo dye Orange G

PAHs – polycyclic aromatic hydrocarbons

PCB – polychlorinated biphenyls

PCP – pentachlorophenol

PFOA - perfluorooctanoic acid

PNA - p-nitroaniline

RR45 - C.I. Reactive Red 45

SCP – sulfachloropyridazine

SD – sulfadiazine

SMT – sulfamethazine

SMX – sulfamethoxazole

TCE – trichloroethylene

TMAH - tetramethylammonium hydroxide

UV_{254} - Spectral Absorption Coefficient is a water quality test parameter which utilizes light at the UV 254nm wavelength to be able to detect organic matter in water and wastewater. This is due to the fact that most organic compounds absorb light at the UV 254nm wavelength.

Introduction

The water situation in Europe as well as in the whole world keeps further deteriorating. Water is no longer the problem of a few regions. Currently, some 770 million people worldwide lack access to an improved water source and 2.5 billion to basic sanitation conditions. In today's industrial world, novel technologies are developed and applied to meet the ever-increasing human demand. Thus, a lot of new hazardous compounds enter continually to our water bodies through different manufacturing units' effluents or through increased use of different chemicals in households, service providers, etc. These compounds contain complex molecules that are bio-refractory in nature. Therefore, they inhibit biological wastewater treatment processes and cannot be completely degraded by conventional biological processes. Thus, it is vital to investigate novel methods for remediation of water and wastewater.

An important method for remediation of water or wastewater is *in situ* chemical oxidation (ISCO). It can be carried out with different oxidants. Most commonly used oxidants for ISCO are permanganate (MnO_4^-), hydrogen peroxide (H_2O_2) and iron (Fe) (Fenton-driven, or H_2O_2-derived oxidation), peroxydisulfate ($S_2O_8^{2-}$) and ozone (O_3). Peroxydisulfate ($S_2O_8^{2-}$), often referred to as simply persulfate, is a novel oxidant being used in ISCO for the remediation of soil and water to receive wide use. Although persulfate based oxidation has shown promising results, it has mainly been investigated at bench-scale.

The persulfate ion ($S_2O_8^{2-}$) is a strong oxidant with high oxidation potential of E°=2.1V and upon activation can produce free sulfate radicals ($SO_4^{\cdot-}$), which are even stronger oxidants (E°=2.6 V) (Tsitonaki, et al., 2010). Therefore, they are capable of degrading several pollutants, even those with high toxicity and persistence, not only in wastewater but also in surface and groundwater. After reaction, the side products generated by sulfate radicals are usually sulfate ions, which may be removed from the water by conventional processes.

The objective of Master's thesis is to review the latest experiences using persulfate for remediation of water and wastewater, to identify best practices and to suggest the direction of future research. The thesis is mainly based on information from peer-reviewed journal papers. Due to the emerging status and the wish to give the latest advances of using persulfate in ISCO processes, some information is from conference proceedings and professional reports.

1. Persulfate

1.1.Physical and Chemical Properties of Persulfate

Peroxydisulfate (hereinafter referred as persulfate) is a strong anion with the formula $S_2O_8^{2-}$. Most common persulfate compounds are ammonium persulfate, potassium persulfate and sodium persulfate. They are inorganic, solid substances with strong oxidizing properties. For ISCO, a solid sodium salt is most commonly used compound. Ammonium persulfate and potassium persulfate solutions are used lesser. Ammonium salt would result in ammonium and nitrate contamination in the subsurface (Siegrist, et al., 2011). Potassium persulfate is less soluble and could be more expensive than sodium persulfate (Siegrist, et al., 2011). Although the salts have different solubility, the dissociations are comparable for all three salts. For example, dissolving sodium persulfate in water, it disassociates into persulfate anions and sodium cations. All three salts decompose before melting upon heating to 100 °C or higher (Siegrist, et al., 2011).

In aqueous solution, at room temperature and at neutral pH persulfate ion is quite stable. The persulfate ion slowly hydrolyzes and forms peroxymonosulfate or hydrogen peroxide at acidic pH. The rate of reaction increases with decreasing pH (Siegrist, et al., 2011). Both, peroxymonosulfate and hydrogen peroxide are highly reactive oxidants that have the potential to oxidize organic compounds. Table 1 summarizes the physical and chemical properties of the most common persulfate salts.

1.2.Traditional Field of Application

In many industrial processes and products persulfates are key components. Approximately 80% of all persulfates are used in two industrial applications. About 60% are used in polymerization reactions. In more detail ammonium, potassium, and sodium persulfates are used in emulsion polymerization reactions in the preparation of neoprene, acrylics, polystyrenes, and polyvinyl chlorides as initiators. Also, they are used in the manufacture of synthetic rubber (styrene butadiene and isoprene) for automobile and truck tires as polymerization initiators. Persulfate initiation is also used to prepare latex polymers for paints, coatings, and carpet backing. In case of soil stabilization, like near buildings, dams and tunnels, ammonium persulfate is used in chemical grout systems as a curing agent. (Corporation, 2001)

About 20% of all persulfates are used in printed circuit manufacture. The persulfate's oxidation capability is used to microetch and clean some of the printed circuit board substrates. They are important oxidants in coating and plating processes. Persulfates can be used as etchants for titanium, zinc and nickel alloys. They are used prior to adhesive bonding or plating to clean and mill aluminium, brass, copper, and many other metal surfaces. Also, persulfates are used to clean and activate charcoal and carbon before and after use of as absorbents. (Corporation, 2001)

Table 1 Physical and Chemical Properties of Persulfate Salts (Corporation, 2001)

Chemical name	Ammonium peroxydisulfate	Potassium peroxydisulfate	Sodium peroxydisulfate
Physical form	Crystalline (monoclinic)	Crystalline (triclinic)	Crystalline (monoclinic)
Melting point	Decomposes at about 120 °C	Decomposes at about 100 °C	Decomposes at about >180 °C
Boiling point	Not applicable	Not applicable	Not applicable
Formula	$(NH_4)_2S_2O_8$	$K_2S_2O_8$	$Na_2S_2O_8$
Molecular weight g/mol	228.2	270.3	238.1
Crystal density at 20 °C (g/cc)	1.98	2.48	2.59
Colour	Off-white	White	White
Odour	None	None	None
Loose bulk density (g/cc)	1.05	1.30	1.12
Solubility (g/100g of H_20) at 25 °C in water	85	6	73
Solubility (g/100g of H_20) at 50 °C in water	116	17	86

Persulfates are used also in cosmetic industry to make hair bleaching performance more effective. Also, persulfates are oxidizing agents in the preparation of aldehydes, carboxylic acids, ketones, quinones and some other compounds. Sodium persulfate can be used in the preparation of antibiotics in the pharmaceutical industry as a reagent. (Corporation, 2001)

Due to their properties, persulfates could be used for soil, water and wastewater remediation or in other environmental applications.

Persulfate is also used in enhanced oil recovery; in the preparation dispersants for toner formulations and ink jetting or metal bonding adhesives and adhesive films; in many photographic applications, including solution regeneration, bleaching solutions, equipment cleaning and wastewater treatment; in nickel and cobalt separation processes; in the preparation of on-site production of an alternative to peroxymonosulfate and potassium caroate; in the sizing of paper, preparation of coatings and binders and production of special papers; in the bleaching and desizing of textiles and the development of dyestuffs; to oxidize non-filterable contaminants in swimming pools and other recreational water, etc. (Corporation, 2001).

For example, in the Nordic Countries (Norway, Sweden and Denmark) the persulfate is used mainly as oxidizers and process regulators in the production of chemicals products, metal coating, the paper industry, the textile industry, the paint industry and in construction.

2. Principles of Advanced Oxidation Processes

In the last two decades a lot of research work has been carried out for the development of new technologies, especially in the area of advanced oxidation processes (AOPs). AOPs are applied as a pre-treatment or for complete mineralization at degradation of complex pollutants. AOPs are defined as processes that involve the generation and use of the hydroxyl radical as a strong oxidant to degrade compounds that cannot be oxidized by conventional oxidants, like gaseous oxygen, ozone, and chlorine. Due to the fact that hydroxyl radicals are reactive electrophiles (electron preferring), that react rapidly and nonselectively with nearly all electron-rich organic compounds, they are effective in destroying organic chemicals. They have an oxidation potential of 2.8 V (Hernandez, et al., 2002) and exhibit to a billion times faster rates of oxidation reactions comparing to conventional oxidants, such as hydrogen peroxide or ozone (Systems, 1994). Once hydroxyl radicals are generated, they can by radical addition (Eq. [1]), hydrogen abstraction (Eq. [2]) and electron transfer (Eq. [3]) attack organic chemicals (Systems, 1994). In the following reactions, R is used to describe the reacting organic compound (Legrini, et al., 1993):

$$R + HO^{\cdot} \rightarrow ROH \qquad [1]$$

$$R + HO^{\cdot} \rightarrow R^{\cdot} + H_2O \qquad [2]$$

$$R^{n} + HO^{\cdot} \rightarrow R^{n-1} + OH^{-} \qquad [3]$$

Different AOPs have been developed and tested for the degradation of different pollutants (inorganic and organic compounds) present in the water or wastewater (Table 1). Advanced oxidation generally uses strong oxidising agents like hydrogen peroxide or ozone, catalysts (iron ions, electrodes, metal oxides) and irradiation (UV light, solar light, ultrasounds) separately or in combination under mild conditions (low temperature and pressure). Among different available AOPs, those driven by light seem to be the most popular technologies for wastewater treatment as shown by the large amount of data available in the literature (Stasinakis, 2008). In regions where water deficit occurs, solar AOP is particularly attractive, thus there is plenty of solar light and therefore AOP has relatively high efficiencies and low costs.

The hydroxyl radical reacts with pollutants, inorganic compounds, that are in the influent matrix, and the origin oxidizers themselves.

The efficiency of pollutant oxidation could be reduced in the presence of mineral scavengers in direct proportion to their concentrations (Hernandez, et al., 2002):

$$^{\cdot}OH + HCO_3^{\cdot} \rightarrow {}^{-}OH + HCO_3^{\cdot} \qquad [4]$$

$$^{\cdot}OH + CO_3^{2-} \rightarrow {}^{-}OH + {}^{\cdot}CO_3^{-} \qquad [5]$$

$$^{\cdot}OH + PO_4^{3-} \rightarrow {}^{-}OH + {}^{\cdot}PO_4^{2-} \qquad [6]$$

Table 1 AOP Technologies

Photochemical	**Non-photochemical**
Ozone/ Ultraviolet Irradiation (O_3/UV)	Ozone water system (HO^-/O_3)
Hydrogen Peroxide/ Ultraviolet Irradiation (H_2O_2/ UV)	Peroxone (H_2O_2/ O_3)
Titanium dioxide catalyzed UV Oxidation (TiO_2/ UV)	Fenton system (H_2O_2/Fe^{2+})
Ozone/ Ultraviolet Irradiation/ Hydrogen Peroxide (O_3/ UV/ H_2O_2)	Ozone/ Titanium Oxide/ Hydrogen Peroxide (O_3/ TiO_2/ H_2O_2)
Photo-Fenton (H_2O_2/Fe^{2+}/UV)	Ozone/ Titanium Oxide (O_3/ TiO_2)
	Sonolysis
	Ozone sonolysis
	Catalytic oxidation
	Supercritical water oxidation

Also, it has been observed that reduced cations and excessive amounts of primary oxidizers can serve as significant scavengers of hydroxyl radical (Hong, et al., 1996). For each oxidant there is an optimum dose. For systems, that use two or more oxidants there is an optimum stoichiometric mass ratio, for example peroxone (Hernandez, et al., 2002).

2.1. Ozone water system

Ozone decomposition in aqueous solution develops through the formation of hydroxide radicals (Hoigne & Bader, 1983). In the reaction mechanism hydroxide ion has the role of initiator (Andreozzi, et al., 1999):

$$HO^- + O_3 \rightarrow O_2 + HO_2^- \qquad [7]$$

$$HO_2^- + O_3 \rightarrow HO_2^{\cdot} + O_3^{\cdot -} \qquad [8]$$

$$HO_2^{\cdot} \rightarrow H^+ + O_2^{\cdot -} \qquad [9]$$

$$O_2^{\cdot -} + O_3 \rightarrow O_2 + O_3^{\cdot -} \qquad [10]$$

$$O_3^{\cdot -} + H^+ \rightarrow HO_3^{\cdot} \qquad [11]$$

$$HO_3^{\cdot} \rightarrow HO^{\cdot} + O_2 \qquad [12]$$

$$HO^{\cdot} + O_3 \rightarrow HO_2^{\cdot} + O_2 \qquad [13]$$

The increase of pH and the addition of hydrogen peroxide to the aqueous ozone solution will result into higher rates of hydroxyl radical production and the attainment of higher steady-state concentrations of hydroxyl radicals in the radical chain decomposition process (Glaze & Kang, 1989).

2.2. Peroxone process

Applying hydrogen peroxide and ozone simultaneously to water, they react to form hydroxyl radicals. The reaction steps during peroxone oxidation for the formation of the hydroxyl radical are (Hernandez, et al., 2002):

$$H_2O_2 + H_2O \leftrightarrow H_3O^{+} + HO_2^{-} \qquad [14]$$

$$O_3 + HO^{-} \rightarrow HO_2^{-} + O_2 \qquad [15]$$

$$O_3 + HO_2^{-} \rightarrow {}^{\cdot}OH + O_2^{\cdot -} + O_2 \qquad [16]$$

$$O_3 + O_2^{\cdot -} \rightarrow O_3^{\cdot -} + O_2 \qquad [17]$$

$$O_3^{\cdot -} + H_2O_2 \rightarrow {}^{\cdot}OH + OH^{-} + O_2 \qquad [18]$$

The system efficiency is affected by many variables such as temperature, scavengers in the influent, pH and pollutant types (Hernandez, et al., 2002).

2.3. Ozone/ Ultraviolet Irradiation process

In this process, aqueous systems saturated with ozone are irradiated with UV light of 254 nm. Hydroxyl radicals are produced through different reaction pathways. There is a general agreement about involved reactions (Peyton & Glaze, 1988):

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 \qquad [19]$$

$$H_2O_2 + h\nu \rightarrow {}^{\cdot}OH + {}^{\cdot}OH \qquad [20]$$

$$2O_3 + H_2O_2 \rightarrow 2{}^{\cdot}OH + 3O_2 \qquad [21]$$

As the above reactions illustrate, photolysis of ozone generates hydrogen peroxide and, thus, O_3/UV involves all of the organic destruction mechanisms present in H_2O_2/O_3 and H_2O_2/UV AOPs (Kommineni, et al., 2008).

2.4.Hydrogen Peroxide/ Ultraviolet Irradiation process

In this process, solutions that are saturated with hydrogen peroxide will be irradiated with UV light of 200 to 280 nm (Stasinakis, 2008). During this process, hydroxyl radical is generated via cleaving the oxygen-oxygen bond by ultraviolet radiation in hydrogen peroxide. The reactions are as follows (Buxton, et al., 1988):

$$H_2O_2 + h\nu \rightarrow 2HO^{\cdot} \quad [22]$$

$$H_2O_2 + HO^{\cdot} \rightarrow HO_2^{\cdot} + H_2O \quad [23]$$

$$H_2O_2 + HO_2^{\cdot} \rightarrow HO^{\cdot} + H_2O + O_2 \quad [24]$$

$$2HO^{\cdot} \rightarrow H_2O_2 \quad [25]$$

$$2HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad [26]$$

$$HO^{\cdot} + HO_2^{\cdot} \rightarrow H_2O + O_2 \quad [27]$$

Process is affected by initial concentration of the target compound, amount of hydrogen peroxide used, pH, presence of bicarbonate and reaction time. Specifically, degradation process's kinetic rate constant is inversely proportional to the pollutant's initial concentration. Although acidic pH values (2.5- 3.5) are usually preferred, the pH values are dependent on the target compounds' acid dissociation constant (Stasinakis, 2008).

2.5.The Fenton's processes

Fenton's reagent is a mixture of ferrous ion, which is a catalyst and hydrogen peroxide, which is an oxidizing agent. The mechanism is as follows (Neyens & Baeyens, 2002; Niaounakis & Halvadakis, 2006):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\cdot} \quad [28]$$

$$Fe^{2+} + HO^{\cdot} \rightarrow Fe^{3+} + OH^- \quad [29]$$

$$HO^{\cdot} + RH \rightarrow H_2O + R^{\cdot} \quad [30]$$

$$R^{\cdot} + Fe^{3+} \rightarrow R^+ + Fe^{2+} \quad [31]$$

Photo Fenton's process involves the formation of hydrogen radical through photolysis of hydrogen peroxide and Fenton's reaction. Ferric ions that are produced (Eq. [28]) in the presence of ultraviolet irradiation, are converted photocatalytically to ferrous ions, with formation of hydroxyl radical of an additional equivalent (Moraes, et al., 2004):

$$Fe^{3+} + H_2O \rightarrow Fe^{2+} + H^+ + HO^{\cdot} \qquad [32]$$

Similarly to the Fenton's process, formed hydroxyl radical will react with organic species. Comparing to conventional the Fenton's process, photo Fenton's process gives higher degrees of mineralization and faster rates, when the process is accelerated by light (Pignatello, et al., 2007). Mainly, the Fenton's process is affected by amount of ferrous ions, solution's pH, initial concentration of the pollutant, concentration of hydrogen peroxide and presence of other ions (Gogate & Pandit, 2004). The optimum pH for the Fenton's processes ranges from 2 to 4. At higher pH, the ferrous ions are unstable and easily transformed to ferric ions, forming complexes with hydroxyl. Moreover, under alkaline conditions, due to its breakdown to oxygen and water, hydrogen peroxide loses its oxidative characteristics (Niaounakis & Halvadakis, 2006). The Fenton's process could be inhibited by sulfate, fluoride, phosphate, chloride ions and bromide. Inhibition by these species may be caused by scavenging of hydrogen radicals, precipitation of iron or transition to dissolve ferric, forming a less reactive complex (Pignatello, et al., 2007).

Electro-Fenton's process includes electrochemical reactions for the *in situ* generation of the reagents used for the Fenton's reaction. The generated reagents depend on solution conditions, cell potential and nature of electrodes (Pignatello, et al., 2007). Ferrous ions may be produced by oxidative dissolution of anodes, e.g. iron metal (Arienzo, et al., 2001) or by reduction of ferric ions at an inert cathode, e.g. platinum (Qiang, et al., 2003). Hydrogen peroxide may be produced by dioxygen reduction at the cathode (Casado, et al., 2005).

3. Persulfate - Novel Oxidant in Advanced Oxidation Processes

3.1.Kinetics and Mechanism of Oxidations by Persulfate

Persulfate salts dissociate in aqueous solutions to form the persulfate anion ($S_2O_8^{2-}$). The decomposition of the persulfate anion in aqueous solution involves the following reactions (Kolthoff & Miller, 1951):

$$S_2O_8^{2-} + H_2O \rightarrow 2HSO_4^- + {}^1/_2\,O_2 \qquad [33]$$

$$H_2O_2O_8 + H_2O \rightarrow H_2SO_5 + H_2SO_4 \qquad [34]$$

$$H_2SO_5 + H_2O \rightarrow H_2O_2 + H_2SO_4 \qquad [35]$$

Persulfate decomposes in dilute acid, neutral and alkaline solutions according to reaction Eq. (33). Reactions Eq. [34] and Eq. [35] apply for strongly acid solutions (Kolthoff & Miller, 1951).

Persulfate anion is a strong oxidant, with the oxidation potential of 2.12 V (House, 1961):

$$S_2O_8^{-2} + 2H^+ + 2e^- \rightarrow 2HSO_4^- \qquad [36]$$

Therefore, it can degrade many environmental contaminants. However, the persulfate anion typically has slow oxidative kinetics at ordinary temperatures for most contaminant species and really can only be applied to a limited number of contaminants, such as TCE or xylene, to be effective. In these circumstances persulfate is typically activated for oxidizing most contaminants or concern. In the presence of various reactants it can be catalyzed to form more powerful oxidant, the sulfate free radical ($SO_4^{-\cdot}$), with the oxidation potential of 2.6 V:

$$S_2O_8^{-2} + activator \rightarrow SO_4^{-\cdot} + (SO_4^{-\cdot}\ or\ SO_4^{-2}) \qquad [37]$$

Catalysis of persulfate anion and sulfate radical can be achieved at elevated temperatures (35 – 40 °C), with ferrous ion, by photo activation, with elevated pH, or with hydrogen peroxide. In addition to ferrous ion, the activators can include also ions of copper, silver, manganese, cerium and cobalt.

Under acidic conditions persulfate anion can hydrolyze to form hydrogen peroxide (Kolthoff & Miller, 1951):

$$S_2O_8^{-2} + 2H_2O \rightarrow H_2O_2 + 2\,HSO_4^- \qquad [38]$$

Hydrogen peroxide has the oxidation potential of 1.77 V and in the presence of various activators, can form the hydroxyl radical, with the oxidation potential of 2.8 V. It is the strongest available oxidant for remediation applications. In addition, also hydroxyl radicals are generated when sulfate radicals react with water. Under stronger acidic conditions, persulfate can form peroxymonopersulfate anions, with the oxidation potential of 1.44 V:

$$S_2O_8^{-2} + H_2O \rightarrow HSO_5^- + HSO_4^- \qquad [39]$$

In this context, persulfate solutions may contain several different oxidant and radical species. This increases the probability of reducing the target contaminant's concentration as mixture of oxidizing species may cause multiple pathways for degradation of the contaminant. However, such diversity of oxidant species makes the assessment of the stoichiometric amount of persulfate needed to decompose the contaminants problematic, and thus it is common practise to revert back to the basic, two electron transfer associated with the persulfate anion (Eq. [36]) to determine the stoichiometric persulfate demand.

In addition, under certain conditions persulfate can also generate the reductive species, super oxide. Under alkaline activation conditions through the addition of hydrogen radical, persulfate generates both sulfate radicals and superoxide (Furman, et al., 2010):

$$2S_2O_8^{-2} + 2H_2O \rightarrow 3SO_4^{-2} + SO_4^{-\cdot} + O_2^{-\cdot} + 4H^+ \qquad [40]$$

Under highly alkaline conditions sulfate radical can react with hydroxide radicals to form hydroxyl radicals (Watts & Teel, 2006):

$$SO_4^{\cdot-} + OH^- \rightarrow SO_4^{-2} + OH^\cdot \qquad [41]$$

Table 2 Potential Reactive Species in an Activated Persulfate System

Species		Potential (V)
Hydroxyl radical	$OH^\cdot$	+2.8
Sulfate radical	$SO_4^{\cdot-}$	+2.6
Persulfate anion	$S_2O_8^{-2}$	+2.1
Hydrogen peroxide	H_2O_2	+1.8
Monopersulfate	HSO_5^-	+1.4
Superoxide	$O_2^{-\cdot}$	-0.2
Perhydroxyl	HOO^-	-0.87

Superoxide can also be generated when persulfate is activated by hydrogen peroxide via the generation of hydroperoxide by iron – activated hydrogen peroxide, and then as in the high pH activation scenario, the hydroperoxide reacts with persulfate anion to form sulfate radical and superoxide species (Ahmad, et al., 2010). The oxidation potential of reactive species potentially present in activated persulfate systems are described in Table 2.

3.2.Activators

Although persulfate is a powerful oxidant, it can be catalyzed with various reactants to form a more powerful sulfate radical.

3.2.1. Base activation

Base activation is at elevated pH. Persulfate decomposes to peroxymonosulfate and sulfate through base-catalyzed hydrolysis. Peroxymonosulfate rapidly decomposes to hydroperoxide and sulfate at basic pH; therefore, no detectable peroxymonosulfate is expected in base-activated persulfate systems (Furman, et al., 2010):

$$S_2O_8^{2-} + 2H_2O + OH^- \rightarrow HO_2^- + 2SO_4^{2-} + 3H^+ \qquad [42]$$

Hydroperoxide reduces another persulfate molecule, resulting in formation of sulfate radical and sulfate, while hydroperoxide is oxidized to superoxide (Furman, et al., 2010):

$$HO_2^- + S_2O_8^{2-} \rightarrow SO_4^{-\cdot} + SO_4^{2-} + H^+ + O_2^{-\cdot} \qquad [43]$$

In highly alkaline conditions, sulfate radical oxidizes hydroxide, resulting in formation of hydroxyl radical (Furman, et al., 2010):

$$SO_4^{-\cdot} + OH^- \rightarrow SO_4^{2-} + OH^{\cdot} \qquad [44]$$

3.2.2. Heat activation

At ambient temperature persulfate oxidation is usually not effective. Commonly persulfate is used with under elevated temperatures (35 to 40 °C) in order to initiate/enhance its radical oxidation mechanisms. Heat-activated persulfate has faster reaction rates, which is especially needed for degradation of resistant contaminants (Waldemer, et al., 2007; Huang, et al., 2002). Sulfate radicals, formed from heat decomposition of persulfate (Eq. [45]), may initiate a series of radical chain reactions (Eqs. [45]-[56]) (Berlin, 1986), where organic compounds (i.e., M in Eq. [46]) are usually degraded.

$$S_2O_8^{2-} + heat \rightarrow 2SO_4^{-\cdot} \qquad [45]$$

$S_2O_8^{2-} + M \rightarrow 2SO_4^{-\cdot} + M^{\cdot}$ [46]

$SO_4^{-\cdot} + H_2O \rightarrow HO^{\cdot} + HSO_4^{-}$ [47]

$SO_4^{-\cdot} + M \rightarrow M^{\cdot} + products$ [48]

$HO^{\cdot} + M \rightarrow M^{\cdot} + products$ [49]

$M^{\cdot} + S_2O_8^{2-} \rightarrow SO_4^{-\cdot} + products$ [50]

$SO_4^{-\cdot} + HO^{\cdot} \rightarrow chain\ termination$ [51]

$SO_4^{-\cdot} + M^{\cdot} \rightarrow chain\ termination$ [52]

$2SO_4^{-\cdot} \rightarrow chain\ termination$ [53]

$HO^{\cdot} + M^{\cdot} \rightarrow chain\ termination$ [54]

$2HO^{\cdot} \rightarrow chain\ termination$ [55]

$2M^{\cdot} \rightarrow chain\ termination$ [56]

3.2.3. Photo activation

Photo activation is similar to heat activation. In the presence of ultraviolet irradiation persulfate can transform to two sulfate radical anions (Dogliotti & Hayon, 1967):

$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{-\cdot}$ [57]

The optical absorption spectrum of this transient has a maximum at 4550 A, a half-life of about 300 μsec (Dogliotti & Hayon, 1967). It is found to be stable in presence or absence of oxygen and in neutral and acid solutions. At pH >8.5 it starts decaying rapidly and has completely disappeared at pH 10.7-10.8 (Dogliotti & Hayon, 1967). In alkaline solutions, the persulfate radical is apparently converted to hydrogen radical (Dogliotti & Hayon, 1967):

$SO_4^{-} + H_2O \leftrightarrow OH + SO_4^{2-} + H^{+}$ [58]

3.2.4. Metal activation

One activation method is activation by transition metal. Metal can initiate a free radical generation through the formation of the sulfate radical (Tsitonaki, et al., 2010):

$S_2O_8^{2-} + M^{n+} \rightarrow SO_4^{-\cdot} + SO_4^{2-} + M^{n+1}$ [59]

$SO_4^{-\cdot} + M^{n+} \rightarrow SO_4^{2-} + M^{n+1}$ [60]

The most common activator is ferrous iron (Buxton, et al., 1997):

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{-\cdot} + SO_4^{2-} \quad [61]$$

$$SO_4^{-\cdot} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{-\cdot} + SO_4^{2-} \quad [62]$$

Other general activators include the ions of copper, silver, manganese, cerium and cobalt.

3.2.5. Combination with other oxidants

Persulfate can also be used in combination with other oxidants, for an example hydrogen peroxide. Combination of hydrogen peroxide and persulfate has several positive effects. Firstly, peroxide generates hydroxyl radicals that will initiate persulfate radical formation and the opposite. Secondly, the degradation of contaminants can be divided between hydrogen peroxide and persulfate radicals. Whereas hydrogen peroxide degrades more susceptible contaminants and the sulfate radicals more recalcitrant compounds. Finally, a higher efficiency in degrading contaminants, including recalcitrant compounds with a combination of hydroxyl and sulfate radicals can be achieved via multi-radical attack mechanism.

After formation of hydroxyl radical upon the decomposition of the hydrogen peroxide followed by the activation of the persulfate to produce sulfate radical:

$$S_2O_8^{2-} + OH^{\cdot} \rightarrow SO_4^{2-} + SO_4^{-\cdot} + {}^1\!/_2\, O_2 + H^+ \quad [63]$$

In practical application, hydrogen peroxide activation is short-lived as the hydrogen peroxide rapidly decomposes, often with considerable off-gassing.

3.2.6. Chelated metal catalysts activation

Transition metal catalyst solubility and availability are important elements in the persulfate activation. At neutral or alkaline conditions chelation is an effective method for maintaining metal activity. It also provides protection under the neutral pH conditions from hydration and further precipitation. Iron (II)-EDTA and iron (III)-EDTA activated persulfate at neutral pH effectively generates sulfate radical, hydroxyl radical, and reductants with potential to rapidly and effectively treat TCE and potentially other biorefractory contaminants.

4. Chemical Oxidation of Water and Waste Water Using Persulfate

The following part of Master's thesis reviews the latest experiences using persulfate for remediation of water and wastewater. The review is based on peer-reviewed articles from different journals, like Chemical Engineering Journal, Environmental Science Technology, Journal of Contaminant Hydrology, Water Research, Separation and Purification Technology, Desalination and Water Treatment, etc. The chosen articles describe the most important activation methods and in a few cases degrading the same contaminants using different activation methods.

The reviewed studies are divided into two parts. Table 3 describes degradation of various contaminants in water and table 4 in wastewater. The division of studies between water and wastewater tables was done considering the most common problems concerning contaminants in water or wastewater. The articles were searched via keywords persulfate and its activation method. Most of the chosen articles have been published less than five years ago. Some studies were chosen due to multiple references in other articles. The main emphasis has been done on different factors affecting the process, e.g. dosage ratio between the contaminant and persulfate, pH, activator's concentration, scavengers, degradation pathways, etc. The possible cost or upscaling of the process was studied rarely.

The following tables bring out the issues described in the peer-reviewed articles. These are the contaminant studied and its initial value at best results achieved; used persulfate compound, e.g. mainly sodium persulfate or potassium persulfate (there were a few studies that did not clarify the exact oxidant used); activation method or activator and its initial value at best results achieved or in case of thermal activation the temperatures tested; results describing the best result achieved, the reaction time and other most important aspects discovered, e.g. effect of pH, persulfate dosage, its injection method, scavenging, mineralization, etc. The final column makes a reference to the reviewed article.

Chapter 4.1 summarizes the results described in tables 3 and 4 through degradation mechanisms, effects of pH, additives, persulfate concentration and degradation by activation type.

Table 3 Degradation of various compounds by activated persulfate in water

Compound	Initial value	Persulfate	Activator	Performance	References
Antipyrine (AP)	0.0265 mM	Sodium persulfate 1.855 mM	Thermally activated (30 – 70°C)	Complete AP degradation occurred at pH = 7.1 after 40 minutes of reaction at 70°C. The AP degradation rate increased with increasing temperature and persulfate dosage, acidic pH, except pH > 11. AP mineralization was insignificant, thus indicating that the intermediate and final oxidation products of AP were recalcitrant to sulfate radical oxidation.	(Tan, et al., 2015)
Atrazine (ATZ)	50 μM	Potassium persulfate 0 - 2 mM	Thermally activated (20 – 60°C)	Complete ATZ degradation was achieved either with higher (2.0 mM) persulfate concentration at 50°C in 120 minutes or at 60°C with lower (1.0 mM) persulfate concentration in 80 minutes, at pH=7.0 The process was highly pH dependent with greater degradation efficiency occurring around neutral pH. Additives had a little effect on ATZ degradation.	(Ji, et al., 2015)
Benzotriazole	0.02 mM	Sodium persulfate 0.5 mM	Weak magnetic field with Fe (0) 0.05 mM	More than 90% degradation rate occurred at pH = 7 less than in 90 minutes.	(Xiong, et al., 2014)
Bisoprolol (BIS)	50 μg	Sodium persulfate 1 mM	Thermally activated (40 – 70°C)	Complete BIS degradation occurred at pH = 7 after 15, 25 and 45 minutes of reaction at 70, 65 and 60°C respectively, whereas 60°C is optimum (the consumption of sodium persulfate was minimal). At lower temperatures the degradation was not complete. The solution had a phosphate buffer (50	(Ghauch & Tuqan, 2012)

				μg). In the absence of buffer, the solution's pH dropped, reaching 4.9 after 1 hour due to the formation of acidic species (H^+, HSO_5^-) after thermal activation. At lower pH the BIS degradation rate decreased to 63%. Inorganic additives had not any negative effect on BIS degradation.	
Caffeine	0.02 mM	Sodium persulfate 0.5 mM	Weak magnetic field with Fe (0) 0.05 mM	Complete degradation occurred at pH = 7 in 60 minutes.	(Xiong, et al., 2014)
Carbamazepine (CBZ)	40 μM	Sodium persulfate 1 mM	Thermally activated (40 – 70°C)	90% CBZ removal occurred at 60°C in 10 minutes, adding 1 mM Fe (II). 87% CBZ removal occurred at 70°C and in 80 minutes. Excessive radical scavengers (e.g. EtOH, phenol, TBA) exerted inhibiting effect. Thus CBZ degradation rate was much lower when EtOH or phenol were present. TBA is the scavenger for hydroxyl radicals, thus CBZ degradation rate is higher than with other scavengers. Degradation rate increased with the increase of persulfate dosage and decreased with the increasing CBZ dosages. Acidic conditions were more favourable. Inorganic anions inhibited degradation of CBZ. Inorganic cations such as Ca^{2+} and Mn^{2+} had no significant impact, however Fe^{2+}, Fe^{3+} and Cu^{2+} could accelerate CBZ degradation.	(Deng, et al., 2013)
Chloramphenicol (CAP)	0.2 mM	Sodium persulfate 4 mM	Thermally activated (50 – 90°C)	Almost complete CAP removal occurred at 80°C in 40 minutes at pH = 5.4. The degradation rate increased with increasing temperatures. Higher persulfate dosages increased CAP degradation rate. At lower pH values CAP degradation rate	(Nie, et al., 2014)

				increased. Adding chloride at molar ratio 1:1 to persulfate enhanced the degradation, but inhibited the treatment at other levels. The presence of the NO_3^-; $H_2PO_4^-$ and HPO_4^{2-} anions significantly slowed down CAP degradation rate. CAP removal efficiencies of 62.2–96.3% in the wastewater matrices were achieved within 160 minutes.	
1,4 – Dioxane (1,4-D)	100 mg/L	Sodium persulfate 5000 mg/L	Thermally activated (40 – 60°C)	Complete 1,4-D removal occurred in 180 minutes at 60°C and at pH = 2.89. Higher persulfate concentrations led to higher 1,4-D degradation rates, but pH adjustment had no significant effect on the 1,4-D degradation rate.	(Zhao, et al., 2014)
Diuron	0.01 mM	Sodium persulfate 0.2 mM	Chelated (sodium citrate) ferrous ion and hydroxylamine	80% diuron degradation rate occurred, when persulfate and ferrous ion were added, with molar ratio 1:1, in 240 minutes at pH = 7, the concentrations of diuron and persulfate were 0.05 mM and 1.0 mM respectively. The degradation rate increased at lower pH (at pH = 3, the rate was 82%, whereas the ferrous ion concentration was 0.2 mM) and decreased at higher pH (at pH = 7, the rate was 65% with the same conditions). Optimum sodium citrate and ferrous ion molar ratio was 1:1, where in 240 minutes at pH = 7 diuron degradation rate was 80%, the ferrous ion concentration was 0.2 mM. Optimum ferrous ion hydroxylamine molar ratio was 1:2, where in 240 minutes at pH = 7 diuron degradation rate was 90%, the ferrous ion concentration was 0.2 mM. Maximum, 92% diuron degradation rate occurred at the following conditions: ferrous ion, hydroxylamine and sodium citrate concentrations	(Tan, et al., 2012)

				were 0.2 mM, 0.4 mM and 0.2 mM respectively in 240 minutes and at pH = 7.	
Diuron	0.02 mM	Sodium persulfate 0.5 mM	Weak magnetic field with Fe (0) 0.05 mM	Complete degradation occurred at pH = 7 in 40 minutes.	(Xiong, et al., 2014)
Diuron	0.0125 - 0.0500 mM	Sodium persulfate 0.0125 - 0.0500 mM	Thermally activated (50 – 70°C)	For diuron level of 0.0125 mM, the pseudo-first-order rate constant was increased from 0.036 to 1.32 min^{-1} with increasing temperature from 50 to 70°C at pH 5.1. Increasing persulfate dosages from 0.0125 to 0.05 mM, the pseudo-first- order rate constant increased from 0.054 to 0.31 min^{-1} at 60°C and at diuron concentration 0.0375 mM. Higher diuron dosages resulted in decreasing of the pseudo-first- order rate constant from 0.87 to 0.15 min^{-1} at 60°C. A weak acid environmental condition (at pH = 6.3, rate constant is 0.18 min^{-1}) more favoured the diuron degradation rate than a weak basic condition, the rate decreased with increasing pH. Adding bicarbonate, the degradation rates decreased as bicarbonate begins to compete with diuron for sulfate radicals. Adding chloride, decreased the degradation rate 25% for diuron as sulfate radicals react with chloride and form less reactive chloride radicals.	(Tan, et al., 2012)
Geosmin	219 nM	Potassium persulfate 10 μM	Ultraviolet (UV) light-activated λ = 254 nm	94.5% geosmin removal was achieved at pH = 7 in 10 minutes. Degradation rate of geosmin decreased with increasing pH from 4.0 to 8.0. It was found that pH did not affect the degradation of geosmin directly, but only through affecting the distribution of $H_2PO_4^-$ and HPO_4^{2-} in the experimental process.	(Xie, et al., 2015)

				Increasing persulfate dosages, the degradation increased. Natural organic matter and bicarbonate are the main radical scavengers.	
Levofloxacin (LVX)	75 μM	Sodium persulfate 1.5 mM	Iron-activated Fe(II)	Complete LVX removal occurred in 90 minutes at pH = 3 and at 21°C. The most effective molar ratio of LVX/persulfate/Fe(II) was 1:20:8. The pH ranges from 3 to 7 did not influence the degradation. At higher pH the LVX degradation decreased.	(Epold, et al., 2015)
Levofloxacin (LVX)	75 μM	Sodium persulfate 0.75 mM	Combined Fenton/persulfate	Complete LVX removal occurred less than 20 minutes at pH = 3 and at 21°C. The most effective molar ratio of LVX/hydrogen peroxide/persulfate/Fe(II) was 1:10:5:2.	(Epold, et al., 2015)
Methyl tert-butyl ether (MTBE)	0.06 mM	Sodium persulfate 31.5 mM	Thermally activated (20 – 50°C)	MTBE degraded rapidly under the experimental conditions at pH = 6.9. Higher temperature resulted in faster MTBE degradation, e.g. at 50°C in 2 hours almost complete MTBE degradation occurs, at 40°C the degradation rate is about 81.6 %. Also higher persulfate concentration and acidic pH enhanced the degradation of MTBE. The bicarbonate ions (which occur in groundwater) acted as radical scavengers.	(Huang, et al., 2002)
2-Methylisoborneol (2-MIB)	238 nM	Potassium persulfate 10 μM	Ultraviolet (UV) light-activated $\lambda = 254$ nm	86.0% 2-MIB was achieved at pH = 7 in 10 minutes. Degradation rate of 2-MIB decreased with increasing pH from 4.0 to 8.0. It was found that pH did not affect the degradation of 2-MIB directly, but only through affecting the distribution of $H_2PO_4^-$ and HPO_4^{2-} in the experimental process. Increasing persulfate dosages, the degradation increased. Natural organic matter and bicarbonate	(Xie, et al., 2015)

				were the main radical scavengers.	
Monochlorobenzene (MCB)	100 mg/L	Sodium persulfate 22.5 g/L	Thermally activated (20 – 60°C)	Complete MCP degradation occurred at 60°C in 120 minutes. Reactivity of persulfate was partly influenced by the presence of background ions such as Cl^{-}, HCO_3^{-}, SO_4^{2-}, and NO_3^{-}. Importantly, a scavenging effect in decreasing rate constant was observed for both Cl^{-} and CO_3^{2-} but not for other ions.	(Luo, 2014)
Naproxen (NAP)	50 μg	Sodium persulfate 1 mM	Thermally activated (40 – 70°C)	Complete NAP degradation occurred at pH = 7.5 after 40 and 90 minutes of reaction at 70 and 60°C respectively. Inorganic additives affected the process. $MgNO_3$ increased by 154% NAP degradation rate constant while $CaCl_2$ decreased the degradation rate constant by 18.5%. NAP mineralization was reached at higher sodium persulfate concentrations (2.5-7.5 mM) at 60°C.	(Ghauch , et al., 2015)
4-Nitrophenol	0.02 mM	Sodium persulfate 0.5 mM	Weak magnetic field with Fe (0) 0.05 mM	More than 95% degradation occurred at pH = 7 within 60 minutes.	(Xiong, et al., 2014)
Pentachlorophenol (PCP)	50 mM	Potassium persulfate 0.115 mM	Electrochemically activated Anode Fe Cathode Fe	38% PCP removal was achieved at pH = 6.5 in 20 minutes at current density 90 mA cm^{-2}. More effective oxidant was peroxymonosulfate (75% PCP removal).	(Govindan, et al., 2014)
Perfluorooctanoic acid (PFOA)	254 μmol/L	Sodium persulfate 10 mmol/L	Microwave irradiation (60 – 130°C)	After 4 hours of microwave irradiation, at 90°C 80.4% of PFOA was degraded. At higher and lower temperature, the degradation rate was lower. Most effective result was achieved at pH = 2,5 and 90°C, where the degradation rate was 85.7% in 4 hours.	(Lee, et al., 2012)

				Addition of zero valent iron had a positive effect on degradation, but not as efficient as acidic pH. Chloride ions decrease the PFOA degradation rate.	
Perfluorooctanoic acid (PFOA)	120.6 μM	Persulfate 6.3 mM	Activated carbon (adsorbent and catalyst, 10 g/L)	In 12 hours 68.2% PFOA removal occurred at pH = 3.8 and 25°C. Although at 45°C the PFOA removal was 70.8%, the defluorination efficiency was only 22.6%, compared to 54.9% at 25°C. The effective molar ratio between persulfate and PFOA was 500:1. With larger persulfate dosages, persulfate ions compete with PFOA on adsorption onto activated carbon surface. Acidic pH enhances the formation of free sulfate radicals and is therefore preferred.	(Lee, et al., 2013)
Propachlor	10 mg/L	Sodium persulfate 5 mM	Cu^{2+} 2.5 mM and Fe^{2+} 2.5 mM	Complete propachlor degradation occurred at 55°C in 32 hours, adding Cu^{2+}. 60.5% propachlor removal occurred at 30°C in 66 hours. Higher Cu^{2+} concentration facilitated degradation rate, however, the equal concentration to persulfate was optimal. Higher Fe^{2+} concentrations facilitated reactions between sulfate radicals and Fe^{2+} ions, therefore decreased the degradation rate. Higher temperature generated more sulfate radicals and also increased reactions with Fe^{2+}, which decreased the degradation of propachlor. On the contrary, in case of Cu^{2+} activation, the removal efficiency increased with increasing temperature. Increasing pH, decreased the degradation of propachlor in case of using both metal ions.	(Liu, et al., 2012)
Sulfachloropyridazine (SCP)	20 mg/L	Persulfate 2 g/L	Nitrogen-doped reduced graphene oxide (N-rGO) 0,2 g/L at 25°C)	Complete SCP degradation occurred in 150 minutes. Using only rGO, 65% of SCP was degraded in 180 minutes. Higher nitrogen level led to better SCP degradation. Process could be	(Kang, et al., 2016)

				accelerated by elevated temperatures, e.g. complete SCP degradation at 25, 35, 45°C was reached respectively in 150, 120 and 45 minutes. Process was practically independent of pH. Increasing the amount of catalyst enhanced SCP degradation. Increasing PS to certain amount increased the process (higher radical concentration triggers self-quenching reactions).	
Sulfadiazine (SD)	20 mg/L	Potassium persulfate 1.84 mM	Ultrasonication λ = 275 nm, 90 W and 0.92 mM Fe(0)	99.1% SD degradation occurred at 20°C in 60 minutes at pH = 7. SD was effectively degraded at pH = 3-7.	(Zou, et al., 2014)
Sulfamethazine (SMT)	0.02 mM	Potassium persulfate 0.2 mM	Ultraviolet (UV) light-activated λ = 254 nm	96.5% SMT removal occurred in 45 minutes at 15°C. The degradation of SMT improved with higher persulfate dosages and 0.5 mM persulfate accomplished 100% degradation of SMT in 15 minutes. The highest SMT degradation rate occurred at pH 6.5, below or beyond which the rate constant decreased.	(Gao, et al., 2012)
Sulfamethoxazole (SMX)	40 μM	Sodium persulfate 2.4mM	Thermally activated (40 – 70°C)	Complete SMX degradation was almost achieved after 45 minutes reaction at 70°C. The SMX degradation rate increased with increasing temperatures and persulfate dose, alkaline pH, and HCO_3^- anions. However, more toxic products were generated.	(Gao, et al., 2015)
Trichloroethylene (TCE)	0,45 mM	Sodium persulfate	Chelated (citric acid) ferrous ion	Complete TCE degradation occurred at pH = 2.8 – 3.3, in 20 minutes when using molar ratios ranging from 20/2/10/1 for persulfate/chelate/ferrous ion/TCE. Higher ferrous ion concentrations increased the degradation of TCE and also persulfate.	(Liang, et al., 2004)

Trichloroethylene (TCE)	100 mg/L	Sodium persulfate 2 g/L	Activated carbon (adsorbent and catalyst, AC) 5 g/L	97% TCE removal occurred at 20°C and pH = 3 in 200 minutes. Elevated AC dosage fastened persulfate degradation. Higher initial persulfate concentration resulted in a decrease of the persulfate degradation rate. Upon persulfate oxidation, the AC surface properties were altered: an increase in acidity of surface concentration, a decrease in pH, a slight decrease in the surface area.	(Liang, et al., 2009)
Trichloroethylene (TCE)	0,46 mM	Sodium persulfate persulfate/TCE molar ratio of 50/1	Thermally activated (20°C)	At neutral pH = 7 (buffered by phosphate) TCE degradation was nearly independent of HCO_3^-/CO_3^{2-} in the range of concentrations of 0 – 9.2 mM. In the (bi)carbonate buffered solution, at pH = 9, the TCE degradation rate was 48% lower and decreased with increasing pH. Chloride concentrations ranging 0 – 0.2 mM had no effect on TCE degradation rate, higher concentrations inhibited the rate.	(Liang, et al., 2006)

Table 4 ***Degradation of various compounds by activated persulfate in wastewater***

Compound	Initial value	Persulfate	Activator	Optimal performance	References
Acid orange 7 (AOS 7)	0.1 mM	Sodium sulfate 12 mM	Electrochemically activated Anode $Ti/RuO_2/IrO_2$ Cathode stainless steel	95.7% AOS 7 removal occurred in 60 minutes adding 1 mM Fe (II) at pH = 3 and current density 16.8 mA cm^{-2}. The degradation efficiency was not significantly affected by pH value and increased with the increase of persulfate and Fe(II) concentration. 57.6% COD removal was achieved after 60 minutes and 90.2% after 600 minutes. Solution's acute toxicity increased during the first stage of the reaction and afterwards decreased with the progress of the oxidation.	(Wu, et al., 2012)
Acid orange 7 (AOS 7)	0.057 mM	Sodium persulfate 5.7 mM	Activated carbon (adsorbent and catalyst, 5 g/L)	More than 97% AOS 7 removal occurred in 5 hours at pH = 5.1 and 25°C. The pH had a significant role in organic degradation, optimal initial pH was near-neutral. Higher persulfate or activated carbon dosages resulted in higher AO7 degradation rates to certain amount. The course of AO7 degradation by the activated carbon/persulfate system occurred in the porous bulk or the boundary layer on the external surface of activated carbon granules.	(Yang, et al., 2011)
Aniline	0.05 mM	Sodium persulfate 2.5 mM	Iron-activated Fe (0) 0.4 g/L	Complete aniline removal occurred in 10 minutes at 25°C at pH = 4 or in 60 minutes at 80°C at pH = 7. The process was affected by radical scavengers	(Hussain, et al., 2014)

				such as EtOH and TBA.	
Aniline	0.05 mM	Sodium persulfate 2.5 mM	Iron activated Fe (II) 0.12 mM	72.8% aniline removal occurred in 4 hours, at pH = 7 and 22.5°C, where the persulfate/Fe(II)/aniline molar ratio was 125/25/1. Excess ferrous ions were scavengers for free sulfate radicals. It could be controlled with chelating agent as citric acid, EDTA and oxalic acid. Citric acid was the most effective.	(Zhang, et al., 2014)
Azo dye Acid Blue 113 (AB113)	50 mg/L	Sodium persulfate 6.3 mM	UV irradiation 14W $\lambda = 254$ nm	97.7% AB113 removal occurred in 120 minutes. The colour removal efficiency and degradation rate decreased with increase of AB113 concentration. pH had no significant effect on removal efficiency. UV intensity affected AB113 removal efficiency significantly.	(Shu, et al., 2015)
Azo dye Orange G (OG)	0.1 mM	Sodium persulfate 4mM	Fe (II) 0.1 mM	Optimum conditions for OG degradation were at pH = 3.5, with persulfate/ferrous ion/(OG) concentrations 4 mM, 4 mM and 0.1 mM, respectively in 30 minutes. The presence of inorganic ions had inhibitory effects on the OG degradation in the following order of NO_3^- <Cl^- <$H_2PO_4^-$ <HCO_3^-.	(Xu & Li, 2010)
Azo dye Orange II	100 mg/L	Persulfate 2.0 g/L	Combination of electrochemical method and heterogeneous activation of persulfate Fe-Co/SBA-15 catalyst 1.0 g/L	95.6% Orange II removal occurred at pH = 6 in 60 minutes when anodic oxidation was combined with the Fe-Co/SBA-15 catalyst. Oxidant was activated by the continuously regenerated Fe(II) and Co(II). At pH 9 to 3, the degradation rate increased from 0.056 to 0.069 mM/min, while the efficiency increased only from 93.7% to 99.8%, because during the process pH dropped	(Cai, et al., 2014)

				almost at the same level (pH = 3). Due to the side reaction between persulfate and free sulfate radical, insignificant increase of persulfate dosages led just to higher consumption of persulfate. Increasing the catalyst dosage accelerated Orange II degradation. Increasing Orange II concentration led to increase of degradation only to certain amount. Dye molecules competed with persulfate to adsorb onto the catalyst surface, and the loading dye molecules on the catalyst surface would decrease the active surface sites available for the activation of persulfate.	
Azo dye C.I. Reactive Red 45 (RR45)	80 mg/L	Potassium persulfate 84.87 mM and 138.43 mM	Iron-activated Fe (II) 1.64 mM or Fe (0) 4.27 mM	> 92% RR45 removal occurred regardless of initial pH, iron activator type and concentration, or oxidant concentration within investigated ranges. The use of Fe (0) avoided loading the wastewater with unnecessary contour anions and enabled a wider pH range of application, having higher mineralization rate of 53% compared to Fe (II) 35%.	(Kusic, et al., 2011)
Beta-lactam antibiotics (penicillins – AMP and cephalosporin – CEP)	25 - 50 µg	Sodium persulfate 1 mM	Ultraviolet (UV) light-activated $\lambda = 254$ nm UV fluence 0 - 320 mJcm^{-2}	75.6% AMP and 90.7% CEP removal occurred at UV fluence 320 and 240 mJcm^{-2}, respectively at 25°C. It was found that chloride ion had a slight positive impact on degradation rate, but inorganic anions such as nitrate and sulfate did not have any impact. Hydrogen peroxide addition also did not have a synergistic effect.	(He, et al., 2014)
Bisphenol A (BPA)	80 µM	Potassium persulfate	Iron-activated Fe (0)	Complete BPA degradation occurred in 45 minutes at pH = 5. Adding 7mg Fe (0) fastened	(Jiang, et al., 2013)

		2 mM	8 mg	the degradation to 30 minutes.	
Bisphenol A (BPA)	80 μM	Potassium persulfate 2 mM	Iron-activated Fe (II), continuous addition 8 mg	Complete BPA degradation occurred in 30 minutes at pH = 5.	(Jiang, et al., 2013)
Bisphenol A (BPA)	80 μM	Potassium persulfate 2 mM	Iron-activated Fe (II), sequential addition 8 mg	97% degradation occurred in 30 minutes at pH = 5.	(Jiang, et al., 2013)
Ciprofloxacin (CIP)	10 mg/L	Sodium persulfate 1.92 g/L	Ultraviolet (UV) irradiation λ = 254 nm intensity 1 mW cm^{-2}	95% CIP was degraded in 30 minutes at pH = 7 and 25°C. Efficiency of degradation was increased with higher persulfate concentration. However, excessive persulfate inhibited the degradation. EtOH and TBA were scavengers and reduced the degradation rate significantly.	(Lin & Wu, 2014)
Ciprofloxacin (CIP)	30 μg	Potassium persulfate 600 μg	Fe (II) 600 μg	95.8 % degradation rate was achieved at pH = 6, in 240 minutes. Adding chelated agents (CA, EDTA or EDDS), the degradation rate decreased. At pH = 6, in 240 minutes the degradation rate decreased from 71.2% to 68.6% using CA, to 60.4% using EDTA and to 42.1% using EDDS, whereas 300 μg potassium persulfate was used.	(Ji, et al., 2014)
Cyanide	50 mg/L	Sodium persulfate 0,8 g/L	UV (h ν = 254 nm)	79% cyanide removal occurred at pH = 11, in 30 minutes and at air flow rate 0.4 L/min. Increasing persulfate concentration slightly increased the removal of cyanide (at 1.5 g/L 86%). It was explained with persulfate being itself scavenger of sulfate radical.	(Moussavi, et al., 2016)
2,4-Dichlorophenol	30 mg/L	Sodium	Iron-activated	92.5% DCP removal occurred within 150	(Li, et al., 2015)

(DCP)		persulfate 12.5 mM	nano-Fe (0) 2.0 g/L	minutes at pH = 3.	
Dimethyl phthalate (DMP)	0.0515 mmol/L	Sodium persulfate 10.3 mmol/L	Thermally activated (20 – 40°C)	Complete DMP removal occurred at 40°C within 18 hours at pH = 3.1.	(Wang, et al., 2014)
p-Hydroxybenzoic acid (HBA)	100 μM	Sodium persulfate 2 mM	Electron beam 3 MeV vertical scan beam, 600 Gy dose	More than 80% HBA was degraded. Addition of persulfate induced a change in the reaction pathway. In the absence of persulfate, the main by-product formed was 3,4-dihydroxybenzoic acid, while in presence of persulfate, 1,4-benzoquinone was detected and the hydroxylated by-products were not present. High pH and dissolved oxygen decreased the HBA degradation.	(Criquet & Karpel Vel Leitner , 2015)
Ibuprofen (IBU)	20.36 μM	Sodium persulfate 1.0 mM	Thermally activated (40 – 70°C)	Complete IBU degradation occurred at pH = 7 after 20 and 40 minutes of reaction at 70 and 65°C respectively. Both, increasing and decreasing pH lowered IBU degradation rate. Increase in sodium persulfate concentration for fixed IBU concentration resulted in faster IBU degradation rate.	(Ghauch , et al., 2012)
Ibuprofen (IBU)	1 mM	Potassium persulfate 20 mM	Gamma irradiation 60-Co radiation chamber, 80 kGy dose	97% IBU removal efficiency occurred at pH = 7. Due to the fact that free sulfate radical reacts directly with the benzene ring forming of benzene radical cation followed by the benzyl type radical, the decay was much faster compared to hydroxyl radical.	(Paul (Guin), et al., 2014)
Landfill leachate	COD 1254 mg/L	Sodium persulfate	Thermally activated (27 –	pH = 3-4, higher temperature, and higher dose of persulfate favoured the removal of COD and	(Deng & Ezyske, 2011)

	Ammonia nitrogen 500 - 2000 mg/L	156.75 mM	50°C)	ammonia. At $S_2O_8^{2-}$:12 COD = 2 and 50°C, the COD removal rates were 79% and 91% at pH = 8.3 and 4, respectively; and the ammonia nitrogen removal reached 100% at both pH values.	
Landfill leachate	COD 1900 mg/L	Sodium persulfate 62.5 mM	Electrochemical: anode Ti/IrO_2-RuO_2-TiO_2, cathode Ti Fe (II) 15.6 mM	62.2% COD removal occurred at pH = 3 in 60 minutes, current density was 13.89 mA/cm^2. At higher pH the degradation rate was lower, e.g. at pH = 9, the removal was only 22%. COD removal efficiency increased with persulfate concentration. However, it led to the side reaction between persulfate and free sulfate radical. Fe (II) dosages were effective until 15.6 mM, in case of higher dosages the Fe (II) acted as a scavenger. Higher densities (>13.89 mA/cm^2) caused side reactions.	(Zhang, et al., 2014)
Landfill leachate	Total organic carbon (TOC) 55 ± 19 mg/L Colour (UV254)	Sodium persulfate 4762 mg/L	Microwave irradiation	TOC removal of 79.4%, colour removal of 88.4%, and UV_{254} removal of 77.1% were reached at power 550W, 85°C and within 30 minutes. Reaction rates increased with microwave power, although at 775W the effect was opposite. Larger persulfate doses had a scavenging effect.	(Chou, et al., 2015)
Landfill leachate (stabilized)	COD 1780 – 2530 mg/L NH_3-N 780 – 1090 mg/L	Sodium persulfate 35 g	Ozone 80 g/m^3	72% COD and 55% NH_3-N removal occurred at pH = 10, in 210 minutes. Increasing the pH, the removal efficiencies for COD and ammonia were also increased. Although the removal of compounds increased with time, the optimal time was 210 minutes. It was found that persulfate and ozone act as oxidants better together than separately.	(Abu Amr, et al., 2013)
Landfill leachate	COD 19180	Sodium	H_2O_2 8.63 g	81% COD and 83% NH_3-N removal occurred	(Hilles, et al.,

(stabilized)	– 20448 mg/L NH_3-N 2450 – 3400 mg/L	persulfate 5.88 g		at pH = 11, in 120 minutes. Elevating pH the removal of compounds was increased, although significant removal efficiency was obtained also at neutral pH. Although the removal of compounds increased with time, the optimal time was 120 minutes. It was found that persulfate and hydrogen peroxide act as oxidants better together than separately.	2016)
Phenol	0.1 mM	Sodium persulfate 50 mM	Ultraviolet (UV) irradiation 20W λ = 295-400 nm UV fluence 0.18 mWcm^{-2}	95% removal occurred in 900 minutes, adding 0.2 g/L magnetite (Fe_3O_4) at pH = 5.	(Avetta, et al., 2015)
Phenol	20 ppm	Potassium persulfate 1.48 g/L	Carbon nanotubes, 0.2 g/L catalyst	Complete phenol removal occurred in 45 minutes and at 45°C. Increase of temperature increased the degradation speed (at 25°C complete removal was achieved in 90 minutes).	(Sun, et al., 2014)
p-Nitroaniline (PNA)	0.2 mM	Sodium persulfate 8 mM	Iron oxide magnetic nanoparticles Fe_3O_4 5.32 g/L	Complete removal occurred at 270 minutes, at 25°C, at pH = 7. The mineralization rate was 67%. Increasing persulfate or Fe_3O_4 concentrations, the degradation rate increased until certain amount -16 mmol/L and 7.98 g/L, respectively. Increasing temperature or decreasing pH, increased PNA degradation rate. The higher was initial concentration of PNA, the lower was the degradation rate.	(Zhao, et al., 2015)
Sulfamethoxazole (SMX)	30 μg	Potassium persulfate 2400 μg	Fe (II) 2400 μg	74.7 % degradation rate was achieved at pH = 6, in 240 minutes. Adding CA and EDTA at pH = 6 whereas 300	(Ji, et al., 2014)

				μg potassium persulfate was used, the degradation rate increased from 29.8% to 35.5% and 49.7%, respectively in 240 minutes. Adding EDDS at the same conditions did not have almost any effect (degradation rate was 29.5%).	
Tetramethylammonium hydroxide (TMAH)	1.1 mM	Sodium persulfate 50 mM	Ultraviolet (UV) irradiation 15 W $\lambda = 254$ nm UV fluence 4.5 mWcm^{-2}	Complete TMAH removal occurred in 130 minutes, at 20°C and at pH = 2. TMAH degradation increased with increasing persulfate dosage till persulfate concentration was 50 mM. Higher reaction temperature and stronger UV irradiation increased also the degradation of TMAH.	(Wang & Liang, 2014)

4.1.Resume for using persulfate in water and wastewater matrix

4.1.1. Degradation mechanisms

The reaction mechanism of persulfate can be led either by sulfate or hydroxyl radical, depending on the contaminant degradation mechanism. It has been proposed that sulfate radical preferably removes electrons from an organic molecule to produce an organic radical cation, whereas hydroxyl radical adds to carbon double bond, aromatic rings or abstracts hydrogen from the carbon hydrogen bond (Antoniou, et al., 2010; Mahdi Ahmed, et al., 2012). Therefore, it was proposed at ciprofloxacin and sulfamethoxazole degradation, that for electron rich compounds, such as ciprofloxacin, both sulfate radical and hydroxyl radical could take part in oxidation; while for less electron rich compounds, such as sulfamethoxazole, only hydroxyl radical could play a dominant role (Ji, et al., 2014).

Mostly the degradation is carried out via sulfate radicals (Lin & Wu, 2014; Deng, et al., 2013; Nie, et al., 2014; Zhao, et al., 2014; Tan, et al., 2012; Epold, et al., 2015; Lee, et al., 2012; Lee, et al., 2013; Liang, et al., 2004; Liang, et al., 2009).

The degradation mechanism and the predominant species can be examined through adding excessive radical scavengers. For example, impact of ethanol (EtOH), phenol and TBA on the CBZ degradation were examined. 87% CBZ was removed in the absence of any scavenger. Adding 400 mM EtOH and phenol, only 21.58% and 0.85% CBZ was removed, respectively (Deng, et al., 2013). Phenol has stronger inhibiting effect because of its higher reaction rate with sulfate radicals. However, 52.58% CBZ removal was observed at the same amount of TBA. TBA demonstrated high reaction rate with hydroxyl radicals and relatively slow reaction rate with sulfate radicals (Deng, et al., 2013). Therefore, it can be concluded that sulfate radicals could be the dominant species for the CBZ degradation.

In some cases persulfate reacts with organics directly and forms sulfate radicals or creates organic radicals (Huang, et al., 2002). Sulfate radicals propagate secondary radicals (Matzek & Carter, 2016). Overall contaminant degradation can be described (Matzek & Carter, 2016):

$$S_2O_8^{2-} + R \rightarrow SO_4^{2-} + SO_4^{-\cdot} + R^{*}\, cr \qquad [64]$$

$$S_2O_8^{2-} + R \rightarrow 2SO_4^{-\cdot} + R^{\cdot} \qquad [65]$$

4.1.2. *Effects of pH*

In most cases, pH had a significant effect on contaminant removal. Acidic pH (2-5) most frequently improves the degradation of the contaminants by forming hydroxyl radicals (Liang & Su, 2009; Xu & Li, 2010; Ji, et al., 2015; Deng, et al., 2013; Nie, et al., 2014):

$$SO_4^{-\cdot} + H_2O \rightarrow SO_4^{2-} + OH^{\cdot} + H^+ \qquad [66]$$

For example, the degradation of Azo dye Orange G showed that reaction's rate constant increased from 0.0037 to 0.04 at pH 9 and 3.5, respectively (Xu & Li, 2010). At antipyrine thermally activated persulfate degradation 54.3% of antipyrine was removed at pH 4.5, 39.4% at pH 7 and 35.8% at pH 9.5 (Tan, et al., 2015). However, the degradation increased at pH 11, being 54.8% (Tan, et al., 2015). Also at CBZ degradation some improvement of removal at pH 11 was observed (Deng, et al., 2013). It was explained with hydroxyl ion activating sulfate radical to hydroxyl radical. Hydroxyl radical has a higher oxidation potential (E_0 = 2.7 V) than sulfate radical (Tan, et al., 2012).

Some improvement of contaminant degradation can also be noted at neutral pH (6-8) (Tan, et al., 2012) and in a few cases slightly alkaline pH (9-10) (Gao, et al., 2015). For example, at diuron removal, it was observed that the highest degradation rate was at pH 6.3 (Tan, et al., 2012). It was explained with generation of less reactive species, like bisulfate, which will reduce sulfate radical level at very acidic condition. At SMX removal, it was observed that increasing pH from 3 to 10, the degradation rate increased from 1.53×10^{-2} to 1.78×10^{-2} min^{-1} (Gao, et al., 2015). It was explained that SMX was at low pH in a major fraction non-protonated and therefore, less susceptible to the sulfate radical oxidation than that of the deprotonated form at higher pH.

4.1.3. *Effects of additives*

Groundwater contains several naturally found ions, which affect contaminants degradation by activated persulfate, usually by decreasing the degradation efficiency (Xu & Li, 2010; Ji, et al., 2015; Deng, et al., 2013). For example, at atrazine degradation, higher chloride, carbonate and bicarbonate concentrations showed inhibitory effect (Ji, et al., 2015), in the case of CBZ degradation, only carbonate and bicarbonate had a considerable effect (Deng, et al., 2013). At CAP degradation bicarbonate, nitrite and hyaluronic acid significantly slowed down the degradation rate (Nie, et al., 2014).

There are also studies that show increase in contaminant degradation when additives are present. For example, at degradation of bisoprolol, none of the additives, except bicarbonate, showed a negative effect (Ghauch & Tuqan, 2012). It was explained with the formation of new radicals that can be involved in oxidation reaction inhibiting bisoprolol degradation.

4.1.4. Effects of persulfate concentration

Mainly, it has been found that higher persulfate concentration increases the contaminants removal (Deng, et al., 2013). Typical concentration ratios of persulfate and contaminant in water and wastewater range from 1:1.3 to 1:525 and from 1:5 to 1:200, respectively, as can be concluded from Tables 3 and 4. The most common ratios in water matrix were from 1:20 to 1:50. In wastewater the concentrations of persulfate were somewhat higher. Some studies suggest that there is an optimum persulfate concentration. Exceeding the optimum concentration, the contaminant degradation is inhibited by the reaction of excess persulfate with persulfate radicals, e.g. the excessive persulfate competes with contaminant (Lin & Wu, 2014; Moussavi, et al., 2016; Wang & Liang, 2014):

$$SO_4^{-\cdot} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{2-} \qquad [67]$$

For optimization, persulfate levels for degradation of contaminants can be customized. However, it is not always feasible as in field conditions there might be more than one contaminants with different degradation rates to be degraded or the water can contain scavenging species. Most of the studies reported pseudo-first order based reactions, which were based on the contaminants concentrations (Tan, et al., 2015; Ji, et al., 2015; Deng, et al., 2013; Nie, et al., 2014). However, reaction rates follow second order kinetics with respect to the contaminant and persulfate concentrations (Matzek & Carter, 2016; Xie, et al., 2015). Using second order kinetics and rate constants could help to minimize the amount of persulfate needed for the desired removal of the contaminant.

Persulfate adding mode can also play a role in the degradation efficiency. For example, at CAP degradation, a single injection compared to sequential addition of persulfate led to the highest degradation efficiency (Nie, et al., 2014).

4.1.5. Degradation by activation type

Persulfate, as a stable oxidant at room temperature or lower, are most commonly activated via heat, transition metals or ultraviolet light, forming highly reactive sulfate radical (He, et al., 2014):

$$S_2O_8^{2-} + activator \rightarrow SO_4^{-\cdot} + (SO_4^{-\cdot}\ or\ SO_4^{2-}) \qquad [68]$$

Without activation, persulfate ion reacts with some organic chemicals, but lesser than with activated persulfate as it has lower oxidation potential (E°=2.01 V). Persulfate activators are also important for enhancing the mineralization of contaminants and the speed of reaction.

4.1.5.1. *Heat activation*

Persulfate forms two sulfate radicals through break-off of peroxide bond due to absorption of heat energy (Kolthoff & Miller, 1951):

$$S_2O_8^{2-} + heat \rightarrow 2SO_4^{-\cdot} \qquad [69]$$

The activation energy depends on pH conditions. At neutral pH conditions the activation energy is 119-129 kJ/mol, at alkaline pH conditions it is 134-139 kJ/mol and at acidic conditions it is 100-116 kJ/mol (House, 1961). Therefore, it can be concluded that preferred environment is acidic or neutral. The rate constant of sulfate radical formation at pH 1.3 varies from 1.0×10^{-7} s^{-1} at 25°C to 5.7×10^{-5} s^{-1} at 70°C (House, 1961). Optimum activation temperature ranges commonly from 50 to 70°C, depending on the contaminant (Nie, et al., 2014; Tan, et al., 2012; Tan, et al., 2015; Ji, et al., 2015; Ghauch & Tuqan, 2012; Deng, et al., 2013; Zhao, et al., 2014; Huang, et al., 2002; Luo, 2014; Ghauch , et al., 2015).

In all studies (tables 3 and 4), where heat was used as a persulfate activator, higher temperatures led to increasing degradation and solubility of the contaminants into the aqueous phase. For example, at antipyrine and CBZ degradation, the degradation rate constant increased over 100 and 60 times, respectively, when the temperature was increased from 40 to 70°C (Tan, et al., 2015; Deng, et al., 2013). However, it is also important to optimize processes and make them feasible. Therefore, due to minimizing the energy consumption, the optimum temperature was not always the highest temperature. For example, 100% removal of bisoprolol was achieved after 15, 25 and 45 minutes of reaction at 70, 65 and 60°C, respectively (Ghauch & Tuqan, 2012). Therefore, for further experiments 60°C was chosen. In addition to energy savings, it was discovered that the overall consumption of persulfate varies depending on the reaction temperature. For example, at bisoprolol removal, at 60°C only 5.0% of the initial persulfate concentration was consumed after only 45 minutes of reaction. However, 8.8% and 9.2% of persulfate were consumed at 65°C and 70°C after a reaction time of about 25 and 15 minutes respectively (Ghauch & Tuqan, 2012).

4.1.5.2. *UV light activation*

Persulfate is activated via UV light forming the sulfate radical (Berlin, 1986):

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{-\cdot} \qquad [70]$$

UV energy breaks the oxygen-oxygen bond similarly to heat-activated persulfate process (Dogliotti & Hayon, 1967). With UV activation, an important role plays the wavelength and UV fluence rate. Most commonly used wavelength is 254 nm as the reaction time is the shortest compared to the other wavelengths (Xie, et al., 2015; Gao, et al., 2012; Shu, et al., 2015; Lin & Wu, 2014; Wang & Liang, 2014).

At SMT removal photolysis, persulfate oxidation, UV/hydrogen peroxide and UV/persulfate processes were compared. In 45 minutes 22.0%, 15.1%, 87.5% and 96.5% SMT removal was achieved, respectively (Gao, et al., 2012). Therefore, it can be concluded, that UV/persulfate process was the most effective treatment for the SMT removal.

AB113 removal study's results indicated that at low-persulfate dosage of 1.05 mM, the colour removal increased from 61.2 to 87.9% in 10 minutes when the UV light intensity increased from 14 to 30 W/l, respectively (Shu, et al., 2015). For the highest persulfate dosage of 6.3 mM, the AB113 removal efficiencies were very close during whole reaction period (Shu, et al., 2015). Therefore, it can be concluded that persulfate dosage played more important role on AB113 degradation than that of UV intensity.

At TMAH removal, as the UV light intensity was increased from 8 W to 15 W, the degradation rate constant of TMAH increased from 0.0117 to 0.0389 min^{-1}, and also for the TOC from 0.0049 to 0.0106 min^{-1} (Wang & Liang, 2014). Hence, it can be concluded that the persulfate degradation is highly dependent upon the intensity of the UV light source.

At beta-lactam antibiotics removal two different UV fluence rates were tested and it resulted in comparable degradation of the target compounds at the same UV fluence (He, et al., 2014). Hence, as long as the UV photons are entered to the solution, the same or comparable target compound degradation can be observed.

At phenol removal the addition of magnetite (Fe_3O_4) to UV light, increased the degradation rate (Avetta, et al., 2015) . Also it was suggested that the addition of magnetite is very useful at low persulfate concentration and much less effective at elevated oxidant levels (Avetta, et al., 2015).

4.1.5.3. Iron activation

Persulfate is activated via one-electron transfer applying metals such as iron, zinc, cobalt, silver, copper and manganese, forming the sulfate radical (Travina, et al., 1999):

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{-\cdot} + SO_4^{2-} + Fe^{3+} \qquad [71]$$

The rate constant for forming sulfate radical is $2.0 \times 10^{1}\ M^{-1}\ s^{-1}$at 22°C (Travina, et al., 1999). As soon as sulfate radical is generated, it reacts with excess ferrous ions in solution and generates ferric form (Buxton, et al., 1997; Hussain, et al., 2014):

$$SO_4^{-\cdot} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} \qquad [72]$$

The rate constant at pH from 3 to 5 for the reaction is $4.6 \times 10^{9}\ M^{-1}\ s^{-1}$at 22°C and activation energy is -18 kJ/mol (Buxton, et al., 1997). The overall reaction can be described as follows (Buxton, et al., 1999):

$$S_2O_8^{2-} + 2Fe^{2+} \rightarrow 2Fe^{3+} + 2SO_4^{2-} \qquad [73]$$

The rate constant for the overall reaction is $3.1 \times 10^{4}\ M^{-1}\ s^{-1}$ at pH less than 0.4 (Buxton, et al., 1999). The activation energy is 50.23 kJ/mol (Fordham & Williams, 1951).
In some studies, indirect persulfate activation with zero-valent iron was used (Hussain, et al., 2014; Jiang, et al., 2013; Li, et al., 2015; Kusic, et al., 2011):

$$Fe^{0} + S_2O_8^{2-} \rightarrow Fe^{2+} + 2SO_4^{2-} \qquad [74]$$

Reaction described by Eq. (74) is followed by reaction described by Eq. (73). Insufficient iron concentration causes inefficient persulfate usage, but too high concentration results in scavenging of sulfate radical (Eq. [72]). Study analyzing the degradation of aniline, showed that increasing zero-valent iron doses aniline degradation efficiency increased (Hussain, et al., 2014). It was explained with more sites for sulfate radical generation at higher zero-valent iron amount. The activation of persulfate took place probably through the electron transfer at the zero-valent iron surface or by ferrous ion. However, the degradation began to decrease at certain level as excess ferrous ions acted as scavengers (Hussain, et al., 2014). Studies show that increase in contaminant concentration decreased the rate constant of degradation (Hussain, et al., 2014). The lower degradation of contaminant was due to excess concentration of contaminant that probably covered the iron surface and active sites for persulfate, retarding the degradation reaction (Hussain, et al., 2014).

Persulfate to iron ratio ranged from 1:1 (Ji, et al., 2014; Xu & Li, 2010) to 59:1 (Jiang, et al., 2013). Exact ratios vary with iron forms, addition methods (sequential, continuous, at time) and target contaminants. For example, using four sequential additions versus a single dose of ferrous ion enhanced the degradation of bisphenol from 49% to 97% and to 100% with continuous addition at the same conditions (Jiang, et al., 2013). At removal of levofloxacin, it was found that increasing persulfate or ferrous ion dosage, the degradation rate was improved, 2.6 and 3.4 times, respectively (Epold, et al., 2015). The efficacy of contaminant degradation was found to decrease with the increase of pH value, although at acidic and neutral conditions the performance was basically the same (Epold, et al., 2015).

In order to overcome the problem, that ferrous ion could act as a scavenger in the process, the stabile concentration of ferrous ions in solution can be achieved by chelating agents. Most commonly used chelates to iron are EDTA, citric acid, sodium thiosulfate and oxalic acid. Citric acid-ferrous ion complex acted as a most effective activator in comparison with EDTA and oxalic acid for the destruction of contaminants, which has determined the broader application prospect of citric acid (Zhang, et al., 2014; Ji, et al., 2014). Also, in comparison with other chelating agents, citric acid has advantages of being environmentally friendly and readily biodegradable (Liang, et al., 2004). The concentration of chelating agent and ferrous ion do not follow a linear relationship with the degradation rate of contaminant (Zhang, et al., 2014).

Using weak magnetic field promotes zero-valent iron corrosion and ferrous ion generation (Xiong, et al., 2014). At weak magnetic field appearance zero-valent iron particles are magnetized and an induced inhomogeneous magnetic field is generated around the zero-valent iron particles (Xiong, et al., 2014). Magnetic field caused an additional convective transfer of paramagnetic ferrous ion due to the Lorentz force and consequently zero-valent iron corroded (Xiong, et al., 2014). Moreover, the field gradient force moved ferrous ions along the field gradient. This caused uneven distribution of ferrous ions on zero-valent iron surface and resulted in localized corrosion (Liang, et al., 2014). It was found that weak magnetic field did not change the radical species primarily responsible for contaminant degradation. It improved significantly the removal of contaminants by accelerating the ferrous ion release from zero-valent iron in the iron-persulfate process (Xiong, et al., 2014). The enhanced ferrous ion generation induced the increased production of sulfate radicals and ferric ions, and thus the improved contaminants removal and faster pH drop. For example, in study concerning the acid orange removal, the rate constants of acid orange removal were raised by 14.6–17.0 times due to the application of a weak magnetic field at the same zero-valent iron dosage (Xiong, et al., 2014).

Also the Fenton-persulfate combination has been studied. It has been concluded, that it is more effective than ferrous-persulfate combination, although the process needs careful optimization of activator’s dosage, especially ratios for hydrogen peroxide and persulfate (Epold, et al., 2015).

4.1.5.4. *Electrochemical activation*

Electrochemical reactions generate sulfate radical at the cathode, similarly to the one-electron transfer redox reaction for iron-activated persulfate (Matzek & Carter, 2016):

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{-\cdot} \qquad [75]$$

Solid iron produces ferrous ions through chemical and anodic reactions, activates the persulfate and can be regenerated at the cathode for additional persulfate activation (Matzek & Carter, 2016):

$$Fe^0 \rightarrow Fe^{2+} + e^- \qquad [76]$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-\cdot} \qquad [77]$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad [78]$$

Applied current is one of the key operating parameter that affected removal efficiency in the electrochemical process. At PCP removal, degradation rate increased with increasing applied current (Govindan, et al., 2014). This was due to the extent of anodic dissolution of iron electrode and consequently the amount of $Fe(OH)_3$ and $Fe(OH)_n$ precipitates available for the attraction of PCP also increased (Govindan, et al., 2014). Current density was also examined at acid orange 7 removal. Increasing the current density from 8.4 to 33.6 mA cm^{-2}, the decomposition percentages of persulfate increased from 42.4% to 67.6% and the decolourization efficiencies increased from 71.2% to 84.3% accordingly (Wu, et al., 2012). However, it was found that at certain elevated level, current density would result in an enhancement in side reactions, e.g. oxygen and hydrogen evolution (Zhang, et al., 2014):

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad [79]$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad [80]$$

These would inhibit the main reactions such as electro-regeneration of ferrous ion from ferric ion and consequently catalytic activation of persulfate by ferric ion (Zhang, et al., 2014).

Decolourization rate and the decolourization efficiency increased with the increase of the ferrous ion concentration (Wu, et al., 2012). The ferrous ion can activate persulfate to produce sulfate radicals.

4.1.5.5. Less common activations

4.1.5.5.1. Microwave activation

In microwave-activated persulfate process the heating is at molecular-level and thus leads to homogeneous and quick thermal reactions (Lee, et al., 2012). Applying microwave irradiation simultaneously with oxidants, free radicals were generated (Chou, et al., 2015). The reaction rate increased in the microwave field due to microwave-specific effects. Till today there is not a common understanding, whether these are non-thermal or thermal effects (Chou, et al., 2015). Persulfate oxidation rates increased with increasing powers. The rate constant (k) can be determined from the Arrhenius equation [$k = A \times \exp(-\Delta G/RT)$]. The microwave field increases molecular vibrations due to orientation of polar molecules that enlarges the value of the constant A (Costa, et al., 2009).

At PFOA removal, the formation of sulfate radical was fastest at 130°C; the same rate was achieved also at 90°C, but in longer time (Lee, et al., 2012). However, the highest PFOA removal was achieved only at 90°C.

Maximum total organic consumption reduction (79%) was achieved at 550 W with a persulfate dose of 4762 mg/L in landfill leachate study (Chou, et al., 2015). Higher power led to generation of excessive persulfate oxidation and therefore the degradation efficiency decreased (Chou, et al., 2015).

4.1.5.5.2. Activation with activated-carbon

Persulfate oxidation was catalysed also with activated-carbon. Activated carbon has a large surface area and a porous structure. Oxygen functional groups on activated-carbon surfaces act as an activator to mediate electron-transfer (Liang, et al., 2009):

$$AC_{surface} - OOH + S_2O_8^{2-} \rightarrow AC_{surface} - OO\cdot + SO_4^{-\cdot} + HSO_4^- \qquad [81]$$

$$AC_{surface} - OH + S_2O_8^{2-} \rightarrow AC_{surface} - O\cdot + SO_4^{-\cdot} + HSO_4^- \qquad [82]$$

The combined use of activated-carbon and persulfate led to a more effective and efficient removal (10 times better than using only persulfate) of perfluorooctanoic acid under lower temperature (25°C) and within a shorter reaction time (Lee, et al., 2013). Also, it is remarkable that only small amounts of short-chain perfluorooctanoic acid's intermediates were detected (Lee, et al., 2013).

It was found that reaction rate constant increased with the increase of activated-carbon dosage (Liang, et al., 2009). At trichloroethylene removal, the variation of activated-carbon surface properties caused by persulfate oxidation included the increase of acidity concentration, a reduced pH, the decrease of activated-carbon surface area, and the alteration of contaminant’s adsorption kinetic behaviour (Liang, et al., 2009). Hence, these changes led to a reduction in adsorption capacity and a weakened intensity of the adsorption reaction, which are related to removal of π-electrons from the activated-carbon matrix by persulfate oxidation (Liang, et al., 2009). Even though the increased number of acidic groups on the activated-carbon surface resulted in weaker adsorption interactions between trichloroethylene and activated-carbon, the presence of activated-carbon could activate persulfate to destroy trichloroethylene during the course of simultaneous adsorption and oxidation reactions (Liang, et al., 2009).

At acid orange 7 removal activated-carbon reuse experiment was carried out. Although efficiencies of acid orange 7 removal for every reuse cycle gradually decreased, the degradation ratio was still over 60% in 5 hour reaction after using activated-carbon for the fourth time (Yang, et al., 2011). The deactivation of activated-carbon could be due to the following reasons: the incomplete removal of acid orange 7 adsorbed on activated-carbon surface inhibited the interaction of persulfate and activated-carbon; the intermediate products of acid orange 7 decomposition remaining on the surface of activated-carbon were not advantageous for the degradation reaction and the adsorbed fraction of organic contaminants on the activated-carbon surface were nearly unreactive.

4.1.5.5.3. Hydrogen peroxide activation

Persulfate was also activated with hydrogen peroxide. It was found that adding persulfate and hydrogen peroxide simultaneously had the best efficiency (81%) for reduction of chemical oxygen demand in landfill leachate at pH 11 (Hilles, et al., 2016). The results demonstrated that the combined persulfate and hydrogen peroxide process could be efficiently used for stabilized leachate treatment also at natural leachate pH (7–9) (Hilles, et al., 2016). Moreover, the biodegradability of the leachate was improved (Hilles, et al., 2016).

4.1.5.5.4. Other

At SD removal, ultrasound was used to activate persulfate and also zero-valent iron was added. It was demonstrated that ultrasound could lead to a significant synergy in the degradation of antibiotic SD as compared to its comparative systems (Zou, et al., 2014). The result revealed that the system could effectively degrade SD with a relatively low persulfate dosage (1.84 mM) at a broad pH range of 3–7 (Zou, et al., 2014). The promotional role of ultrasound could be described as follows: acceleration in the heterogeneous zero-valent iron corrosion reactions in the zero-valent iron – water interphase, through enhancements in the reaction mass transfer and the regeneration of zero-valent iron surface; enhancement in the bulk radical reactions caused by the sonochemical cavitation effect (Zou, et al., 2014).

At SCP removal persulfate was activated with nitrogen doped reduced graphene oxide. Complete SCP degradation occurred in 45 minutes at 45°C (Kang, et al., 2016).

4.2. Advantages, Disadvantages and Cost of Persulfate Application

4.2.1. Advantages

Persulfate as a novel oxidant has many advantages over the other well-known oxidants. The following describes advantages resulting from persulfate physical properties. An important advantage is high aqueous solubility (saturated solution: 2.5M $Na_2S_2O_8$ at 20 °C) (Ji, et al., 2014; Liang, et al., 2006). Persulfate also has no odour and due to its powder form and stability is also easy to transport. Also due to the previously mentioned properties persulfate can be transferred more effectively to the contaminated zones to react with the contaminants (Huang, et al., 2002).

The following describes advantages resulting from persulfate chemical properties. One of the most important property is effectiveness of oxidation. Persulfate has the redox potential of 2.01V over a wide range of pH (Liang, et al., 2006). Activating persulfate results to forming of sulfate and hydroxyl radicals, which have even more higher redox potential, 2.6V and 2.7V, respectively. In most cases the sulfate radical is predominant radical. Nonetheless hydroxyl radical has a slightly higher redox potential than sulfate radical, the hydroxyl induced oxidation is unselective (Tan, et al., 2012). For example, with increasing pH hydroxyl radicals may be completed and thereby lowering the treatment rate by many other co-existing species, like bicarbonate and carbonate (Tan, et al., 2012).

Some studies compared persulfate to other common oxidants as hydrogen peroxide and ozone and found persulfate more stable in the subsurface (Huang, et al., 2002; Huling & Pivetz, 2006). This is due to the fewer mass transfer and mass transport limitations (Huling & Pivetz, 2006). Also the natural oxidant demand for persulfate is low. The stability of the persulfate also allows it to be injected at high concentrations, storage and transport it easily, even to contamination in hard to reach places (Huling & Pivetz, 2006; Waldemer, et al., 2007; Ji, et al., 2014). Persulfate will undergo density-driven and diffusive transport into low-permeability materials (Huling & Pivetz, 2006).

It is noteworthy that the slow activation of persulfate by Fe (II) was reported to be suitable for subsurface application (Ji, et al., 2014). The reactivity-saving characteristics of persulfate-Fe(II) system would be beneficial to systems that are required to respond to prolonged and low level discharge of contaminants to the aquatic environment (Tsitonaki, et al., 2010).

Activating persulfate with irradiated magnetite leads to lower persulfate application and therefore to lower cost of the oxidant (in case using sunlight for radiation) and lesser need to eliminate the excess oxidant after treatment (Avetta, et al., 2015).

4.2.2. Disadvantages

The main disadvantage is the high cost of the persulfate. Sodium persulfate costs more than hydrogen peroxide and potassium permanganate. Persulfate also it requires activation, e.g. a catalyst. Due to the lack of naturally occurring catalysts and difference in transport behaviour of these reagents upon injection, it is difficult to achieve optimal mix of reagents in the subsurface (Huling & Pivetz, 2006). Although persulfate is more stable that some oxidants, it is less stable than permanganate and therefore will not persist as long in subsurface systems (Huling & Pivetz, 2006).

Persulfate based oxidation works very efficiently for clean water matrices. However, the oxidation efficiency decreases as water or wastewater matrices become more complex. It has been noted that substances, that contain high molecular weight compounds, high salts and high particulates, cannot be oxidized efficiently by persulfate.

4.2.3. Cost

The cost for persulfate processes has been studied very vaguely. There are only few studies that have examined operating cost for persulfate based processes. For example, in study investigating the removal of p-nitrophenol using a hybridized photo-chemical activated persulfate process, it was found that the most cost effective condition for the process was at persulfate concentration 1452 mg/l, at pH 4.5 and 25ºC (Zarei, et al., 2015). With the described condition 89% of p-nitrophenol was degraded after 120 minutes. The operation cost for the process was USD$ 3.7/m^3 (Zarei, et al., 2015).

Another example is treatment of stabilized landfill leachate with combined sodium persulfate and hydrogen peroxide based advanced oxidation process. It was concluded that around USD$10.7 was required to remove 81% of organics (there was 1 kg of COD in landfill leachate) from 50 liters of leachate (Hilles, et al., 2016). Major part of the costs was related to the chemicals used, e.g. sodium persulfate and hydrogen peroxide. It was concluded that although the cost is high, the process achieved significant organics removal and it worked efficiently at leachate’s natural pH (Hilles, et al., 2016).

Somewhat comparably to the previous example is the treatment of high-strength wastewater by ferrous ion activated persulfate and hydrogen peroxide. It was concluded that 50.2 Euro/m^3 was required to decrease chemical oxidant demand by 52% (Kattel, et al., 2016).

In case of more energy consuming activation processes, like heat, ultraviolet light, etc. in some cases the cost for energy has been calculated. For example, the study investigating landfill leachate treatment with microwave-enhanced persulfate oxidation, it was concluded that the energy cost was USD$ 6.03/m^3 and using conventional heating oxidation at the same conditions the energy cost was almost the same, USD$ 6.10/m^3 (Chou, et al., 2015).

Although there are only a few data regarding operating costs, it could be concluded that focusing on one specific contaminant removal is more cost efficient. Therefore, the persulfate oxidation processes are more suitable as a part of water or wastewater treatment process.

5. Conclusions

Based on reviewed articles it can be concluded that activated-persulfate is a viable method for destruction of contaminants in water and wastewater. With optimized conditions, in some cases, 100% contaminant removal can be accomplished. Persulfate is effective for degrading relatively concentrated pollutants and recalcitrant organics. More resistant contaminants require longer time for reaction and a higher persulfate dosage. The efficiency of contaminants degradation depends also on the competition kinetics between contaminants, activator and reactive species in the water or wastewater.

There are many challenges to optimize the process for efficient, timely and cost-effective contaminant removal in practical systems. One key issue in optimizing the process is the slow release of persulfate. It could be achieved with special physical techniques. However, it needs further experiments with broader range of chemicals and reaction conditions. Another issue that does not have a solution is how to reuse the residual persulfate. Also a little work has been done regarding removal of excessive sulfate ions in treated water.

While there could be a challenge with redundant sulfate ions, an excessive iron could also become a problem. By today, the only solution found is using iron-chelator. Exploiting magnets after persulfate activation with nano-iron-chelator enables also reuse of iron-chelator. Therefore, abovementioned process could have a great potential and should be investigated further.

Although the outcomes typically improve with increased persulfate concentrations, it can lead to inefficient resource management and depletion of reactants, also limiting the degradation of contaminants. Better knowledge on reaction rates of both persulfate and contaminant, could allow persulfate usage’s optimization in specific systems. Also, it has been found that electrochemical persulfate activation could minimize the usage of persulfate or iron via regeneration. This brings along also better mineralization.

A novel promising technique is persulfate activated by activated-carbon. Activated-carbon acts as a catalyst for persulfate activation and for removal of some contaminants and by-products as an adsorbent. Also, it is the most environmentally friendly solution.

An important factor is also the characteristics of water or wastewater matrix. It could be concluded that mainly, in cases, where the contaminant degradation process was favoured by acidic conditions, additives, which raised the solution’s pH had a significant scavenging effect, e.g. bicarbonate and *vice versa*.

For the final conclusion, the implementation of these novel methods requires follow-up studies that should verify their usefulness for promoting effective persulfate degradation and advanced process characteristics for practical application, especially for upscaling the applications and the cost-effectiveness. Based on the studies examined, persulfate has a great potential as a novel oxidant in treatment of the contaminated water and wastewater, but more research is necessary to confirm that.

6. Abstract

Considerable amount of hazardous and bio-refractory natured complex molecules have been detected in the environment due to the developing industry and ever-increasing human demand. Therefore, conventional biological processes are not capable of degrading all the contaminants anymore and new effective treatment methods have to be adopt. Thus, the objective of Master’s thesis is to review the latest experiences for using persulfate in AOPs for remediation of water and wastewater, and also to identify the best practices and suggest the possible direction of future research.

In the last two decades a lot of research work has been carried out in the area of AOPs. It generally uses strong oxidising agents, catalysts (iron ions, electrodes, metal oxides) and irradiation (UV light, solar light, ultrasounds) separately or in combination under mild conditions (low temperature and pressure). A novel AOP is persulfate-based oxidation. Persulfate is a stabile and strong oxidant, with oxidation potential of 2.01 V. As persulfate anion has slow oxidative kinetics at ordinary temperatures for most contaminant species and can be applied to a limited number of contaminants, it is typically activated. At persulfate activation more powerful oxidant, sulfate free radical with oxidation potential of 2.6 V is formed. Most common activation methods are heat activation, UV light activation, iron activation, including using chelates and magnetic fields and electrochemical activation.

It can be concluded that activated-persulfate is an effective method for degrading relatively concentrated pollutants and recalcitrant organics. More resistant contaminants require longer time for reaction and a higher persulfate dosage. The efficiency of contaminants degradation depends also on the competition kinetics between contaminants, activator and reactive species in the water or wastewater. In most cases elevated temperature and acidic or neutral pH enhanced the degradation process of the contaminants. Using chelates in iron-activated processes made possible the activators regeneration. The same effect can be achieved with using weak magnetic fields or electrochemical technology. A novel promising and environmentally friendly technique is persulfate activated by activated-carbon. Activated-carbon acts as a catalyst for persulfate activation and for removal of some contaminants and by-products as an adsorbent.

Most important advantages are persulfate’s high solubility; stability; high oxidation potential and even higher potential when forming a sulfate and hydroxyl radical. Key issues that need further research in optimizing the process are the slow release and reuse of residual

persulfate. Also the cost of the process and *in situ* solutions have been poorly dealt with and need further research.

7. Kokkuvõte

Suure nõudluse tõttu toodetakse üha enam ohtlikke ning bioloogiliselt raskesti lagunevaid aineid. Seetõttu selliste ainete looduslik lagunemine on pea võimatu ning on vaja arendada ja rakendada uusi tõhusaid tehnoloogilisi puhastusmeetodeid. Magistritöö eesmärgiks on anda kirjanduse põhjal ülevaade viimastest persulfaadi kasutuskogemustest süvaoksüdatsiooniprotsessides (SOP) vee ja reovee puhastamiseks. Samuti on eesmärgiks kirjeldada olemasolevat parimat praktikat ning selle põhjal teha ettepanekuid uute uuringusuundade kohta.

Viimasel paarikümnel aastal on SOP palju uuritud. Tavaliselt kasutatakse sellistes protsessides tugevaid oksüdante, katalüsaatoreid (metalli ioonid, elektroodid, metalloksiidid) ja kiirgust (UV, päike, ultraheli), nii eraldi kui ka kombineeritult, mõõdukatel tingimustel (madal temperatuur ja rõhk). Persulfaadil põhinev oksüdatsioon on uuenduslik SOP. Persulfaat on stabiilne ja tugev oksüdant, mille oksüdatsioonipotentsiaal on 2,01 V. Persulfaadi aniooni oksüdatsioon on enamike saasteainete korral tavalisel temperatuuril aeglane ja seda võib kasutada piiratud arvu saasteainete lagundamiseks. Seetõttu on vaja persulfaati aktiveerida. Aktiveerimisel moodustub suurema oksüdatsioonipotentsiaaliga (2,6 V) sulfaadivaba radikaal. Enamasti aktiveeritakse persulfaat soojusega, UV kiirgusega ja metalliga, sealhulgas kasutades kelaate, magnetvälja või elektrokeemilisi protsesse.

Uuritud teadusartiklite põhjal võib järeldada, et aktiveeritud persulfaat on tõhus meetod kõrge kontsentratsiooniga ja püsivate orgaaniliste saasteainete lagundamisel. Püsivamad saasteained vajavad pikemat reaktsiooniaega ja kõrgemaid persulfaadi doose. Saasteainete lagundamise tõhusus sõltub samuti saasteainete, aktivaatori ja reageerivate ainete omavahelisest konkureerimisest vees või reovees. Paljudel juhtudel soodustavad saasteainete lagunemist veel kõrgem temperatuur ja happeline või neutraalne pH. Kelaatide kasutamine metalliga aktiveeritud protsessides muutis võimalikuks ka aktivaatorina kasutatud metalli regenereerimise piiratud ajaks. Sama tulemus saavutati kasutades nõrka magnetvälja või elektrikeemilist protsessi. Uuenduslik ja perspektiivikas tehnoloogia on aktiivsöe kasutamine aktivaatorina. See toimib nii persulfaadi lagunemise katalüsaatorina, mõningate saasteainete lagundajana, ent ka mõnede kõrvalsaaduste adsorbendina.

Teiste oksüdantidega võrreldes on persulfaadi olulisim eelis kõrge lahustuvus veekeskkonnas, stabiilsus, kõrge oksüdatsioonipotentsiaal ja veelgi kõrgem oksüdatsioonipotentsiaal moodustades aktiveerumisel sulfaat- ja hüdroksüülradikaali. Edasistes uuringutes on aga oluline keskenduda protsesside optimeerimisele, näiteks persulfaadi jääki taaskasutades või aeglaselt lahusesse vabastades, võttes arvesse nii nende protsesside maksmust kui ka *in situ* kasutamise reaalseid võimalusi.

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