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COBALT/PEROXYMONOSULFATE AND RELATED OXIDIZING REAGENTS FOR WATER TREATMENT

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Abstract

This dissertation explores the fundamentals of a novel advanced oxidation technology, the cobalt/peroxymonosulfate (Co\textsuperscript{II}/KHSO\textsubscript{5}) reagent, for the treatment of persistent and hazardous substances in water. Co\textsuperscript{II}/KHSO\textsubscript{5} is based on the chemistry of the Fenton Reagent and proceeds via the generation of sulfate radicals, which similarly to hydroxyl radicals, readily attack and degrade organic and microbial contamination in water. Very few studies have exploited the reactivity of sulfate radicals for environmental applications. Compared to the extensively investigated hydroxyl radicals, sulfate radicals are not fully understood. Following this approach, the coupling of nine transition metals with hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), potassium peroxymonosulfate (KHSO\textsubscript{5}) and persulfate (K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}) was also explored. The objective was again the generation of inorganic radicals and the efficient degradation of organic contaminants in water. The determination of reactive metal-oxidant couples and the identification of the transient species formed by such interactions significantly contribute to the better understanding of oxidation-reduction phenomena and provide new tools for decontamination of specialty wastewater. Additional use of germicidal ultraviolet (UV) radiation led to the development of several other novel systems. All the reagents explored here can be classified in the following three general categories of advanced oxidation processes:

M/Ox: Fe(II)/H\textsubscript{2}O\textsubscript{2}, Fe(III)/H\textsubscript{2}O\textsubscript{2}, Co(II)/KHSO\textsubscript{5}, Ag(I)/K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}

UV/Ox: UV/H\textsubscript{2}O\textsubscript{2}, UV/KHSO\textsubscript{5}, UV/K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}

UV/M/Ox: UV/Fe(II)/H\textsubscript{2}O\textsubscript{2}, UV/Fe(III)/H\textsubscript{2}O\textsubscript{2}, UV/Co(II)/KHSO\textsubscript{5}, UV/Ag(I)/K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}

Many of these technologies, never tested before, demonstrated several operational advantages against established ones. Those were due to the high oxidizing strength of the sulfate radicals formed, the high photosensitivity of the peroxides used and the pure catalytic activity of cobalt.
both homogeneously and heterogeneously. This study is also one of the very few dealing with intermediates formed via sulfate radical attack on phenolic compounds. It is also the first that explores the sulfate radical mechanism of oxidation, when sulfate radicals are generated via the Co^{II}/KHSO₅ reagent and provides strong evidence on the interaction of chloride ions with sulfate radicals leading to the formation of free available chlorine in water. It also includes the very first documented heterogeneous activation of peroxymonosulfate using Co₃O₄. Previous investigations on the metal activation of peroxymonosulfate are limited to homogeneous systems.
Extended Summary

A highly efficient advanced oxidation process for the destruction of organic contaminants in water is reported. The technology is based on the cobalt-mediated decomposition of peroxymonosulfate (Co/KHSO₅) leading to the formation of very strong oxidizing species (sulfate radicals) in the aqueous phase. The system is a modification of Fenton Reagent, since an oxidant is coupled with a transition metal in a similar manner. The study was initially focused on comparing the Co/KHSO₅ with the traditional Fenton Reagent, Fe(II)/H₂O₂, in the dark, at the pH range 2.0-9.0 with and without the presence of buffers such as phosphate and carbonate. Three model contaminants that show diversity in structure were tested: 2,4-dichlorophenol (2,4-DCP), atrazine and naphthalene. Co/KHSO₅ was consistently proven to be more efficient than Fenton Reagent for the degradation of 2,4-DCP and atrazine, at all the conditions tested. At high pH values, where the efficiency of Fenton Reagent was diminished, the reactivity of the Co/KHSO₅ system sustained at high values. When naphthalene was treated with the two oxidizing systems in comparison, Fenton Reagent demonstrated higher degradation efficiencies than Co/KHSO₅ at acidic pH, but at higher pH (neutral), the latter was proven much more effective. The extent of mineralization, as total organic carbon removed, was also monitored and again the Co/KHSO₅ reagent demonstrated higher efficiencies than Fenton Reagent. Cobalt showed true catalytic activity in the overall process, since extremely low concentrations (in the range of µg/L) were sufficient for the decomposition of the oxidant and thus the radical generation.

To further evaluate the compatibility of metals with inorganic peroxides, nine transition metals were coupled with hydrogen peroxide (H₂O₂), potassium peroxymonosulfate (KHSO₅) and potassium persulfate (K₂S₂O₈). From the twenty-seven combinations, fourteen M/Ox couples
demonstrated significant reactivity toward transforming 2,4-DCP. It was found that Co(II) and Ru(III) are the best metal-catalysts for the activation of KHSO$_5$. Fe(III) and Fe(II) were the most efficient transition metals for the activation of H$_2$O$_2$. Finally, Ag(I) showed the best results toward activating K$_2$S$_2$O$_8$. Quenching studies with specific alcohols were also performed to identify the primary radical species formed from the reactive M/Ox interactions. The determination of these transient species allowed us to postulate the rate-determining step of the redox reactions taking place when a metal is coupled with an oxidant in aqueous solution. It was found that when Co(II), Ru(III) and Fe(II) interact with KHSO$_5$, freely diffusible sulfate radicals are the primary species formed. The same was proven for the interaction of Ag(I) with K$_2$S$_2$O$_8$ but in this case caged or bound to the metal sulfate radicals might be formed as well. The conjunction of Ce(III), Mn(II) and Ni(II) with KHSO$_5$ showed also to generate caged or bound to the metal sulfate radicals. A combination of sulfate and hydroxyl radicals was formed from the conjunction of V(III) with KHSO$_5$ and from Fe(II) with K$_2$S$_2$O$_8$. Finally, the conjunction of Fe(III), Fe(II) and Ru(III) with H$_2$O$_2$ led primarily to the generation of hydroxyl radicals. The redox behavior of a particular metal in solution cannot be predicted based exclusively on its size and charge. Additional phenomena such as metal hydrolysis as well as complexation with other counter ions present in solution might affect the thermodynamics of the overall process.

This study also explores the effect of ultraviolet (UV) light radiation for oxidant activation. H$_2$O$_2$, KHSO$_5$ and K$_2$S$_2$O$_8$ were combined with Fe, Co and Ag, respectively, and/or with UV light (254 nm) and were tested for the treatment of 2,4-DCP. From the combined use of UV, the oxidants and the transition metals, four general categories of advanced oxidation technologies were evaluated and compared for the degradation and mineralization of 2,4-DCP. Those were (i) the dark conjunction of each oxidant with its favorable metal activator (M/Ox),
(ii) the use of UV alone, (iii) the combination of UV with each oxidant (UV/Ox) and, (iv) the use of UV combined with each metal/oxidant systems (UV/M/Ox). The comparison of the 2,4-DCP treatment results with respect to the transformation of the parent contaminant and the extent of organic carbon removal led to the construction of the following order of efficiencies: UV/K₂S₂O₈ > UV/KHSO₅ > UV/H₂O₂ for the UV/Ox processes and UV/Fe(III)/H₂O₂ > UV/Fe(II)/H₂O₂ > UV/Co(II)/KHSO₅ > UV/Ag(I)/K₂S₂O₈ for the UV/M/Ox processes tested here. The relative absorbance of the species participating in the reactions supports this order, since K₂S₂O₈ followed by KHSO₅ were proven more photosensitive than H₂O₂. Among the metals tested, only Fe species such as Fe(OH)²⁺ were found to absorb strongly at 254 nm and to this is attributed the higher efficiencies obtained with the photo-Fenton reagents.

This study also reports on the sulfate radical pathway of room temperature degradation of two phenolic compounds in water. The radicals were produced by Co/KHSO₅. The major intermediates formed from the transformation of 2,4-DCP were 2,4,6-trichlorophenol, 2,3,5,6-tetrachloro-1,4-benzenediol, 1,1,3,3-tetrachloroacetone, pentachloroacetone and carbon tetrachloride. Those resulting from the transformation of phenol with the presence of chloride in solution were 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 1,1,3,3-tetrachloroacetone and pentachloroacetone. In the absence of chloride, phenol transformed into 2,5-cyclohexadiene-1,4-dione (quinone), 1,2-benzenediol (catechol) and 1,4-benzenediol (hydroquinone). Several parameters were varied and their impact on the transformation of the organic compounds is also discussed. Those were the initial concentration of the organic-substrate, the dose of Oxone® (KHSO₅) used, the cobalt counter anion and the quenching agent utilized for terminating the reaction. The study also provides strong evidence on the interaction
of chloride ions with sulfate radicals leading to the formation of free available chlorine and the halogenation of organic compounds in water.

The potential of heterogeneous activation of Oxone® (KHSO₅) in water using cobalt oxides is also explored. Two commercially available cobalt oxides, CoO and Co₃O₄ (CoO·Co₂O₃) were tested for the activation of KHSO₅ and the subsequent oxidation of 2,4-DCP via a sulfate radical mechanism. Both systems, CoO/Oxone and Co₃O₄/Oxone, were tested at acidic and neutral pH and compared with the homogeneous Co(NO₃)₂/Oxone. The activity of these systems was evaluated on the basis of the induced transformation of 2,4-DCP as well as the dissolution of Co. It was observed that only Co₃O₄ activates KHSO₅ heterogeneously, with its heterogeneity being more pronounced at neutral pH. Both CoO and Co₂O₃ contained in Co₃O₄ might be responsible for the observed heterogeneity and the relative mechanisms are further discussed.
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\[
\begin{align*}
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^- & (1.1) \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{HO}_2^\cdot + \text{H}^+ & (1.2) \\
\text{Fe(OH)}^{2+} + \text{hv} & \rightarrow \text{OH}^\cdot + \text{Fe}^{2+} & (1.3) \\
\text{Fe}^{III} (\text{C}_2\text{O}_4)_3^{3-} + \text{hv} & \rightarrow \text{Fe}^{2+} + 2\text{C}_2\text{O}_4^{2-} + \text{C}_2\text{O}_4^\cdot & (1.4) \\
\text{C}_2\text{O}_4^\cdot & \rightarrow \text{CO}_2^\cdot + \text{CO}_2 & (1.5) \\
\text{CO}_2^\cdot + \text{Fe}^{III} (\text{C}_2\text{O}_4)_3^{3-} & \rightarrow \text{Fe}^{2+} + \text{CO}_2 + 3\text{C}_2\text{O}_4^{2-} & (1.6) \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 + 3\text{C}_2\text{O}_4^{2-} & \rightarrow \text{Fe}^{III} (\text{C}_2\text{O}_4)_3^{3-} + \text{OH}^\cdot + \text{OH}^- & (1.7) \\
\text{Co}^{2+} + \text{H}_2\text{O} & \leftrightarrow \text{CoOH}^\cdot + \text{H}^+ & (1.8) \\
\text{CoOH}^\cdot + \text{HSO}_5^- & \rightarrow \text{CoO}^\cdot + \text{SO}_4^\cdot + \text{H}_2\text{O} & (1.9) \\
\text{CoO}^\cdot + 2\text{H}^+ & \leftrightarrow \text{Co}^{3+} + \text{H}_2\text{O} & (1.10) \\
\text{Co}^{3+} + \text{HSO}_5^- & \rightarrow \text{Co}^{2+} + \text{SO}_5^\cdot + \text{H}^+ & (1.11) \\
\text{Co}^{2+} + \text{SO}_4^\cdot & \rightarrow \text{Co}^{3+} + \text{SO}_4^{2-} & (1.12) \\
2\text{SO}_5^\cdot & \leftrightarrow \cdot\text{O}_3\text{SOOOOSO}_3^- \rightarrow [\text{SO}_4^\cdot\text{O}_2\text{SO}_4^\cdot] & (1.13) \\
[\text{SO}_4^\cdot\text{O}_2\text{SO}_4^\cdot] & \rightarrow \text{O}_2 + \text{S}_2\text{O}_8^{2-} & (1.14) \\
[\text{SO}_4^\cdot\text{O}_2\text{SO}_4^\cdot] & \rightarrow \text{O}_2 + 2\text{SO}_4^\cdot & (1.15) \\
\text{S}_2\text{O}_8^{2-} + \text{hv} & \rightarrow 2\text{SO}_4^\cdot & (1.16) \\
\text{Co}^{2+} + \text{HSO}_5^- & \rightarrow \text{Co}^{3+} + \text{SO}_4^\cdot + \text{OH}^- & (2.1) \\
\text{HSO}_5^- + \text{e}^- & \rightarrow \text{SO}_4^\cdot + \text{OH}^- & (2.2) \\
\text{HSO}_5^- + \text{e}^- & \rightarrow \text{SO}_4^{2-} + \text{OH}^\cdot & (2.3) \\
\text{HSO}_5^- & \rightarrow \text{SO}_5^\cdot + \text{H}^+ + \text{e}^- & (2.4)
\end{align*}
\]
\[ \text{Ag}^+ + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Ag}^{2+} + \text{SO}_4^\bullet + \text{SO}_4^{2-} \quad (3.1) \]

\[ \text{Ag}^+ + \text{S}_2\text{O}_8^{2-} \rightarrow [\text{Ag}^{II}(\text{SO}_4^\bullet)]^+ + \text{SO}_4^{2-} \quad (3.2) \]

\[ \text{M}^{n+} + \text{HSO}_5^- \rightarrow \text{M}^{(n+1)} + \text{OH}^- + \text{SO}_4^\bullet \quad (3.3) \]

\[ \text{V}^{3+} + \text{HSO}_5^- \rightarrow \text{V}^{4+} + \text{OH}^- + \text{SO}_4^\bullet \quad (3.4) \]

\[ \text{V}^{3+} + \text{HSO}_5^- \rightarrow \text{V}^{4+} + \cdot \text{OH} + \text{SO}_4^{2-} \quad (3.5) \]

\[ \text{Ce}^{3+} + \text{HSO}_5^- \rightarrow [\text{Ce}^{IV}(\text{SO}_4^\bullet)]^{3+} + \text{OH}^- \quad (3.6) \]

\[ \text{Ce}^{4+} + \text{HSO}_5^- \rightarrow \text{Ce}^{3+} + \text{SO}_5^\bullet + \text{H}^+ \quad (3.7) \]

\[ \text{Fe}^{3+} + \text{HSO}_5^- \rightarrow \text{Fe}^{2+} + \text{SO}_5^\bullet + \text{H}^+ \quad (3.8) \]

\[ \text{Mn}^{2+} + \text{HSO}_5^- \rightarrow [\text{Mn}^{III}(\text{SO}_4^\bullet)]^{2+} + \text{OH}^- \quad (3.9) \]

\[ \text{Ni}^{2+} + \text{HSO}_5^- \rightarrow [\text{Ni}^{III}(\text{SO}_4^\bullet)]^{2+} + \text{OH}^- \quad (3.10) \]

\[ 2\text{Mn}^{3+} + 2 \text{H}_2\text{O} \rightarrow \text{Mn}^{2+} + \text{MnO}_2 + 4\text{H}^+ \quad (3.11) \]

\[ \text{Mn}^{3+} + \text{HSO}_5^- \rightarrow \text{Mn}^{2+} + \text{SO}_5^\bullet + \text{H}^+ \quad (3.12) \]

\[ \text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Fe}^{3+} + \text{SO}_4^\bullet + \text{SO}_4^{2-} \quad (3.13) \]

\[ 2\text{H}_2\text{O} + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{HSO}_4^- + \text{H}_2\text{O}_2 \quad (3.14) \]

\[ \text{Ru}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Ru}^{4+} + \text{OH}^- + \cdot \text{OH} \quad (3.15) \]

\[ \text{M}^{n+} + \text{SO}_4^\bullet \rightarrow \text{M}^{(n+1)} + \text{SO}_4^{2-} \quad (3.16) \]

\[ \text{M}^{n+} + \cdot \text{OH} \rightarrow \text{M}^{(n+1)} + \text{OH}^- \quad (3.17) \]

\[ \text{M}^{(n+1)+} + \text{HSO}_5^- \rightarrow \text{M}^{n+} + \text{SO}_5^\bullet + \text{H}^+ \quad \text{where M= Co, Ce and Mn} \quad (3.18) \]

\[ \text{M}^{n+} + \text{H}_2\text{O} \leftrightarrow \text{MOH}^{(n-1)} + \text{H}^+ \quad (3.19) \]

\[ \text{HO} \rightarrow \text{OH} \quad \overset{hv}{\rightarrow} \quad 2 \cdot \text{OH} \quad (4.1) \]

\[ \begin{array}{c}
\text{O} \\
\cdot \text{O} \\
\text{O} \\
\cdot \text{OH} \\
\hline
\text{O} \\
\cdot \text{O} \\
\text{S} \\
\cdot \text{O} \\
\hline
\text{O} \\
\cdot \text{O} \\
\text{S} \\
\cdot \text{O} \\
\hline
\text{O} \\
\cdot \text{O} \\
\text{S} \\
\cdot \text{O} \\
\hline
\end{array} \quad \overset{hv}{\rightarrow} \quad \begin{array}{c}
\text{O} \\
\cdot \text{O} \\
\text{S} \\
\cdot \text{O} \\
\hline
\text{O} \\
\cdot \text{O} \\
\text{S} \\
\cdot \text{O} \\
\hline
\end{array} + \cdot \text{OH} \quad (4.2) \]
\[
\text{Fe}^{III}(\text{C}_2\text{O}_4)^{3-} + \text{hv} \rightarrow \text{Fe}^{2+} + 2.5\text{C}_2\text{O}_4^{2-} + \text{CO}_2
\]  
(4.3)

\[
\text{SO}_4^{2-} + \text{Organics} \rightarrow [...\text{many steps}...] \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\]  
(5.1)

\[
\text{SO}_4^{2-} + \text{Cl}^- \leftrightarrow \text{SO}_4^{2-} + \text{Cl}^* \\
4.7 \times 10^8
\]  
(5.2)

\[
\text{Cl}^* + \text{Cl}^- \rightarrow \text{Cl}_2^* \\
8 \times 10^9
\]  
(5.3)

\[
\text{Cl}_2^* + \text{Cl}_2^* \rightarrow \text{Cl}_2 + 2\text{Cl}^- \\
9 \times 10^8
\]  
(5.4)

\[
\text{Cl}^* + \text{Cl}^* \rightarrow \text{Cl}_2 \\
8.8 \times 10^7
\]  
(5.5)

\[
\text{Cl}_2(\text{aq}) + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- 
\]  
(5.6)

\[
\text{HOCl} \rightarrow \text{OCl}^- + \text{H}^+ \\
pK_{\alpha} = 7.5
\]  
(5.7)

\[
\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^- \\
1.36 \text{ V}
\]  
(5.8)

\[
\text{HClO} + \text{H}^+ + 2\text{e}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O} \\
1.48 \text{ V}
\]  
(5.9)

\[
\text{HSO}_5^- + \text{H}^+ + 2\text{e}^- \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} \\
1.75 \text{ V}
\]  
(5.10)

\[
\text{HSO}_5^- + \text{Cl}^- \rightarrow \text{SO}_4^{2-} + \text{HOCl} \\
0.27 \text{ V}/ 1.4 \times 10^{-3}
\]  
(5.11)

\[
\text{HSO}_5^- + 2\text{Cl}^- + \text{H}^+ \rightarrow \text{SO}_4^{2-} + \text{Cl}_2 + \text{H}_2\text{O} \\
0.39 \text{ V}
\]  
(5.12)

\[
\text{R}^* + \text{Cl}_2^* \rightarrow \text{R-Cl} + \text{Cl}^- 
\]  
(5.13)

\[
\text{R-H} + \text{HOCl} \rightarrow \text{R-Cl} + \text{H}_2\text{O}
\]  
(5.14)

\[
\text{SO}_4^{2-} + \text{NO}_2^- \rightarrow \text{SO}_4^{2-} + \text{NO}_2^* 
\]  
(5.15)

\[
\text{HSO}_5^- + \text{NO}_2^- \rightarrow \text{HSO}_4^- + \text{NO}_3^- \\
1.80 \text{ V}
\]  
(5.16)

\[
\text{HSO}_5^- + \text{NO}_2^- + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{NO}_3^- + \text{H}_2\text{O} \\
1.74 \text{ V}
\]  
(5.17)

\[
\text{HSO}_5^- + 2\text{H}^+ + 2\text{S}_2\text{O}_3^{2-} \rightarrow \text{HSO}_4^- + \text{S}_4\text{O}_6^{2-} + \text{H}_2\text{O} \\
1.73 \text{ V}
\]  
(5.18)

\[
\text{HSO}_5^- + \text{H}^+ + 2\text{S}_2\text{O}_3^{2-} \rightarrow \text{SO}_4^{2-} + \text{S}_4\text{O}_6^{2-} + \text{H}_2\text{O} \\
1.67 \text{ V}
\]  
(5.19)
S_2O_3^{2-} + 2H^+ \rightarrow S + SO_2 + H_2O \quad (5.20)

SO_4^{2-} + Ag^+ \rightarrow SO_4^{2-} + Ag^{2+} \quad (5.21)

SO_4^{2-} + CH_3OH \rightarrow HSO_4^- + CH_2OH \quad (5.22)

SO_4^{2-} + CH_3CH_2OH \rightarrow HSO_4^- + CH_3CHOH \quad (5.23)

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CHAPTER 1

Introduction

1.1 Motivation: The Need for Effective Destructive Technologies in Water Treatment

The presence of many organic contaminants in wastewater, surface water, and groundwater may result from contaminated soil, agricultural runoff, industrial discharges, waste disposal, soil erosion, hazardous-compounds storage leak, or the residues from waste treatment. Examples of such chemicals include chlorinated aromatics, polycyclic aromatic hydrocarbons, pesticides, herbicides, endocrine disrupting chemicals, toxins, and warfare agents. The presence of organic pollutants in water poses serious threat to public health since most of them exhibit properties that classify them as toxic, endocrine disrupting, mutagenic or potentially carcinogenic to humans, animals and aquatic life in general. Many organic pollutants are considered toxic and detrimental to public health and the environment, even when present at very small concentrations. For this reason, such organic pollutants are regulated by USEPA, and their removal from the contaminated water is of high priority. Consequently, the need for efficient treatment of these contaminants is imperative. In certain cases, conventional treatment methods, such as biological processes, are not effective due to the high toxicity of the contaminants to the microorganisms (1-4). On the other hand, there are other technologies that demonstrate satisfying results for the removal of low concentrations of several of these contaminants from the aqueous phase to
another phase (activated carbon adsorption, activated alumina adsorption, air stripping), but not for their complete destruction, thus further treatment is needed afterwards (adsorbent regeneration, gas phase treatment). Other processes, such as membranes, can also be effective for the removal of the majority of these chemicals but again this is a physical removal process and the contaminants remain intact and at higher concentrations in the waste stream (i.e., concentrate stream). Other conventional separation technologies (i.e., distillation, evaporation) are proven ineffective and costly due to the large quantities of water that needs to be treated and the relatively small concentration of contaminants in the steam (i.e., usually in the level of mg/L) (5). The conclusion is that more powerful and efficient technologies must be explored and applied for the degradation of recalcitrant organic substances in water such as pesticides, herbicides, insecticides, natural organic matter, endocrine disrupting chemicals, and other synthetic or naturally occurring toxic chemicals.

1.2 Background

1.2.1 Advanced Oxidation Technologies

Chemical oxidation is a treatment technology that has the potential to completely destroy harmful non-biodegradable and biocidal organic contaminants in water. The so-called Advanced Oxidation Technologies (AOTs) are among the most effective chemical oxidation processes and play a crucial role in water treatment. In AOTs, the reactions follow a specific oxidation pathway, which, in most of the cases, includes the formation of free hydroxyl radicals. The hydroxyl radicals are extremely reactive and readily attack organic molecules. Conditions that
favor the formation of those radicals are conducive to elimination of the most harmful contaminants. The final products formed are carbon dioxide, water and, depending upon the chemical composition of the precursor, other ionic inorganic residues such as chloride and nitrate. The latter species are considered environmentally acceptable, since their final concentration is not high. The process of the complete oxidation of the parent contaminants is called “mineralization” and is a feasible outcome at optimum conditions of most AOTs. Typical examples of Advanced Oxidation Technologies (AOTs) include ozonation (6-8), UV/H₂O₂ (9), sonolysis (10), the Fenton Reagent (Fe²⁺/H₂O₂) (11-15), Fenton-like reactions (Fe³⁺/H₂O₂ with and without UV-light radiation) (16-19), electron beams and γ-irradiation (20) and TiO₂-photocatalysis (21). The formation of hydroxyl radicals occurs spontaneously but slowly in natural systems. With these processes we simulate nature but in this case we elaborate appropriate modifications in order to achieve acceleration of the redox reactions (22).

1.2.2 Fenton Reagent and its Modifications

The treatment of organic contaminants using the Fenton reagent is based on the formation of hydroxyl free radicals that readily attack and degrade organic pollutants in water. The fundamental Fenton reaction involves the addition of dilute hydrogen peroxide (H₂O₂) to a degassed solution of ferrous iron, but it is also extensively applied in systems open to the atmosphere (1,2,4,11,12,18,23-27). The reagent can also be applied with a slight modification where ferric replaces ferrous iron (16,19). The hydroxyl radicals are generated according to the following chemical equations (14):
Fe^{2+} + H_{2}O_{2} \rightarrow Fe^{3+} + \cdot OH + OH^{-} \quad (1.1)

Fe^{3+} + H_{2}O_{2} \rightarrow Fe^{2+} + HO_{2}^{-} + H^{+} \quad (1.2)

Although the homogeneous Fenton Reagent is a very powerful oxidizing agent and is used in several industrial applications for the treatment of contaminated water discharges, it faces several and significant limitations:

- **Narrow range of operational pH**: The Fenton Reagent is only effective at a pH range between 2 and 6 and has a maximum reactivity at pH 2.8. Increase in solution pH results in iron speciation and precipitation and therefore in much lower efficiencies. Such precipitates include iron hydroxide, iron oxide, and iron oxyhydroxides. Above pH 6, the reactivity of the Fenton Reagent is diminished (4,18,25-29). In the presence of oxygen, ferrous iron is oxidized to ferric which easily forms iron oxides that precipitate. This is a significant disadvantage, since most natural waters that potentially require treatment have pH above 6 and in addition buffering species are present.

- **Large amounts of iron needed**: Iron is not acting as a true catalyst in the overall process, since high concentrations are needed for the decomposition of hydrogen peroxide (stoichiometric amounts) (18).

- **Limited organic carbon removal**: In most of the cases and due to the intense iron speciation phenomena, the extent of mineralization using the Fenton Reagent cannot exceed 60% (incomplete mineralization).

- **Quenching of hydroxyl radicals by naturally occurring carbonate species**: It has been reported that carbonate species present in water act as hydroxyl radical scavengers (30). Consequently, the presence of carbonates in the aqueous phase leads to a decrease in Fenton
reactivity as well as that of other hydroxyl radical-based AOTs (i.e., TiO$_2$ photocatalysis) (31).

Due to these limitations, scientists and engineers have recently been investigating and using various modified Fenton reactions. The additional use of ultraviolet radiation with the previous system may lead for instance to complete mineralization of the contaminants under certain conditions. The simplest modified Fenton reaction is the so-called photo-Fenton that involves ultraviolet (UV) radiation for the photolysis of Fe(OH)$_2^+$. The process proceeds according to chemical reactions 1.1 and 1.3 (16-18,28):

\[
\text{Fe}^{III}(\text{OH})^2^+ + \text{hv} \rightarrow \text{Fe}^{II} + \cdot\text{OH} \quad \Phi=0.15 \quad (1.3)
\]

The advantage of this method is that iron is not depleted as in the case of the conventional Fenton reaction. The ferric ion is initially reduced to ferrous but is subsequently oxidized back to ferric forming a catalytic loop of reactions. However, the quantum yield (fraction of the absorbed photons that result in a photochemical reaction) of reaction 1.3 is not very high (only 0.15) and Fe(OH)$_2^+$ absorbs UV up to about 400 nm, where the visible range begins (visible: 400-700 nm) (22).

One even more enhanced Fenton-like reaction has been developed where the radicals are generated via the UV-vis/Ferrioxalate/H$_2$O$_2$ system. The quantum yield achieved thereby for the production of Fe(II) is 1.25 and the ferrioxalate complex can absorb at wavelengths of the visible light region up to 500-550 nm (18,22,29,32,33). The problem with the latter technology is that it requires the addition of the oxalate component, which is also degradable under these conditions.
Fe^{III} (C_{2}O_{4})_{3}^{3-} + hv \rightarrow Fe^{2+} + 2C_{2}O_{4}^{2-} + C_{2}O_{4}^{•-} \quad (1.4)

C_{2}O_{4}^{•-} \rightarrow CO_{2}^{•-} + CO_{2} \quad (1.5)

CO_{2}^{•-} + Fe^{III} (C_{2}O_{4})_{3}^{3-} \rightarrow Fe^{2+} + CO_{2} + 3C_{2}O_{4}^{2-} \quad (1.6)

Fe^{2+} + H_{2}O_{2} + 3C_{2}O_{4}^{2-} \rightarrow Fe^{III} (C_{2}O_{4})_{3}^{3-} + OH^{•} + OH^{-} \quad (1.7)

Other modifications of the Fenton reagent that have been applied to achieve higher destruction efficiencies for organic contaminants include: (i) slow addition, in-situ generation or addition of excess hydrogen peroxide, (ii) addition of chelators and pyrosulfates, and (iii) heterogeneous or immobilized iron to avoid precipitation (34-39). The selections of these modifications are usually based upon the specific conditions and aims of the particular treatment objective.

1.2.3 Inorganic Peroxides in Water Treatment

The main focus of this study is the cobalt-mediated activation of peroxymonosulfate but hydrogen peroxide and potassium persulfate were also tested in comparison with potassium peroxymonosulfate. As they are, with no further activation, these three peroxides demonstrate high oxidizing strength as demonstrated by their respective redox potentials shown in Table 1.1. They are in fact stronger electron acceptors than the majority of common oxidants used in water treatment. The basis of this study however is the activation of these inorganic peroxides towards the formation of free radicals. The latter are even stronger and more reactive oxidizing species than the parent compounds they come from.
<table>
<thead>
<tr>
<th>Half reaction</th>
<th>$E^\circ$, V</th>
<th>Half reaction</th>
<th>$E^\circ$, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O}_3 + 2\text{H}^+ + 2\text{e} \rightarrow \text{O}_2 + \text{H}_2\text{O}$</td>
<td>2.08</td>
<td>$\text{BrO}^- + 2\text{H}^+ + 2\text{e} \rightarrow \text{Br}^- + \text{H}_2\text{O}$</td>
<td>1.59</td>
</tr>
<tr>
<td>$\text{S}_2\text{O}_8^{2-} + 2\text{H}^+ + 2\text{e} \rightarrow 2\text{HSO}_4^-$</td>
<td>2.08</td>
<td>$\text{HClO} + \text{H}^+ + 2\text{e} \rightarrow \text{Cl}^- + \text{H}_2\text{O}$</td>
<td>1.48</td>
</tr>
<tr>
<td>$\text{S}_2\text{O}_8^{2-} + 2\text{e} \rightarrow 2\text{SO}_4^{2-}$</td>
<td>1.96</td>
<td>$\text{NH}_2\text{Cl} + \text{H}^+ + \text{e} \rightarrow \text{Cl}^- + \text{NH}_4^+$</td>
<td>1.40</td>
</tr>
<tr>
<td>$\text{HSO}_5^- + 2\text{H}^+ + 2\text{e} \rightarrow \text{HSO}_4^- + \text{H}_2\text{O}$</td>
<td>1.82</td>
<td>$\text{Cl}_2(\text{g}) + 2\text{e} \rightarrow 2\text{Cl}^-$</td>
<td>1.36</td>
</tr>
<tr>
<td>$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e} \rightarrow 2\text{H}_2\text{O}$</td>
<td>1.78</td>
<td>$\text{HBrO} + \text{H}^+ + 2\text{e} \rightarrow \text{Br}^- + \text{H}_2\text{O}$</td>
<td>1.33</td>
</tr>
<tr>
<td>$\text{HSO}_5^- + \text{H}^+ + 2\text{e} \rightarrow \text{SO}_4^- + \text{H}_2\text{O}$</td>
<td>1.75</td>
<td>$\text{O}_2(\text{aq}) + 2\text{H}^+ + 2\text{e} \rightarrow \text{H}_2\text{O}$</td>
<td>1.23</td>
</tr>
<tr>
<td>$\text{MnO}_4^- + 4\text{H}^+ + 3\text{e} \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$</td>
<td>1.68</td>
<td>$\text{Br}_2(\text{aq}) + 2\text{e} \rightarrow 2\text{Br}^-$</td>
<td>1.09</td>
</tr>
<tr>
<td>$\text{ClO}^- + 2\text{H}^+ + 2\text{e} \rightarrow \text{Cl}^- + \text{H}_2\text{O}$</td>
<td>1.64</td>
<td>$\text{ClO}_2(\text{aq}) + \text{e} \rightarrow \text{ClO}_2^-$</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Specifically, the activation of peroxymonosulfate with the use of transition metals and/or UV radiation has never been investigated before for environmental applications. Potassium peroxymonosulfate (KHSO$_5$) is a component of the triple salt, 2KHSO$_5$.KHSO$_4$.K$_2$SO$_4$, which is best known under the commercial name OXONE$^\text{®}$ (DuPont). The use of peroxymonosulfate itself (without cobalt or other transition metal) as an alternative electron acceptor, other than oxygen, “free chlorine” or hydrogen peroxide, has not been fully investigated for environmental applications either. OXONE$^\text{®}$ is a known alternative to chlorine bleaching agent and is currently used in the paper and pulp industry. The presence of transition metals in solution during kraft pulp bleaching with peroxymonosulfate has been of recent interest (44-46). The coupling of transition metals (cobalt included) with peroxymonosulfate was proven too strong with respect to oxidizing power and finally had a detrimental effect in the overall process. Although the radicals generated by the transition metal mediated peroxymonosulfate decomposition led to effective delignification, significant losses in pulp strength due to cellulose degradation were detected. OXONE$^\text{®}$ is also used as a cleaning agent in pools and spas (47). Persulfate is commonly used in
TOC analyzers (48,49) where it is activated with UV radiation (254 nm) or heating and was recently suggested that could be effective against the SARS virus (50). The coupling of various catalysts with peroxydisulfate (persulfate) has been recently investigated for the destruction of organic wastes (51). However, the pH was acidic and the temperature was rather elevated. Compared to the other two, hydrogen peroxide is a more widely used oxidant in water treatment (along with Fe, UV or O3) due to the fact that is a “green” and relatively inexpensive chemical.

In the environmental field, there have been some previous studies dealing with TiO2 photocatalytic (solar or UV radiation) degradation of water contaminants that reported the role of certain inorganic additives as alternative electron acceptors (52-55). Those were the ones that inspired us for undertaking this research. Most of the contaminants were of aromatic structure and the oxidants tested were hydrogen peroxide, peroxymonosulfate, peroxydisulfate (or persulfate), periodate and bromate. Photolysis of periodate has also been tested for the reduction of chemical oxygen demand (COD) of an industrial wastewater (56). All the studies agree that the addition of electron acceptors enhances the rate of contaminant degradation. Al-Ekabi et al. suggested that among the additives tested, peroxymonosulfate was proven to be the most effective for the photocatalytic degradation of 1,1,2-trichloroethane (52). In all the other cases, persulfate was proven the most efficient. Either way however, the fact that the sulfate containing oxidants are proven the most effective leads to the speculation that the sulfate radicals generated by the photo-induced decomposition of peroxymonosulfate and persulfate are stronger oxidizing species than hydroxyl or other radicals, under certain conditions.
1.2.4 Cobalt/Peroxymonosulfate

Since 1956 when Ball and Edwards first reported the cobaltous-mediated decomposition of peroxymonosulfate, there have been several studies investigating the kinetics and the mechanisms of this highly oxidizing system (57-62). Only recently however, the significant reactivity of this particular reagent has been exploited in chemistry and biology. More specifically, it has been applied for the cleavage of DNA (63-65) as well as in a chemiluminescence system for the detection of fluorescent organic compounds (66,67). It is also of interest in the paper and pulp industry, where peroxymonosulfate is tested as a bleaching agent alternatively to chlorine (44-46). All studies agree on the same radical mechanism, with sulfate radicals being the primary oxidizing species formed:

\[
\begin{align*}
    \text{Co}^{2+} + \text{H}_2\text{O} & \leftrightarrow \text{CoOH}^+ + \text{H}^+ \quad (1.8) \\
    \text{CoOH}^+ + \text{HSO}_5^- & \rightarrow \text{CoO}^+ + \text{SO}_4^- + \text{H}_2\text{O} \quad (1.9) \\
    \text{CoO}^+ + 2\text{H}^+ & \leftrightarrow \text{Co}^{3+} + \text{H}_2\text{O} \quad (1.10) \\
    \text{Co}^{3+} + \text{HSO}_5^- & \rightarrow \text{Co}^{2+} + \text{SO}_5^- + \text{H}^+ \quad (1.11) \\
    \text{Co}^{2+} + \text{SO}_4^\cdot & \rightarrow \text{Co}^{3+} + \text{SO}_4^{2-} \quad (1.12) \\
    2\text{SO}_5^\cdot & \leftrightarrow \cdot\text{O}_3\text{SOOOOSO}_5^- \rightarrow [\text{SO}_4^\cdot\text{O}_2\text{SO}_4^\cdot] \quad (1.13) \\
    [\text{SO}_4^\cdot\text{O}_2\text{SO}_4^\cdot] & \rightarrow \text{O}_2 + \text{S}_2\text{O}_8^{2-} \quad (1.14) \\
    [\text{SO}_4^\cdot\text{O}_2\text{SO}_4^\cdot] & \rightarrow \text{O}_2 + 2\text{SO}_4^- \quad (1.15)
\end{align*}
\]

It must be mentioned here that per oxydisulfate (persulfate) is a reported termination product of the catalytic decomposition of peroxymonosulfate, as shown in equation (1.14).
1.3 Specific Research Objectives - Hypothesis and Rationale

Driven by the limitations of the Fenton Reagent and motivated by the potential the Co/peroxymonosulfate reagent has demonstrated in our preliminary investigations, this study aimed at further exploring the Co/peroxymonosulfate system and various alternative combinations for the oxidation of model environmentally important compounds. Alternative reagents, some of which are introduced for the first time in the field of AOTs, include the following combinations: Metal/Oxidant, UV/Oxidant and UV/Metal/Oxidant. Hence, this study complies with our overall objective as a research group of developing novel and efficient AOTs for water purification. Following a systematic experimental and analytical plan, I sought to explore the mechanism and fundamentals of the newly developed chemical reagents, compare their efficiencies against water contaminants, investigate the impact of important process parameters and water quality characteristics, and optimize their application both from economical and environmental point of view. Description and rationale of the specific research studies undertaken is provided below.

1.3.1 Catalytic Behavior of Cobalt in Co/Peroxymonosulfate

As already stated, iron is not really acting as a catalyst in the Fenton reaction, since it is needed in large amounts for the decomposition of hydrogen peroxide. On the other hand, cobalt was reported to catalytically decompose peroxymonosulfate towards sulfate radical formation. This study investigates the kinetics of the reaction with respect to the catalyst. The kinetics with
respect to the oxidant were also explored. In this approach, conditions at which the reaction of Co with peroxymonosulfate is slow enough had to be determined. Radical processes proceed very fast and only at extreme conditions (i.e., low pH), we were able to monitor the rate of reaction.

1.3.2 Radical Identification

The radicals formed by each method were identified with specific quenching studies following the specific properties of each radical. It is thoroughly established in the literature that alcohols containing alpha hydrogen such as methanol and ethanol readily react with hydroxyl and sulfate radicals. Peroxymonosulfate radicals however are relatively inert towards alcohols. Moreover, although alcohols with no alpha hydrogen such as tert-butyl alcohol are effective quenching agents for hydroxyl radicals, they react 1000-fold slower with sulfate radicals (64,68-72).

1.3.3 Type of Transition Metal

In general, the efficiency of the pairing of a transition metal with an oxidant depends upon the pH, the concentration of dissolved oxygen and the metal anion or ligand. Moreover, the transition metal has to demonstrate high redox potential to be able to reduce the inorganic oxidant in the reverse electron transfer reaction such as equation 1.11. The conjunction of several other metals with peroxymonosulfate was also tested for the destruction of organic contaminants. The objective was to propose an order of efficiency of the catalysts that decompose peroxymonosulfate. The same was also performed with the other two oxidants, potassium
persulfate and hydrogen peroxide. Similarly to what I have investigated with cobalt, I sought to prove that by lowering the transition metal dose, the efficiency of an oxidation process does not significantly decrease when sufficient reaction time is allowed. This provided further information of the amounts of catalyst needed to achieve degradation (or even mineralization) of a specified quantity of a contaminant (or a mixture of them) and under a specified treatment time.

1.3.4 Type of Oxidant

The three inorganic oxidizing species, peroxymonosulfate, hydrogen peroxide and persulfate, were also tested, catalyzed by the same transition metal. The efficiency of the oxidants with respect to the contaminant degradation was also compared. Again specific quenching studies with alcohols provided information regarding the type of the dominant radicals generated.

1.3.5 Effect of Ultraviolet Light

Photolysis of inorganic peroxides with ultraviolet (UV) radiation is also an important variation for the treatment of organic contaminants in water. It has been reported that, when photolyzed, persulfate also generates sulfate radicals. Obviously, the mechanism of its decomposition (reaction 1.16) should be similar to that of peroxymonosulfate:

\[ S_{2}O_{8}^{2-} + hv \rightarrow 2SO_{4}^{-} \]  

(1.16)
In this study, UV radiation was coupled with the transition metal-based chemical system and the effectiveness of such combination was evaluated in detail. The effect of such combination was examined for the degradation and mineralization of the parent contaminant. The influence of UV radiation wavelength on the activation of the photosensitive species was an additional parameter of investigation. The conventional Fenton Reagent at optimum conditions (pH close to 3.0 and high doses of iron and hydrogen peroxide) leads to complete destruction of the parent contaminant but not to complete mineralization of the organic carbon load, measured as TOC removal. Normally the TOC removal efficiency when Fenton Reagent is applied does not exceed 60%. Complete mineralization leading to carbon dioxide and water is achieved with additional use of ultraviolet (UV) radiation (18). It is anticipated that the role of UV radiation in the process is important from both a fundamental point of view and from the development of alternative promising chemical oxidation processes.

1.3.6 Degradation Intermediates of Sulfate Radical Attack (SRA)

Important objective of the study was also the identification of the major intermediate compounds formed following degradation of 2,4-DCP with Co/peroxymonosulfate. It was anticipated that such intermediates would be different than those formed during the hydroxyl-radical mediated degradation of 2,4-DCP using other AOTs (i.e., Fenton reagent, TiO$_2$ photocatalysis, UV/H$_2$O$_2$). In fact, such study is one of the very few to include byproduct formation of sulfate radical-mediated degradation reactions of organic contaminants. Furthermore, identifying and quantifying the reaction intermediates is crucial for assessing the toxicity of the treated stream to humans and animals and the effective integration of the process with biological treatment.
processes that may follow in a wastewater treatment train (i.e., when not aiming at complete mineralization).

### 1.3.7 Chlorine Formation

Chlorine formation when chlorine-containing compounds react with sulfate radicals has been reported in the literature (51) and was also sensed (chlorinous smell) in our preliminary investigations. Since sulfate radicals exhibit high enough redox potential to oxidize chloride ions to chlorine radicals, they may combine in a termination reaction and form free available chlorine species. Following this hypothesis, several control studies were performed to examine whether chlorine formation follows a rational pathway, quantify the species and examine alternatives of treating or reusing it.

### 1.3.8 Treatment of Environmentally Important Compounds

The reagents developed and tested within this study are novel and some of them appear for the first time in the environmental field. For this, this dissertation is mainly focused on the proof of concept of each technology, rather than the destruction of many and diverse water pollutants. Nonetheless, apart from the treatment of 2,4-dichlorophenol (2,4-DCP), which was the model contaminant tested throughout this study, several other compounds of environmental significance were also tested for degradation. The contaminants tested in this study fall in the general categories of synthetic organic, endocrine disrupting, and toxic chemicals and are:
- **2,4-Dichlorophenol**: The contaminant has been included in the drinking water contaminant candidate list by the USEPA and is a well-known intermediate used for the synthesis of 2,4-dichlorophenoxyacetic acid (2,4-D), a regulated and widely used herbicide (73). Conversely, 2,4-DCP is a major intermediate resulting from the degradation of 2,4-D with advanced oxidation technologies (74-77). Like all chlorinated phenols, 2,4-DCP demonstrates very low biodegradability and there have been several studies exploring the use of advanced oxidation technologies (mainly photocatalysis) for its treatment (78-82).

- **4-Nitrophenol**: 4-nitrophenol was observed to be more toxic than 2-nitrophenol in animal studies. However, there is much less information about the toxicological effects of nitrophenols compared to the rest of the chemical pollutants tested here.

- **Phenol**: Phenol, a widely used chemical, ranks in the top 50 in production volumes for chemicals produced in the United States. To protect human health from ingestion of contaminated water, the USEPA has suggested that phenol concentrations should not exceed 3.5 mg/L in natural waters (83).

- **Atrazine**: Atrazine is a herbicide used on row crops and is released in natural waters during runoff. It is already regulated for drinking water and has an assigned MCL of 0.003 mg/L.

- **Naphthalene**: The first molecule in the series of polycyclic aromatic hydrocarbons (PAHs), made of two benzene rings. PAHs are released in the environment as byproducts from the incomplete combustion of organic substances and are already regulated by the USEPA (MCL: 0.2 ppb), since they may cause serious health effects to humans (84,85).
1.3.9 Carbonate Species

As stated earlier, naturally occurring bicarbonate and carbonate species have demonstrated a scavenging effect on hydroxyl radical processes. It is very important therefore to examine whether the sulfate radicals formed by the Co/peroxymonosulfate process are affected by the presence of such species. If not, the proposed process will demonstrate an additional advantage over the Fenton Reagent.

1.3.10 Heterogeneous Catalysis

Special restrictions with respect to cobalt addition were considered, since, although a necessary element, it can be proven toxic when found at high concentrations in water. The developed Co(II)/KHSO\textsubscript{5} reagent is homogeneous, since it was compared with an already established homogeneous system such as the Fenton Reagent. Nevertheless, our investigations were focused on using extremely low concentrations of cobalt that are currently found in drinking water. For example, we found that as low as 72.3 µg/L of dissolved cobalt were sufficient for the complete destruction of 50 mg/L of 2,4-DCP and approximately 30% organic carbon removal (see Chapter 2). Certainly after the investigation of the homogeneous system our approach was modified towards applying a heterogeneous system that included the use of cobalt oxides.
1.3.11 Preliminary Economics

The development of all these new advanced oxidation technologies and their efficiency toward treating persistent organic contaminants has increased our treatment options for water decontamination. It is imperative, however, to determine the economics of these processes, especially in the cases that relatively expensive treatment options such as addition of chemicals and use of UV are proposed here. Consequently, the equivalent costs of the three oxidants used as well as the energy requirements from the application of UV light radiation for the processes utilizing the UV component were compared. The latter was determined by measuring the total electrical power or flux entering the UV reactors used in our studies. Subsequently, established figures-of-merit such as electrical energy per order (EE/O) was determined for each process and this will facilitate the comparison of the developed technologies (22,86).

1.4 Dissertation Organization

Each chapter of this study corresponds to a peer-reviewed journal article already published or submitted for publication. This particular structure was chosen for the obvious ease it provided for preparing this dissertation but more importantly the ease it provides to interested scientists and engineers to read it through, since each paper/chapter is a logical continuation of the previous one. Even if the papers were not prepared in advance, the structure of this dissertation would have been similar to the one chosen.

Chapter 2: This chapter deals with the fundamentals of the Co/peroxymonosulfate reagent. This novel oxidizing system is also compared with an established technology, the Fenton Reagent, for
the degradation of 2,4-dichlorophenol, atrazine and naphthalene. It was published in *Environ. Sci. Technol.* in 2003 (87).

**Chapter 3:** This chapter explores the coupling of nine transition metals with the three oxidants (peroxymonosulfate, persulfate and hydrogen peroxide) with the objective of identifying similar to the Fenton and the Co/peroxymonosulfate reagents. It was published in *Environ. Sci. Technol.* in 2004 (88).

**Chapter 4:** The component of ultraviolet (UV) radiation is now introduced either alone or in combination with the favorable transition metal for the activation of the three oxidants and the oxidation of organic contamination in water. The study was published in *Appl. Cat. B: Environ.* in 2004 (89).

**Chapter 5:** This chapter deals with the sulfate radical pathway of degradation of phenolic compounds in water. Major intermediates are identified and mechanistic schemes are provided. The study was accepted for publication in *Environ. Sci. Technol.* in November 2005.

**Chapter 6:** This chapter deals with the heterogeneous activation of peroxymonosulfate using cobalt oxides. It is the first attempt towards developing a friendlier to the environment oxidizing reagent, where the catalyst is not dissolved in solution. The study was published in the *J. Phys. Chem. B.* in 2005.

**Chapter 7:** This chapter provides suggestions for future research in the field related to the cobalt/peroxymonosulfate reagent and the advanced oxidation technologies in general. Process optimization and environmental friendliness should guide any future work based on this dissertation.
Additional research work was also performed as part of a research contract between DuPont Chemical Solutions Enterprise and the University of Cincinnati. The contract-project lasted for one year, October 1, 2003 – September 30, 2004. At this moment, the results still remain proprietary information and consequently, they have not been included in this dissertation. They have been summarized however in a manuscript and upon authorization will be submitted to *Water Research*.
CHAPTER 2

Degradation of Organic Contaminants in Water with Sulfate Radicals Generated by the Conjunction of Peroxymonosulfate with Cobalt

A highly efficient advanced oxidation process for the destruction of organic contaminants in water is reported in this chapter. The technology is based on the cobalt-mediated decomposition of peroxymonosulfate that leads to the formation of very strong oxidizing species (sulfate radicals) in the aqueous phase. The system is a modification of Fenton Reagent, since an oxidant is coupled with a transition metal in a similar manner. Sulfate radicals were identified with quenching studies using specific alcohols. The study was primarily focused on comparing the cobalt/peroxymonosulfate (Co/KHSO5) reagent with the traditional Fenton Reagent [Fe(II)/H2O2] in the dark, at the pH range 2.0-9.0 with and without the presence of buffers such as phosphate and carbonate. Three model contaminants that show diversity in structure were tested: 2,4-dichlorophenol, atrazine and naphthalene. Cobalt/peroxymonosulfate was consistently proven to be more efficient than Fenton Reagent for the degradation of 2,4-dichlorophenol and atrazine, at all the conditions tested. At high pH values, where the efficiency of Fenton Reagent was diminished, the reactivity of the Co/peroxymonosulfate system sustained at high values. When naphthalene was treated with the two oxidizing systems in comparison, Fenton Reagent demonstrated higher degradation efficiencies than cobalt/peroxymonosulfate at acidic pH, but at higher pH (neutral), the latter was proven much more effective. The extent of
mineralization, as total organic carbon removed, was also monitored and again the Co/peroxymonosulfate reagent demonstrated higher efficiencies than Fenton Reagent. Cobalt showed true catalytic activity in the overall process, since extremely low concentrations (in the range of µg/L) were sufficient for the decomposition of the oxidant and thus the radical generation. The advantage of Co/peroxymonosulfate compared to the traditional Fenton Reagent is attributed primarily to the oxidizing strength of the radicals formed, since sulfate radicals are stronger oxidants than hydroxyl, and the thermodynamics of the transition metal-oxidant coupling.

2.1 Introduction

As stated earlier, the Fenton Reagent is considered a very powerful oxidizing agent and is used at several industrial applications for the treatment of contaminated water discharges. The process however faces several and significant limitations. The major constraint is the requirement for acidic pH. The reaction is effective only at pH values close to 3. At higher pH, such as greater than 6, the efficiency of the Fenton Reagent is dramatically decreased due to iron speciation and precipitation (4,12-14,16,18,26,28). Furthermore, it is suggested that iron does not demonstrate true catalytic activity in the reaction and the concentrations needed for the decomposition of hydrogen peroxide are high (18). There are also some species that show resistance to oxidation by the fundamental Fenton reaction and the total organic carbon (TOC) removal is believed that cannot exceed 60% (mineralization) (18).
Driven by the need of overcoming the limitations of Fenton Reagent and seeking for a process that introduces stronger oxidants than hydroxyl radicals, generated by almost all AOTs, this work explores an alternative oxidation technology. The system includes the generation of sulfate radicals through the cobalt-mediated decomposition of peroxymonosulfate, according to the following reaction:

\[
\text{Co}^{2+} + \text{HSO}_5^- \rightarrow \text{Co}^{3+} + \text{SO}_4^{2-} + \text{OH}^- \quad (2.1)
\]

The technology is a modification of the Fenton Reagent, since a transition metal is coupled with an oxidant. However, the removal efficiencies achieved thereby for the degradation of typical carcinogenic contaminants, such as 2,4-dichlorophenol (2,4-DCP) and atrazine, were higher than those obtained using the Fenton Reagent at all the conditions tested, even at those that are optimum for the latter (pH 3). In the case of naphthalene, Fenton Reagent was proven more efficient at acidic pH. Finally, Co/peroxymonosulfate demonstrated very high efficiencies for the destruction of the contaminants at a much wider pH range (2-8) regardless the presence or not of buffering species.

Depending upon the transition metal used for the catalysis as well as its oxidation state, hydroxyl radicals or even peroxymonosulfate radicals can be the reactive species formed. The cobalt-mediated decomposition follows a sulfate radical mechanism with peroxymonosulfate radicals formed as intermediates only. The same was suggested when iron(II), titanium(III) and oxovanadium(IV) were used whereas with copper(I), hydroxyl radicals were the primary oxidizing species (90-92). Other transition metals that have been reported to catalyze the
peroxymonosulfate decomposition include manganese, ruthenium, iridium, molybdenum, tungsten, nickel and cerium (57,58,60,70,71,93-96).

This study explores the reactivity of Co/peroxymonosulfate at certain conditions and compares its efficiency with the Fenton Reagent for the destruction of three typical organic contaminants in water: 2,4-dichlorophenol, atrazine and naphthalene. Specific investigations with respect to the catalytic behavior of cobalt and the primary radicals formed are also reported.

2.2 Materials and Methods

The degradation experiments were conducted at ambient temperature in 0.5 and 2L batch-reactors. The reaction was monitored in most of the cases for 4 hours (240 min). The experiments were performed in the hood where visible light penetration was very limited. It was decided not to cover the vessel, with aluminum foil for example, in order to be able to watch the color development in the reactor, which is indicative for the progress of the reaction (catalyst speciation, complexation etc.). The initial concentrations of the contaminants were 50 mg/L (0.307mM) for 2,4-DCP, 8 mg/L (0.037mM) for atrazine and 5 mg/L (0.039mM) for naphthalene. The concentration of the contaminants with time was monitored with an Agilent 1100 Series HPLC System with a QuatPump and a UV-vis diode array detector. The column used for the analysis of 2,4-DCP and atrazine was an Eclipse XDB-C8 column, obtained from Agilent. A Discovery RP Amide C-16 from Supelco was used for the analysis of naphthalene. Excess sodium nitrite or methanol solutions were added in the samples that were removed from the reactor at specific time intervals for the quenching of the Co/peroxymonosulfate reaction and
the Fenton Reagent. Methanol is a well-known quenching agent for both sulfate and hydroxyl radicals but it interferes with the analysis of total organic carbon (TOC). Sodium nitrite demonstrated similar quenching properties and it was used instead of methanol in the cases that TOC analysis followed. Reaction of nitrite with residual peroxymonosulfate resulted in the formation of nitrate and sulfate. Consequently, nitrate formation in the samples was indicative of the peroxymonosulfate consumption and thus the extent of the reaction. A Dionex DX 500 Ion Chromatography System with a CD 25 Conductivity Detector and a GP 50 Gradient Pump was used for the measurement of chloride, nitrite, nitrate and sulfate ions that were present in the reaction solution (97). The anion analysis was performed with an IonPac AS 14 4-mm (10-32) analytical column and an IonPac AG 14 4-mm (10-32) guard column. The objective was to monitor the chloride release in solution resulted from the degradation of 2,4-DCP. However, after an initial increase, the chloride concentration decreased even below the concentration that corresponds to the chloride initially present in solution. For this reason, ion chromatography results were used only for qualitative purposes. Rationale of the chloride loss is provided in a consecutive section of this study. A Shimadzu TOC 5050 Analyzer and a VCSH-ASI system were used for the measurement of TOC (as non-purgeable organic carbon, NPOC) present in the samples.

DuPont’s triple salt, OXONE® (2KHSO₅.KHSO₄.K₂SO₄), purchased from Aldrich, was the compound providing the strong oxidant, peroxymonosulfate (HSO₅⁻). The transition metals Co(II) and Fe(II) were in the forms of cobalt chloride (CoCl₂.6H₂O) and ferrous sulfate (FeSO₄.7H₂O), respectively. Experimental conditions such as concentrations of reagents and pH values are provided in the figure captions. The error bars presented in several figures represent
experiments that were conducted in triplicate. In most comparative experiments, it was decided to use stoichiometric amounts (1:1 molar ratios) of the transition metal with respect to the oxidant. The objective was not to be limited in any case by the concentration of the transition metal. The fact that iron does not demonstrate real catalytic activity in the Fenton reaction along with literature information suggesting that Fe(II):H₂O₂ molar of 1:1 is a typical and sometimes optimum ratio for the Fenton Reagent were the main reasons for selecting it (12,17,18,23,36,98-100). In general, iron does not demonstrate a negative role when used at high concentrations as in the case of hydrogen peroxide, which normally above a certain concentration shows detrimental effects (101). Moreover, the initial ratio of the oxidizing system (metal and electron acceptor) versus 2,4-DCP was 2:1, versus atrazine 4:1 and versus naphthalene 1:1. The three latter molar ratios were selected so that the degradation of the contaminants could be monitored throughout the reaction time. When calculating molar ratios the fact that 1 mole of OXONE® gives 2 moles of peroxymonosulfate was considered, as shown by its chemical formula. Other transition metal salts such as ferrous chloride (FeCl₂·4H₂O) and nickel sulfate (NiSO₄·6H₂O) were also used as received. Concentrated H₂SO₄ was used to adjust the pH in the acidic region. The following pairs: NaOH/K₂HPO₄, H₂SO₄/NaHCO₃ Na₂CO₃/NaHCO₃ and KH₂PO₄/K₂HPO₄ at various molar ratios were the buffering species introduced in solution for pH adjustment in the range of 5.8-9.0 (102). The efficiency of the oxidizing systems in comparison was based on the extent of degradation of the parent contaminant and the organic carbon mineralization achieved after certain reaction time.
2.3 Results

2.3.1 Co/Peroxymonosulfate vs. Fenton Reagent

Initially, the objective was to evaluate the efficiency of peroxymonosulfate using Fe(II) as the transition metal catalyst for the degradation of 2,4-DCP. Our aim by that way was to modify the Fenton Reagent, get comparative results of the two systems in the dark and examine whether higher 2,4-DCP removal efficiencies could be achieved with this modification. In our preliminary investigations, it was proven that, in the dark, the conjunction of H₂O₂ with Fe(II), or else the Fenton Reagent, led to higher degradation efficiencies of the chlorophenol than the interaction of HSO₅⁻ with Fe(II). The limiting factor of the Fenton Reagent process is iron speciation and precipitation. Therefore our approach was modified towards finding a more efficient catalyst for the decomposition of peroxymonosulfate and seeking to explore whether the new coupling would result in higher degradation efficiencies of the contaminants tested than those achieved with Fenton Reagent. It has been reported that the catalyst-mediated decomposition of peroxymonosulfate can proceed according to the following radical formation reactions (60,103,104):

\[
\begin{align*}
\text{HSO}_5^- + e^- &\rightarrow \text{SO}_4^{*} + \text{OH}^- \quad (2.2) \\
\text{HSO}_5^- + e^- &\rightarrow \text{SO}_4^{2*} + \text{OH}^* \quad (2.3) \\
\text{HSO}_5^- &\rightarrow \text{SO}_5^{*} + \text{H}^+ + e^- \quad (2.4)
\end{align*}
\]
As a result, we aimed at finding a catalyst that favors reaction (2.2) instead of (2.3) with the objective of exploring whether the activation of peroxymonosulfate via the sulfate radical pathway would result in higher degradation efficiencies of the contaminant. Besides iron, nickel and cobalt coordinated with simple anions such as chloride and sulfate were also tested. As shown in Figure 2.1, cobalt proved to be the most efficient among the three. The 2,4-DCP removal efficiency achieved with Co/peroxymonosulfate was by far higher than the ones achieved with the other two metals. This finding agrees with the studies of Ball and Edwards who first suggested that cobalt is the best catalyst for the decomposition of peroxymonosulfate (58).
Figure 2.1. Effect of different transition metals for the catalysis of peroxymonosulfate and the degradation of 2,4-DCP. Conditions: [2,4-DCP]₀ = 50 mg/L (0.307mM), [NiSO₄·6H₂O]₀ = 0.307mM, [KHSO₅]₀ = 0.616mM; [2,4-DCP]₀ = 0.308mM, [FeCl₂·4H₂O]₀ = 0.312mM, [KHSO₅]₀ = 0.617mM; [2,4-DCP]₀ = 0.307mM, [CoCl₂·6H₂O]₀ = 0.307mM, [KHSO₅]₀ = 0.613mM; initial pH = 5.1, no buffering species present.

Following the latter result, the Co/peroxymonosulfate system was compared with the Fenton Reagent for the degradation of 2,4-DCP in an open to the atmosphere batch-reactor, under several conditions. Figure 2.2a shows the limitations of Fenton Reagent with respect to pH for the treatment of 2,4-DCP. Significant degradation efficiencies of 2,4-DCP were achieved only at acidic pH (6.0 and below). This was not the case when the chlorophenol was treated with Co/peroxymonosulfate, as shown in Figure 2.2b. Throughout the whole pH range (2.0-8.0) Co/peroxymonosulfate demonstrated better results than the Fenton Reagent. Figure 2.2c merges the results obtained from the treatment of 2,4-DCP with the two oxidizing systems at pH 3.0,
which is within the well-known optimum pH range for the Fenton Reagent. It is shown that, allowing sufficient reaction time, the Co/peroxymonosulfate process gives higher degradation efficiencies even at that particular pH.

Figure 2.2a. Degradation of 2,4-DCP with the Fenton Reagent at different initial pH values. Conditions: [2,4-DCP]₀=0.307mM, molar ratio of the oxidizing system versus 2,4-DCP 2:1, pH buffered at 7.0 with [KH₂PO₄]= 19.72 mM and [NaOH]= 8 mN.
Figure 2.2b. Degradation of 2,4-DCP with the Co/peroxymonosulfate reagent at different initial pH values. Conditions: \([2,4\text{-DCP}]_0=0.307\text{mM}\), molar ratio of the oxidizing system versus 2,4-DCP = 2:1, pH buffered at 7.0 with \([\text{KH}_2\text{PO}_4]= 19.72 \text{mM}\) and \([\text{NaOH}]= 8 \text{mN}\).
Figure 2.2c. Comparative degradation of 2,4-DCP with the Co/peroxymonosulfate system and the Fenton Reagent at initial pH 3.0. Conditions: [2,4-DCP]₀=0.307mM, molar ratio of the oxidizing system versus 2,4-DCP = 2:1, no buffering species present.

When atrazine was the model contaminant tested, similar results were obtained as shown in Figure 2.3. Again, at the suggested optimum pH of Fenton Reagent, the treatment with Co/peroxymonosulfate resulted in higher degradation efficiencies of atrazine. Testing the two systems at neutral pH the difference in the efficiencies achieved was dramatically increased in favor of the Co/peroxymonosulfate system as in the case of the 2,4-DCP treatment. In addition to the studies with 2,4-DCP and atrazine, the degradation of naphthalene was also examined. Figure 2.4 shows comparative degradation of naphthalene using the two oxidizing systems in comparison at pH 3.0. In this case, Fenton Reagent showed better results than the Co/peroxymonosulfate process. However, when tested for the treatment of naphthalene, at neutral pH buffered with phosphates, the Co/peroxymonosulfate system sustained its high
reactivity. Beltran et al. (1998) have reported that relatively high doses of hydrogen peroxide (H₂O₂/PAHs=200/1 molar) can also result in successful treatment of PAHs with Fenton Reagent at neutral pH (105).

Figure 2.3. Comparative degradation of atrazine with the Co/peroxymonosulfate system and the Fenton Reagent at initial pH 3.0. Conditions: [C₈H₁₄ClN₅]₀=8mg/L (0.037mM), molar ratio of the oxidizing system versus atrazine = 4:1, no buffering species present.
Figure 2.4. Comparative degradation of naphthalene with the Co/peroxymonosulfate system and the Fenton Reagent at initial pH 3.0. Conditions: \([C_{10}H_8]_0=5\text{mg/L (0.039mM)},\) molar ratio of the oxidizing system versus naphthalene = 1:1, no buffering species present.

It is expected that by using higher molar ratios of the oxidant and the catalyst versus the chlorophenol, the removal efficiency of the target compound would increase. Eventually, using a molar ratio of 3:1, the Co/peroxymonosulfate process resulted in 99% transformation of the 2,4-DCP while the Fenton Reagent achieved only 90%. Data obtained by varying the molar ratio of the compared oxidizing reagents versus the contaminant are depicted in Figure 2.5. It must be noted here that in this study, Fenton Reagent was found to be slightly more reactive at pH 5.1 than at pH 3.0 (Figure 2.2a). It seems that pH 5.1 was proven better than pH 3 with respect to the reactivity of the Fenton Reagent due to inhibition of the complexation of Fe(III) with hydrogen peroxide, a reaction that also leads to activation of hydrogen peroxide, at the latter pH (16). Most
probably complexation of Fe(III) with sulfate ions (released from the addition of sulfuric acid for pH adjustment) occurs at pH 3 and competes with the peroxide activation reaction.

Figure 2.5. Comparative degradation of 2,4-DCP with the Co/peroxymonosulfate system and the Fenton Reagent. Effect of the molar ratio of the oxidizing system versus the contaminant. Conditions: [2,4-DCP]₀=0.307mM, molar ratio of the oxidant versus the transition metal = 1:1, initial pH=5.1, no pH adjustment, reaction time 1h.

In Figure 2.6, the two processes were compared at buffered solutions in the pH range of 6-8. Along with the chlorophenol concentration, the total organic carbon present in solution was also monitored. Throughout this pH range and under certain loading of oxidizing system, 2,4-DCP was completely destroyed when treated with the Co/KHSO₅ reagent. In the case of the Fenton Reagent, the removal efficiency of 2,4-DCP decreased from 55% at pH just below 6.0 to 15% at
pH close to 8.0. The Co/ KHSO$_5$ process also achieved from 20 to 30% TOC removal while the Fenton Reagent achieved only up to 5% and at pH values below 6.5.

Figure 2.6. Comparative TOC (reaction time, 4h) and 2,4-DCP (1h) removal efficiencies achieved from the treatment of 2,4-DCP with the Co/peroxymonosulfate process and the Fenton Reagent. Effect of pH in the range 6.0-8.0. Conditions: [2,4-DCP]$_0$=50mg/L (0.307mM), MR=10:1, 0.1M phosphate buffer.

The Co/peroxymonosulfate reagent was also tested for the removal of organic carbon resulting from the degradation of 2,4-DCP in water buffered with carbonates. A summary of the results is provided in Table 2.1. It seems that the sulfate radicals generated by the Co/peroxymonosulfate process are not affected by carbonate species, since the removal efficiencies of chlorophenol and TOC were still at high values. They were also comparable to the values obtained when phosphates were the buffering species introduced in solution (Figure 2.6). The higher TOC removal at pH 9.0 as compared to pH 6.5 with the Co/peroxymonosulfate reagent is attributed to
different kinetics at these particular conditions. In general, 2,4-DCP degradation and TOC removal demonstrated higher rates at higher pH values. At pH 6.5 and for 4h, TOC removal had not reached steady state as in the case of the experiment at pH 9.0. Allowing further reaction time similar TOC values were obtained at both pH conditions. Fenton Reagent showed also significant reactivity at pH 6.7 buffered with carbonates. It is believed that the particular order of the reagents addition plays a crucial role in the efficiency of the Fenton Reagent. At pH 6.7 buffered with carbonates, hydrogen peroxide was added before iron to avoid iron species precipitation. This particular order of addition was also suggested being optimum by Beltran et al. (1998) who investigated PAHs degradation with Fenton Reagent at neutral pH (105). It must be also underlined that during the experiments at pH 6.5 and 6.7 the pH increased instead of decreasing, as in the cases of most AOTs due to the formation of organic acids from the degradation of the contaminants and the proton release from the hydrolysis of the transition metals. This is because the system was initially close to the pKa value of the first dissociation of carbonic acid (pKa1=6.35) and carbon dioxide was generated that escaped the solution (bubble formation observed). Consequently, hydrogen and bicarbonate ions were consumed to maintain equilibrium leading to an increase of the pH.
Table 2.1. Comparative degradation of 2,4-DCP using the Fenton Reagent and the Co/peroxymonosulfate system in water buffered with carbonates. Conditions: [2,4-DCP]₀=50 mg/L, molar ratio (MR) of the oxidant and catalyst vs. the contaminant = 10:1, 0.1M carbonates (pH=9.0), 0.1M carbonates and 14mM sulfuric acid (pH=6.5), reaction time 4h, triplicate experiments.

<table>
<thead>
<tr>
<th>Process</th>
<th>pH₀</th>
<th>pH_f</th>
<th>% 2,4-DCP Rem. Effic.</th>
<th>% TOC Rem. Effic.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fenton</td>
<td>6.7</td>
<td>8.2 ± 0.4</td>
<td>N/A</td>
<td>25.7 ± 0.8</td>
</tr>
<tr>
<td>Co/KHSO₅</td>
<td>6.5</td>
<td>7.8 ± 0.6</td>
<td>99</td>
<td>32.1 ± 10.5</td>
</tr>
<tr>
<td>Co/KHSO₅</td>
<td>9.1</td>
<td>8.8 ± 0.1</td>
<td>99</td>
<td>41.0 ± 4.6</td>
</tr>
</tbody>
</table>

Another aim of this study was also to test whether the Co/peroxymonosulfate process faces the barrier of mineralization that Fenton Reagent does, believed to be approximately 60% (18). For this, the oxidizing system loading (here represented as molar ratio of the oxidizing system vs. the contaminant) was significantly increased. Figure 2.7 shows comparative results from the mineralization of 2,4-DCP with the Fenton Reagent and the Co(II)/KHSO₅ system. While Fenton Reagent at pH 3.0 (optimum) and at a 80:1 mol ratio of H₂O₂:2,4-DCP achieves 55% of organic carbon removal (measured as non-purgeable organic carbon, NPOC), the Co(II)/KHSO₅ at neutral pH and at the same oxidant to contaminant mol ratio (same dose of H₂O₂ and KHSO₅; KHSO₅:2,4-DCP=80:1) mineralizes almost 90% of the initial organic loading. In this case again, Fenton Reagent fails to exceed 60% mineralization of the contaminant while the Co(II)/KHSO₅ reagent does not demonstrate such limitation. At higher pH, the reactivity of Fenton Reagent decreases and gradually diminishes above pH 6.
Figure 2.7. Comparative mineralization of 2,4-DCP with the Co(II)/KHSO₅ system at pH 7.0 and the Fenton Reagent at pH 3.0. Conditions: [2,4-DCP]₀=50 mg/L (0.307mM) corresponding to 22.1 mg/L of NPOC (normalized); KHSO₅/Co(II)=1000/1 and H₂O₂/Fe(II)=1/1 mol, the Co(II)/KHSO₅ experiments were conducted at pH 7.0, adjusted with 0.1M phosphate buffer, while for the adjustment of the Fenton reaction at pH 3.0, concentrated sulfuric acid was used.

2.3.2 Fundamental Investigations of the Co/Peroxymonosulfate Reagent

Testing the Co/peroxymonosulfate reagent at different pH values for the treatment of 2,4-DCP it was found that the kinetics of the contaminant decay were significantly slower at pH 2.0 than at higher pH values. Figure 2.8 shows that at pH 2.0 and for the first 60 min the decay of 2,4-DCP with the Co/peroxymonosulfate system follows pseudo-first order reaction kinetics. As expected, the removal efficiency became 10% higher for an extended reaction time of 24h at that particular pH (not shown). For a reaction time of 4h there were still significant amounts of unreacted
peroxymonosulfate. This was indicated by the nitrate formation in the samples as nitrite was oxidized by peroxymonosulfate to form nitrate. Faster kinetics exist at pH values above 2.0. It was found that by increasing the pH up to a value of 4.0-5.0, higher degradation rates are achieved. The initial reaction rate, for example, for the first 15 min was calculated to be 0.0052, 0.0269 and 0.0310 mmol/min, for initial pH values of 2.0, 3.0 and 4.0, respectively.

![Graph showing the decay of 2,4-DCP with the Co/peroxymonosulfate system at pH 2.0 and at two different oxidant loadings.](image)

**Figure 2.8.** Kinetic analysis of the 2,4-DCP decay with the Co/peroxymonosulfate system at pH 2.0 and at two different oxidant loadings represented as peroxymonosulfate:2,4-DCP molar. Conditions: [2,4-DCP]₀=0.307mM, molar ratio of cobalt versus 2,4-DCP = 2:1, no buffering species present.

It has been reported that the decomposition of peroxymonosulfate is catalytic with respect to cobalt (62,64). The objective therefore was to prove that even very low concentrations of Co(II) are enough for the degradation of 2,4-DCP. The catalytic behavior of cobalt in the process is
presented in Figure 2.9a. The concentration of peroxymonosulfate was kept constant and the cobalt dose was lowered from 1.227 mM (~72.3 mg/L) to 1.227 µM or (72.3 µg/L). The results obtained at buffered solution of pH 7.0 were similar regardless of the cobalt concentration; the 2,4-DCP transformation was again almost complete and the TOC removal was around 30%. Figure 2.9b shows results with respect to 2,4-DCP degradation kinetics represented as moles degraded per reaction time (calculated) versus the molar ratio of peroxymonosulfate:Co. The concentration of peroxymonosulfate was again kept constant and the cobalt dose was lowered gradually. It is shown that by decreasing cobalt dose a critical concentration of 0.72 mg/L (corresponding to peroxymonosulfate:Co molar of 100) is reached. Below this value and for the first 5 minutes, the reaction was significantly slowed down.

Figure 2.9a. 2,4-DCP and TOC removal efficiencies achieved with the Co/peroxymonosulfate chemical oxidation process. Effect of cobalt dose. Conditions: [KHSO₅]₀=1.227 mM, [2,4-DCP]₀=0.307 mM, 0.1M phosphate buffer (pH=7.0), reaction time 4h.
Figure 2.9b. Effect of cobalt dose in the kinetics of 2,4-DCP destruction with the Co/peroxymonosulfate method. Number of moles degraded per reaction time versus peroxymonosulfate:Co molar. Conditions: [KHSO$_5$]$_0$=1.227mM, [2,4-DCP]$_0$=0.307mM, 0.1M phosphate buffer (pH=7.0).

The primary radicals formed from the cobalt-mediated decomposition of peroxymonosulfate were identified with specific quenching studies. It is thoroughly established in the literature that alcohols containing alpha hydrogen such as methanol and ethanol readily react with hydroxyl and sulfate radicals. Peroxymonosulfate radicals, however, are relatively inert towards alcohols. Moreover, although alcohols with no alpha hydrogen such as tert-butyl alcohol (TBA) are effective quenching agents for hydroxyl radicals, they react 1000-fold slower with sulfate radicals (64,69-72). The following Table 2.2 summarizes the quenching experiments. When ethanol was used at molar ratios of 500:1 and 1000:1 versus the oxidant, the system
demonstrated 88% and 95% decrease in the 2,4-DCP removal efficiencies respectively, compared to the efficiencies when no alcohol was used. This indicates that peroxymonosulfate radicals should be excluded from being the primary species formed. To differentiate between hydroxyl and sulfate radicals TBA was used at the same molar ratios. In this case, the system demonstrated only 9% decrease in the removal efficiency of 2,4-DCP. The latter indicates that sulfate radicals are indeed the primary oxidizing species formed, since the TBA addition did not affect significantly the degradation efficiency of the model contaminant.

Table 2.2. % change in the 2,4-DCP removal efficiency when specific alcohols were present in solution.

<table>
<thead>
<tr>
<th></th>
<th>Et-OH</th>
<th>TBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar ratio of the alcohol vs. KHSO\textsubscript{5}</td>
<td>503</td>
<td>998</td>
</tr>
<tr>
<td>Alcohol Concentration, M</td>
<td>0.617</td>
<td>1.225</td>
</tr>
<tr>
<td>Reaction Time</td>
<td>%change in 2,4-DCP removal efficiency</td>
<td></td>
</tr>
<tr>
<td>1h</td>
<td>-88</td>
<td>-95</td>
</tr>
<tr>
<td>2h</td>
<td>-88</td>
<td>-95</td>
</tr>
<tr>
<td>3h</td>
<td>-88</td>
<td>-95</td>
</tr>
<tr>
<td>4h</td>
<td>-88</td>
<td>-95</td>
</tr>
</tbody>
</table>

Conditions: \([2,4-\text{DCP}]_0=0.307\text{mM (50mg/L)}, [\text{CoCl}_2.6\text{H}_2\text{O}]_0=1.229\times10^{-3}\text{mM}, [\text{KHSO}_3]_0=1.227\text{mM, 0.1M phosphate buffer (pH=7.0)}\).
2.4. Discussion

The efficiency of the developed process lies primarily upon the high oxidizing strength of the sulfate radicals formed. The sulfate radicals are stronger oxidants than the hydroxyl, especially at neutral (natural) pH, considering the comparison of their redox potential, as shown in Table 2.3.

<table>
<thead>
<tr>
<th>Radical Reaction</th>
<th>Redox Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SO}_4^* + e^- \rightarrow \text{SO}_4^{2-} )</td>
<td>2.5-3.1 V (106)</td>
</tr>
<tr>
<td>( \text{OH}^* + e^- \rightarrow \text{OH}^- )</td>
<td>1.985 V (41)</td>
</tr>
<tr>
<td>( \text{OH}^* + e^- + H^+ \rightarrow \text{H}_2\text{O} )</td>
<td>2.38V (41) or 2.72V (107)</td>
</tr>
<tr>
<td>( \text{SO}_5^* + e^- \rightarrow \text{SO}_5^{2-} )</td>
<td>1.1 V (106,108)</td>
</tr>
</tbody>
</table>

According to Neta et al. (1988), sulfate radicals are also more efficient oxidants than hydroxyl for many organic compounds, since they are more selective for oxidation (electron transfer) (106). Hydroxyl radicals may react rapidly also by hydrogen abstraction and addition. The selectivity of sulfate radicals against hydroxyl radicals for degrading certain organic compounds was verified in the case of 2,4-DCP and atrazine. In the case of naphthalene though and at pH 3.0, hydroxyl radicals generated with the Fenton Reagent were proven more efficient than sulfate radicals resulted from the conjunction of cobalt with peroxymonosulfate. This suggests that sulfate radicals are not indeed universally more effective than hydroxyl in degrading organic compounds. The structure of the contaminant-substrate affects the reactivity of sulfate radicals more greatly than that of hydroxyl.
Sulfate radicals are such strong oxidants that can oxidize chloride ions to form chlorine radicals (106). In our experimental investigations there was indication of chlorine formation (odor) that was quantified in a future work. Chlorine formation, when chloride species present in solution react with sulfate radicals, has also been reported by other researchers (109).

Furthermore, the reduction of Co(III) to Co(II) mediated by the oxidation of peroxymonosulfate (reaction 1.11) is thermodynamically feasible (0.82 V), fast and the process proceeds cyclically many times until peroxymonosulfate is consumed (61,62). It is noted that cobalt (II) is the dominant species at least up to pH 6, but even at higher pH values, when Co(III) was also present initially, the process demonstrated the same 2,4-DCP removal efficiencies as with Co(II) only present. The color development of the solution before the addition of peroxymonosulfate was indicative of the cobalt speciation: Co(II) pink, Co(III) blue, co-presence purple. The respective reaction of the Fenton Reagent (reaction 1.2), on the other hand, is very slow (16,18,29). It is also thermodynamically unfavorable, since demonstrates a negative redox potential of -0.724 V. Furthermore, in open systems and above pH 5, iron(II) is oxidized to iron(III) and most of the latter precipitates in the form of the respective hydroxides and oxyhydroxides, leading to further lower catalytic activity (18).

The high efficiency at elevated pH values of the process proposed herewith is a very important advantage for its future applicability in the large scale. This is because the pH of most contaminated natural waters is in the range of 6 to 8. It is also important to state that cobalt is needed only in small-catalytic amounts, thus its potential toxicity may be overcome. As low as 72.3 µg/L of dissolved cobalt were sufficient for the complete transformation of 50 mg/L of 2,4-
DCP and approximately 30% organic carbon removal (Figure 2.9a). This value is between cobalt concentrations found in drinking water and below those tested in a recent study that reported the role of dissolved cobalt as a catalyst in an ozonation process \((110)\). The development of a heterogeneous system would be certainly more appropriate, especially for drinking water applications. Sol-gel techniques for surface immobilization of cobalt are currently under investigation in our laboratories.

With respect to the oxidants, hydrogen peroxide is more environmentally friendly than peroxymonosulfate. However, peroxymonosulfate, although releases additional sulfate ions in the aqueous phase, is easier to handle (crystalline form) and sulfate radicals are stronger oxidants than hydroxyl, especially at elevated pH. Preliminary cost analysis based on prices derived from major production companies of hydrogen peroxide and potassium peroxymonosulfate in the US showed that the former is much cheaper than the latter. Hydrogen peroxide costs $1.52 per kg of pure substance while OXONE® costs approximately $2.20 per kg \((47,111)\). However, the use of Fenton Reagent includes the costs for iron and hydrogen peroxide addition as well as for pH adjustment at the acidic region. Furthermore, the costs of post neutralization and sludge treatment due to the iron species precipitation must be included. Iron precipitation can have a positive effect however, since many contaminants can be adsorbed and co-precipitate with the sludge. The cost of Co/peroxymonosulfate includes only the cost of peroxymonosulfate, since cobalt is needed in very small amounts and no pH adjustment or sludge treatment are required. Hence, it is believed that the Co/peroxymonosulfate reagent might be proven an attractive alternative remediation technology for practitioners in the field.
In many cases, the quality of industrial wastewater demonstrates such diversity that it is very difficult to propose an overall efficient method for the removal of COD, parameter that is usually of major concern when treating industrial discharges (usually a series of different processes is required). From the general idea, however, of the described technology, many more alternatives have been raised. Depending upon the dominant transition metal present in the wastewater, we may be able to propose the addition of the oxidant that decomposes favorably with this as a catalyst.

In general, the efficiency of the pairing seems to depend on several factors such as the pH, the nature of the metal ligand and the ionic strength. Moreover, the transition metal has to demonstrate high redox potential in order to oxidize the inorganic oxidant in the similar to equation 1.11 redox reaction. Some other parameters that are currently under investigation in our laboratories include the initial concentration of the contaminant, the concentration and the selectivity of the oxidant and the concentration of dissolved oxygen (DO) in solution.
CHAPTER 3

Radical Generation by the Interaction of Transition Metals with Common Oxidants

Nine transition metals were tested for the activation of three oxidants and the generation of inorganic radical species such as sulfate, peroxymonosulfate and hydroxyl radicals. From the twenty-seven combinations, fourteen M/Ox couples demonstrated significant reactivity toward transforming a model organic substrate such as 2,4-dichlorophenol and are further discussed here. It was found that Co(II) and Ru(III) are the best metal-catalysts for the activation of peroxymonosulfate. As expected on the basis of the Fenton Reagent, Fe(III) and Fe(II) were the most efficient transition metals for the activation of hydrogen peroxide. Finally, Ag(I) showed the best results toward activating persulfate. Quenching studies with specific alcohols (tert butyl alcohol and ethanol) were also performed to identify the primary radical species formed from the reactive M/Ox interactions. The determination of these transient species allowed us to postulate the rate-determining step of the redox reactions taking place when a metal is coupled with an oxidant in aqueous solution. It was found that when Co(II), Ru(III) and Fe(II) interact with peroxymonosulfate, freely diffusible sulfate radicals are the primary species formed. The same was proven for the interaction of Ag(I) with persulfate but in this case caged or bound to the metal sulfate radicals might be formed as well. The conjunction of Ce(III), Mn(II) and Ni(II) with peroxymonosulfate showed also to generate caged or bound to the metal sulfate radicals. A combination of sulfate and hydroxyl radicals was formed from the conjunction of V(III) with
peroxymonosulfate and from Fe(II) with persulfate. Finally, the conjunction of Fe(III), Fe(II) and Ru(III) with hydrogen peroxide led primarily to the generation of hydroxyl radicals. It is also suggested here that the redox behavior of a particular metal in solution cannot be predicted based exclusively on its size and charge. Additional phenomena such as metal hydrolysis as well as complexation with other counter ions present in solution might affect the thermodynamics of the overall process and are further discussed here.

3.1 Introduction

The dual role of common oxidants (i.e. chlorine, ozone, hydrogen peroxide, persulfate salts) for decontamination as well as disinfection is well known in water treatment applications. The potential though of further activating these oxidants for the generation of transient species that demonstrate much greater oxidizing strength than the parent oxidant is far less explored. Advanced Techniques such as photolysis and radiolysis are used for the activation of the oxidants and thus provide a clean way of generating highly oxidizing radical species. The use of transition metals, in most cases in catalytic amounts, provides another option of radical generation. Perhaps the most well known of such systems is Fenton reagent that leads to the generation of hydroxyl radicals according to reaction 1.1. The technology is currently applied for the treatment of industrial discharges, soil and groundwater remediation.

Chapter 2 demonstrated that sulfate radicals, generated by the conjunction of cobalt with peroxymonosulfate as shown in reaction 2.1, are even more efficient oxidants than hydroxyl radicals at least for the transformation of 2,4-dichlorophenol (2,4-DCP), atrazine and
naphthalene, under certain conditions. Sulfate radicals demonstrate higher standard reduction potential than hydroxyl radicals, at neutral pH and to this is mainly attributed their superiority in degrading several organic compounds. At acidic pH, they both demonstrate almost similar reduction potentials but in general sulfate radicals are more selective towards oxidation than hydroxyl. Hydroxyl radicals react rapidly with organic substrates by hydrogen abstraction or addition (106). The difference in oxidizing power for these two radicals at neutral pH and their similarity at acidic has been rationalized by Steenken (112). On the basis of Brønsted catalysis law it was suggested that the difference between the two radicals lies in the abilities of their redox partners as leaving groups; the bisulfate and sulfate ions for the sulfate radical and the water molecule for the hydroxyl radical.

On the basis of the Fenton Reagent and the cobalt/peroxymonosulfate system, several transition metals were coupled with common oxidants. Ag(I), Ce(III), Co(II), Fe(II), Fe(III), Mn(II), Ni(II), Ru(III) and V(III) were tested for the activation of three inorganic oxidants: hydrogen peroxide, potassium peroxymonosulfate and persulfate. OXONE® is the commercial name of the triple salt $2\text{KHSO}_5\cdot\text{KHSO}_4\cdot\text{K}_2\text{SO}_4$, which is the source of the strong oxidant peroxymonosulfate ($\text{KHSO}_5$). Hydrogen peroxide is extensively used in water treatment (along with UV or O$_3$) due to the fact that is a “green” chemical and is more economic than the other two. Persulfate is commonly used in TOC analyzers where it is activated with UV radiation (254 nm) or heating and was recently suggested that could be effective against SARS (50). The objective was to identify the couples that demonstrate significant reactivity toward transforming a model organic substrate (2,4-DCP), identify the major transient species formed from each coupling and rationalize their formation and reactivity. To our knowledge, this is the first study that investigates radical formation
reactions and the induced thereby transformation of a model chlorinated aromatic compound at such great extent. First, the comparison of the reactivity resulting from the coupling of so many different reagents (nine transition metals and three oxidants) has not been attempted before. Moreover, this study introduces to the environmental field a novel and accurate technique, already applied with great results in the fields of biochemistry, for identifying radical species formed by the interaction of a metal with an oxidant. The generation and utilization of inorganic radical species such as sulfate radicals increase our options for developing new decontamination technologies. In several cases, these species have been proven much more efficient oxidants than the extensively investigated hydroxyl radicals toward degrading organic and inorganic contaminants. More specifically, the determination of reactive metal-oxidant couples and the identification of the transient species formed by these interactions significantly contribute to the better understanding of oxidation-reduction phenomena and provide new tools for decontamination of specialty wastewater (i.e., paper and pulp, photographic, automotive, nuclear). These wastewaters are contaminated with metals (i.e., Mn, Fe, Cu, Ag, Ni, Co). The latter, before being removed, can be used for the treatment of other harmful compounds that are also present.

3.2 Materials and Methods

The transition metals tested were in the form of simple salts except for vanadium: Ag$_2$SO$_4$ (100%, Fisher), CeCl$_3$.7H$_2$O (99.9%, Aldrich), CoCl$_2$.6H$_2$O (98%, Aldrich), FeCl$_3$ (97%, Aldrich), FeSO$_4$.7H$_2$O (100.4%, Fisher), MnCl$_2$.4H$_2$O (98%, Aldrich), NiSO$_4$.6H$_2$O (99.6%, Fisher), RuCl$_3$.xH$_2$O (47% as Ru$^{3+}$, Aldrich) and V$_2$O$_5$ (99%, Aldrich). All metals were selected
at their lowest reported oxidation state that normally occurs in solution. Stock solutions of the metal salts were prepared with concentrations varying from 5 mM to 100 mM depending upon the solubility of each salt. In some cases the pH of the stock solution was adjusted in the acidic region with the corresponding acid of the metal counter ion to facilitate complete dissolution of the salt.

Specific aliquots of the solutions were added to the reactor in order to achieve an initial metal concentration of 1.244 mM (except for Ru: 2.553 mM), corresponding to a 4:1 molar ratio of the metal (8.2:1 for Ru) versus the substrate or 1:1 versus the oxidant. It must be noted here that this ratio is not necessarily optimum for each metal/oxidant couple. It was selected based on literature information suggesting that Fe(II)/H2O2 molar of 1/1 (stoichiometric) is a typical and sometimes optimum ratio for the Fenton Reagent (see Chapter 2). In addition, some metals (i.e., Fe, Ag, V, Ce) did not demonstrate true catalytic activity in the overall process and rather elevated metal concentrations were required to achieve oxidant decomposition. This however might make critical the impact of the competing, non-favorable reactions between the metals and the radicals formed (see reactions 18 and 19). In any case, when designing environmental applications, it is imperative that the metal concentration is as low as possible (i.e., not exceeding levels higher than ppb) and hence a metal has to be tested beforehand whether it can activate the respective oxidant at such low concentrations.

The oxidants used were potassium peroxymonosulfate (from OXONE®), hydrogen peroxide (H2O2, 30% solution) and potassium persulfate (K2S2O8). All chemicals were used as received. 100 mM stock solution of each oxidant was previously prepared and a specific aliquot was
diluted in the reaction vessel to achieve an initial concentration of 1.244 mM, which also corresponds to a 4:1 molar ratio of the oxidant versus the substrate. The solution pH plays a major role in the overall process, especially due to solubility limitations of certain transition metal salts. Metals such as Ag(I), Fe(II), Fe(III) require acidic conditions to remain in solution and thus were tested at pH~3.0, while all the other metals such as Co(II), Ce(III), Mn(II), Ni(II), Ru(III) and V(III) did not demonstrate such limitation and it was decided to be tested at neutral pH. In the latter case, the pH was buffered at 6.8-7.1 with 0.1 M of phosphates (H₂PO₄⁻/HPO₄²⁻). In the other cases, it was adjusted at 2.8-3.1 with either sulfuric or hydrochloric acid, depending upon the counter ion of each transition metal salt.

The initial concentration of the substrate (2,4-DCP) was approximately 50.7 mg/L (0.311 mM) and its transformation was monitored with an Agilent 1100 Series HPLC System with a QuatPump and a UV-vis diode array detector. The column used for the analysis of the substrate was an Eclipse XDB-C8 column, obtained from Agilent. All experiments were batch and were conducted in 500 mL flasks at ambient room temperature. First, the substrate and the acid or the buffering species were added, followed by the metal addition. Finally and immediately at the oxidant addition (thus the initiation of the reaction), time monitoring was initiated. Samples (10 mL) were taken at specific time intervals for 4 h and were immediately quenched with excess of methanol solution (5 mL of 2.46 M). Several experiments were conducted in triplicate and thus some figures show error bars.

Once a reactive couple was identified, two sets of quenching experiments were performed to determine the radical species formed by each particular metal-oxidant couple. The experimental
procedures were repeated as previously with the addition of (i) tert-butyl alcohol (TBA) and (ii) ethanol (EtOH) being the only difference from before. A specific amount of each alcohol was added in the reactor before the metal and the oxidant addition to obtain a concentration of 622 mM, corresponding to a 500:1 molar ratio of the alcohol versus the oxidant.

3.3 Results and Discussion

3.3.1 Metal-Oxidant Reactivity

First, the reactivity resulting from the interaction of the nine transition metals with each of the three oxidants was determined by monitoring the transformation of the substrate (2,4-DCP). The results are depicted in Figures 3.1-3.9.

Ferrous and ferric iron were the only metals able to activate all three oxidants at a significant extent as shown in Figures 3.1 and 3.2, respectively. The Fenton and Fenton-like reagents led to high transformation of the substrate; 91% and 95%, respectively in 4 h reaction time. The coupling of KHSO5 with ferrous and ferric iron led to 75% and 35% of substrate transformation while the same metals coupled with K2S2O8 led to 21% and 15% transformation, respectively.
Figure 3.1: 2,4-DCP transformation by the interaction of Fe(II) and three different oxidants at initial pH 3.0. Conditions: \([2,4\text{-DCP}]_0= 0.311 \text{ mM}, [\text{FeSO}_4\cdot 7\text{H}_2\text{O}]_0= [\text{H}_2\text{O}_2]_0= [\text{KHSO}_5]_0= [\text{K}_2\text{S}_2\text{O}_8]_0= 1.244 \text{ mM}.\)
**Figure 3.2**: 2,4-DCP transformation by the interaction of Fe(III) and three different oxidants at initial pH 3.0. Conditions: \([2,4-\text{DCP}]_0= 0.311 \text{ mM}, [\text{FeCl}_3]_0= [\text{H}_2\text{O}_2]_0= [\text{KHSO}_5]_0= [\text{K}_2\text{S}_2\text{O}_8]_0= 1.244 \text{ mM}.

Figure 3.3 shows the transformation of the chlorophenol when Co(II) was coupled with each oxidant at pH 7.0. As expected, the Co(II)/KHSO₅ couple showed very high reactivity since 98% of the chlorophenol was transformed in less than 1 min. The very fast kinetics of the chlorophenol degradation with the Co(II)/KHSO₅ couple are, as discussed in Chapter 2, due to the high concentration of cobalt used and the neutral pH of the solution. The coupling of the metal with the other two oxidants did not show any ability in degrading the substrate.
**Figure 3.3:** 2,4-DCP transformation by the interaction of Co(II) and three different oxidants at pH 7.0, buffered with 0.1M phosphates. Conditions: [2,4-DCP]₀=0.311 mM, [CoCl₂·6H₂O]₀=[H₂O₂]₀=[KHSO₅]₀=[K₂S₂O₈]₀= 1.244 mM.

Ru(III) coupled with KHSO₅ showed almost the same fast reactivity as the Co(II)/KHSO₅ couple towards transforming the substrate (Figure 3. 4). In addition Ru(III) coupled with H₂O₂ led, at a much lesser extent though, to some transformation of the chlorophenol (20%) in 4 h of reaction time. Finally, the Ru(III)/K₂S₂O₈ reagent did not demonstrate any appreciable ability to transform 2,4-DCP in 4 h of reaction time.
Figure 3.4: 2,4-DCP transformation by the interaction of Ru(III) and three different oxidants at pH 7.0, buffered with 0.1M phosphates. Conditions: $[\text{2,4-DCP}]_0=0.311 \text{ mM}$, $[\text{RuCl}_3\cdot x\text{H}_2\text{O}]_0=2.553 \text{ mM}$, $[\text{H}_2\text{O}_2]= [\text{KHSO}_5]_0= [\text{K}_2\text{S}_2\text{O}_8]_0=1.244 \text{ mM}$.

Figure 3.5 shows that Ag(I) is a very efficient activator of the decomposition of K$_2$S$_2$O$_8$ since their interaction led to 85% transformation of the chlorophenol in 4 hours of reaction time. The Ag(I)/KHSO$_5$ couple was proven far less reactive since it demonstrated only 8% transformation while the coupling of Ag(I) with H$_2$O$_2$ showed practically no reactivity against the chlorophenol throughout the treatment time.
Figure 3.5: 2,4-DCP transformation by the interaction of Ag(I) and three different oxidants at initial pH 3.0. Conditions: [2,4-DCP]$_0$= 0.311 mM, [Ag$_2$SO$_4$]$_0$= 0.622 mM, [H$_2$O$_2$]$_0$= [KHSO$_5$]$_0$= [K$_2$S$_2$O$_8$]$_0$= 1.244 mM.

Figures 3.6-3.9 show the induced transformation of 2,4-DCP with the coupling of Ce(III), V(III), Mn(II) and Ni(II) with the three oxidants tested here. The interaction of these metals with KHSO$_5$ only and not with any of the other two oxidants, led to higher than 10% transformation of 2,4-DCP in 4 h of reaction time. The values obtained were 32%, 26%, 24% and 16%, respectively.
**Figure 3.6:** 2,4-DCP transformation by the interaction of Ce(III) and three different oxidants at pH 7.0, buffered with 0.1M phosphates. Conditions: $[\text{2,4-DCP}]_0 = 0.311$ mM, $[\text{CeCl}_3\cdot7\text{H}_2\text{O}]_0 = [\text{H}_2\text{O}_2]_0 = [\text{KHSO}_5]_0 = [\text{K}_2\text{S}_2\text{O}_8]_0 = 1.244$ mM.
Figure 3.7: 2,4-DCP transformation by the interaction of V(III) and three different oxidants at pH 7.0, buffered with 0.1M phosphates. Conditions: \([2,4\text{-DCP}]_0 = 0.311\, \text{mM}, [\text{V}_2\text{O}_3]_0 = 0.622\, \text{mM}, [\text{H}_2\text{O}_2]_0 = [\text{KHSO}_5]_0 = [\text{K}_2\text{S}_2\text{O}_8]_0 = 1.244\, \text{mM}.\)
**Figure 3.8:** 2,4-DCP transformation by the interaction of Mn(II) and three different oxidants at pH 7.0, buffered with 0.1M phosphates. Conditions: [2,4-DCP]₀=0.311 mM, [MnCl₂.4H₂O]₀= [H₂O₂]₀= [KHSO₅]₀= [K₂S₂O₈]₀= 1.244 mM.
**Figure 3.9:** 2,4-DCP transformation by the interaction of Ni(II) and three different oxidants at pH 7.0, buffered with 0.1M phosphates. Conditions: $[2,4-\text{DCP}]_0=0.311 \text{ mM}$, $[\text{NiSO}_4.6\text{H}_2\text{O}]_0=\ [\text{H}_2\text{O}_2]= [\text{KHSO}_5]= [\text{K}_2\text{S}_2\text{O}_8]_0= 1.244 \text{ mM}$

A summary of the most reactive couples is provided in Table 3.1. From the 27 combinations (9 metals tested, with 3 oxidants), 14 couples demonstrated relatively high reactivity, as evaluated based on the removal efficiency achieved of the model organic contaminant (above 10% transformation within 4 hours of reaction time). Table 3.1 is divided in three parts with each part corresponding to the reactive couples of different transition metals with a particular oxidant. In each part the couples are placed in order of decreasing reactivity.
Table 3.1. Summary of the results from the transformation of 2,4-DCP by the interaction of metals with oxidants - Identification of the primary radical species formed by each interaction

<table>
<thead>
<tr>
<th>Metal</th>
<th>Counter Ion</th>
<th>Oxidant</th>
<th>pHo</th>
<th>Overall (4h) % transf. of 2,4-DCP</th>
<th>Init. (30 min) % transf. of 2,4-DCP</th>
<th>% change in transf. (30 min.) of 2,4-DCP due to</th>
<th>Major oxidiz. species</th>
<th>Metal Redox Couple</th>
<th>E⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Co(II)</td>
<td>Cl⁻</td>
<td>KHSO₅</td>
<td>7.0</td>
<td>98</td>
<td>98</td>
<td>-4</td>
<td>-84</td>
<td>SO₄⁻</td>
</tr>
<tr>
<td>2</td>
<td>Ru(III)</td>
<td>Cl⁻</td>
<td>KHSO₅</td>
<td>7.0</td>
<td>98</td>
<td>97</td>
<td>-3</td>
<td>-91</td>
<td>SO₄⁻</td>
</tr>
<tr>
<td>3</td>
<td>Fe(II)</td>
<td>SO₄²⁻</td>
<td>KHSO₅</td>
<td>2.9</td>
<td>75</td>
<td>66</td>
<td>-6</td>
<td>-90</td>
<td>SO₄⁻</td>
</tr>
<tr>
<td>4</td>
<td>Ce(III)</td>
<td>Cl⁻</td>
<td>KHSO₅</td>
<td>7.0</td>
<td>32</td>
<td>15</td>
<td>+27</td>
<td>-42</td>
<td>[SO₄⁻]³</td>
</tr>
<tr>
<td>5</td>
<td>V(III)</td>
<td>O²⁻</td>
<td>KHSO₅</td>
<td>7.0</td>
<td>27</td>
<td>15</td>
<td>-35</td>
<td>-71</td>
<td>SO₄⁻*OH</td>
</tr>
<tr>
<td>6</td>
<td>Mn(II)</td>
<td>Cl⁻</td>
<td>KHSO₅</td>
<td>7.0</td>
<td>24</td>
<td>12</td>
<td>-17</td>
<td>-27</td>
<td>[SO₄⁻]</td>
</tr>
<tr>
<td>7</td>
<td>Fe(III)</td>
<td>Cl⁻</td>
<td>KHSO₅</td>
<td>3.0</td>
<td>21</td>
<td>14</td>
<td>-46</td>
<td>-30</td>
<td>Fe(III)/SO₄⁻</td>
</tr>
<tr>
<td>8</td>
<td>Ni(II)</td>
<td>SO₄²⁻</td>
<td>KHSO₅</td>
<td>7.0</td>
<td>16</td>
<td>6</td>
<td>-7</td>
<td>-2</td>
<td>[SO₄⁻]</td>
</tr>
<tr>
<td>9</td>
<td>Ag(I)</td>
<td>SO₄²⁻</td>
<td>K₂S₂O₈</td>
<td>3.1</td>
<td>85</td>
<td>21</td>
<td>-18</td>
<td>-53</td>
<td>SO₄⁻/[SO₄⁻]</td>
</tr>
<tr>
<td>10</td>
<td>Fe(II)</td>
<td>SO₄²⁻</td>
<td>K₂S₂O₈</td>
<td>2.8</td>
<td>35</td>
<td>20</td>
<td>-48</td>
<td>-94</td>
<td>SO₄⁻*OH</td>
</tr>
<tr>
<td>11</td>
<td>Fe(III)</td>
<td>Cl⁻</td>
<td>K₂S₂O₈</td>
<td>3.0</td>
<td>15</td>
<td>7</td>
<td>+77</td>
<td>+47</td>
<td>Fe(III)</td>
</tr>
<tr>
<td>12</td>
<td>Fe(II)</td>
<td>Cl⁻</td>
<td>H₂O₂</td>
<td>3.0</td>
<td>95</td>
<td>56</td>
<td>-81</td>
<td>-79</td>
<td>*OH</td>
</tr>
<tr>
<td>13</td>
<td>Fe(II)</td>
<td>SO₄²⁻</td>
<td>H₂O₂</td>
<td>2.9</td>
<td>91</td>
<td>91</td>
<td>-99</td>
<td>-99</td>
<td>*OH</td>
</tr>
<tr>
<td>14</td>
<td>Ru(III)</td>
<td>Cl⁻</td>
<td>H₂O₂</td>
<td>6.8</td>
<td>20</td>
<td>8</td>
<td>-81</td>
<td>-77</td>
<td>*OH</td>
</tr>
</tbody>
</table>

¹Conditions: [2,4-DCP]₀ = 50.7 mg/L (0.311 mM), Metal (except for Ru: 2.553 mM) and Oxidant concentration = 1.244 mM, [TBA] = [EtOH] = 622 mM.
²In all experiments at pH~7.0 the presence of the buffering species H₂PO₄⁻ and HPO₄²⁻ acting as counter ions should also be included.
³The brackets denote caged or bound to the metal radical species.
Overall, six couples demonstrated very high reactivity (above 70% transformation) and from an environmental point of view they already provide established technologies (Fenton and Fenton-like) or may provide in the future alternatives for remediation technologies to practitioners in the field. As expected, the Fenton (Fe$^{II}$/H$_2$O$_2$), Fenton-like (Fe$^{III}$/H$_2$O$_2$) and the Co(II)/KHSO$_5$ reagents were among the 6 highly reactive couples. In addition, Ru(III)/KHSO$_5$, Fe(II)/KHSO$_5$ and Ag(I)/K$_2$S$_2$O$_8$ also demonstrated very high reactivity toward transforming the substrate. It was also proven here that cobalt(II) is the best catalyst for the activation of peroxymonosulfate. The same can be claimed for iron at either oxidation states for the activation of hydrogen peroxide (the Fenton and Fenton-like reagents) as well as for silver(I) for the activation of persulfate.

The results also showed that peroxymonosulfate is more universal than the other two oxidants, since it showed significant reactivity with the majority of the metals tested, especially at neutral pH. Although the distance of the O-O bond is comparable with that of solid hydrogen peroxide (113), it is believed that this non-symmetrical peroxide can be more easily activated than the other two oxidants tested here (114). Among the transition metals tested, only iron in both the divalent and trivalent forms showed reactivity in mediating the decomposition of all three oxidants at a significant extent.

3.3.2 Effect of Metal Dose as Mol Ratio of the Metal vs. the Oxidant

The objective of this study was to determine whether a particular metal/oxidant coupling has the potential of being used for water decontamination and if so, what are the primary radical species
formed from such interaction. Certainly further investigation is required with respect to optimum ratios of reagents used and one can propose several other parameters that can be varied such as the pH, type and concentration of buffer used, reaction time, dissolved oxygen, just to name a few. It must be noted therefore that the 1/1 metal/oxidant (or 4/1 metal/2,4-DCP) is not necessarily the optimum for all the metal/oxidant couples. Instead, it was chosen such for the reasons addressed in the Materials and Methods section (Section 3.1). Ideally, the higher the metal concentration, the faster the kinetics of oxidant activation and thus the contaminant degradation will be. This however has been proven so far only for the case of Co(II) with peroxymonosulfate (see Chapter 2), but not for all the metal/oxidant couples, since some of the metals failed to activate appreciably some of the oxidants or some metals do not demonstrate true catalytic activity. In such cases, competing reactions such as 3.16 and 3.17 might become more dominant than the reactions of the radicals with the organic material. For instance, rather elevated concentrations of Fe(II), Fe(III), Ag(I) and V(III) are needed for the activation of the oxidants tested here. The couples that might have a potential for environmental applications will be those that require the use of metals at extremely low concentrations (in the levels of ppb) but many of the metals cannot activate the respective oxidants at these concentrations.

To obtain an idea on the impact of the metal dose on the reactivity of a M/Ox couple, three metals, Fe(II), V(III) and Ce(III), known to react very fast via the competing, unfavorable reaction 3.16 were tested at four different doses for the activation of peroxymonosulfate. The metal concentration was varied accordingly while the oxidant concentration remained constant to obtain the following M/KHSO₅ ratios: 2/1; 1/1; 1/10; 1/100 (or the following metal vs. 2,4-DCP
molar ratios: 8/1; 4/1; 1/2.5; 1/25). Figures 3.10a-c summarize the results from the treatment of 2,4-DCP with these three M/KHSO₅ couples at four different metal doses used.

**Figure 3.10a:** Effect of Fe(II) dose as mol ratio of Fe(II):KHSO₅ on the transformation of 2,4-DCP at initial pH 3.0. Conditions: [2,4-DCP]₀ = 0.311 mM, [KHSO₅]₀ = 1.244 mM.
Figure 3.10b: Effect of V(III) dose as mol ratio of V(III):KHSO₅ on the transformation of 2,4-DCP at pH 7.0, buffered with 0.1M phosphates. Conditions: [2,4-DCP]₀ = 0.311 mM, [KHSO₅]₀ = 1.244 mM.
Figure 3.10c: Effect of Ce(III) dose as mol ratio of Ce(III):KHSO₅ on the transformation of 2,4-DCP at pH 7.0, buffered with 0.1M phosphates. Conditions: [2,4-DCP]₀ = 0.311 mM, [KHSO₅]₀ = 1.244 mM.

It is shown that among those tested, the optimum M:Ox ratio for the Fe(II):KHSO₅ was 1:1, as already suggested in the Materials and Methods section. The optimum ratio for V(III):KHSO₅ was 2:1 and it appears that the more V(III) is used the higher the efficiency of the process. Finally at all Ce(III) doses tested, the Ce(III):KHSO₅ demonstrated limited activity within the 30 min of reaction with the 1:10 mol ratio appearing to be slightly the best case, although the differences are within experimental error as shown by the error bars of Figure 3.10c.
3.3.3 Quenching Studies for Radical Identification

After identifying the most reactive couples, quenching experiments were conducted with the addition of TBA and EtOH for identifying the primary radical species formed from each couple. These results are also summarized in Table 3.1. The conditions of the experiments were identical to those described previously (Figures 3.1-3.9) with the addition of the alcohol being the only difference from before. The alcohols (either EtOH or TBA) were added at certain amounts in solution to obtain a concentration of 622 mM, which corresponds to a 500:1 molar ratio of the alcohol versus the oxidant or the transition metal. The technique has been extensively used by the research group of Burrows (63,64,70-72,115) and is based on the differences in the reactivity and the rates of the reactions between the potential radical species formed and the particular alcohol-additive. The transition-metal-mediated activation of hydrogen peroxide and potassium persulfate is known to generate hydroxyl and sulfate radicals respectively. In the case of potassium peroxymonosulfate however, there are three different radicals that can be formed: sulfate, hydroxyl and peroxymonosulfate (see reactions 2.2-2.4). Literature information suggests that alcohols containing alpha hydrogen, such as ethanol, react at high and comparable rates with hydroxyl and sulfate radicals; the rate with hydroxyl radicals \(1.2\times10^9 - 2.8\times10^9 \text{ M}^{-1}\text{s}^{-1}\) is approximately 50-fold greater than that with sulfate radicals \(1.6\times10^7 - 7.7\times10^7 \text{ M}^{-1}\text{s}^{-1}\) \((106,116,117)\). Peroxymonosulfate radicals, however, are relatively inert towards alcohols, since their reaction rate with ethanol is less than \(10^3 \text{ M}^{-1}\text{s}^{-1}\) \((117)\). Moreover, although alcohols with no alpha hydrogen, such as tert-butyl alcohol are effective quenching agents for hydroxyl radicals, they react much slower with sulfate radicals; the reaction rate with hydroxyl radicals \(3.8\times10^8 - 7.6\times10^8 \text{ M}^{-1}\text{s}^{-1}\) is approximately 1000-fold greater than that with sulfate radicals \(4\times10^5 - 9.1\)
Based on these properties, the experiments with ethanol would allow us to differentiate between the formation of peroxymonosulfate and sulfate/hydroxyl radicals. Peroxymonosulfate radicals however demonstrate very low reaction rates with phenols and, if formed, are not expected to induce any appreciable transformation of the substrate. Consequently, the effect of the presence of TBA is much more critical, rather than that of EtOH, and the change in the % transformation of the substrate due to the addition of TBA allowed us to differentiate between sulfate and hydroxyl radicals. The latter are much stronger oxidants than peroxymonosulfate radicals and are expected to be the major species responsible for the transformation of 2,4-DCP. The effect of EtOH served only as supporting information to the information derived from the effect of TBA and in some cases allowed us to differentiate between the formation of freely diffusible or bound to the metal radical species.

The results from the reactive couples depicted in lines 1, 9, 12 and 13 of Table 3.1 can serve as controls for the determination of the radical species formed from the other couples. It is already established that Co(II)/KHSO₅ (59-64) as well as Ag(I)/K₂S₂O₈ (60,61,118) lead to the formation of sulfate radicals while Fenton and Fenton like reagents lead to the generation of hydroxyl radicals. The same results were obtained from the quenching experiments performed in this study as shown in Table 3.1. The transformation of 2,4-DCP by the Co(II)/KHSO₅ reagent, for example, was not affected by the presence of TBA, since almost the same % transformation (only 1% decrease) was achieved with and without TBA. On the other hand, when ethanol was added in solution, the transformation of the substrate decreased 84%, indicating that the species formed reacted with EtOH and not with the substrate. From the combined effect of TBA and EtOH it is concluded that the major species formed from the Co(II)/KHSO₅ interaction, and
hence those that are responsible for the transformation of the substrate, are the sulfate radicals. The rate-determining step for the sulfate radical generation via the Co(II)/KHSO5 system is depicted in reaction 2.1. The results from the quenching experiments with the use of the Ag(I)/K2S2O8 couple are slightly different however. In this case, the 2,4-DCP transformation decreased only 18% due to the presence of TBA indicating that sulfate radicals are the oxidizing species formed. The addition of ethanol however did not have the same dramatic effect as in the case of the Co(II)/KHSO5 couple, since the decrease in the % transformation of 2,4-DCP was 53%. These results suggest that the sulfate radicals are indeed the primary species formed by the Ag(I)/K2S2O8 reagent but in this case a combination of freely diffusible and bound to the metal sulfate radicals are generated according to reactions 3.1 and 3.2.

\[
\text{Ag}^+ + S_2O_8^{2-} \rightarrow \text{Ag}^{2+} + \text{SO}_4^{*} + \text{SO}_4^{2-} \quad (3.1)
\]

\[
\text{Ag}^+ + S_2O_8^{2-} \rightarrow \text{[Ag}^{II}(\text{SO}_4^{*})]\text{]}^+ + \text{SO}_4^{2-} \quad (3.2)
\]

In the case of the treatment of 2,4-DCP with the Fenton and the Fenton-like reagents, hydroxyl radicals were found to be the primary species formed. When TBA was present, 81% and 99% decrease in the transformation of the substrate was observed while the decrease due to EtOH was 79% and 99%, respectively. These values indicate that hydroxyl radicals are the primary species formed by both reagents. The slight difference in the percent decrease may be accounted for the hydroperoxyl radical formation at an initiation step with the Fe(III)/H2O2, which is a less reactive radical compared to hydroxyl and is the only difference between the two systems according to reactions 1.1 and 1.2.
Of particular interest are the results from the transformation of 2,4-DCP with KHSO₅ and different metals (Table 3.1, lines 1-8). It can be seen that the decrease in the transformation efficiency from one couple (M/KHSO₅) to another is followed by an increase in the % change of the substrate transformation when TBA is present and a decrease in the % change of the substrate transformation when ethanol is present, in absolute values. These results indicate that the formation of freely diffusible sulfate radicals by a particular M/Ox couple and their participation as the major species for the transformation of the substrate is decreasing as one proceeds from line 1 to 9. Co(II)/KHSO₅, Ru(III)/KHSO₅ and Fe(II)/KHSO₅ generate almost exclusively freely diffusible sulfate radicals via general reaction 3.3.

\[
M^{n+} + \text{HSO}_5^- \rightarrow M^{(n+1)} + \text{OH}^- + \text{SO}_4^- \cdot \quad (3.3)
\]

As one proceeds to consecutive couples the freely diffusible sulfate radicals are being replaced by hydroxyl radicals and bound to the metal or caged sulfate radicals. The effect of TBA and EtOH on the % transformation of 2,4-DCP with the V(III)/KHSO₅ reagent suggests that sulfate radicals as well as hydroxyl radicals (at a lesser extent) are generated by the latter interaction according to reactions 3.4 and 3.5.

\[
V^{3+} + \text{HSO}_5^- \rightarrow V^{4+} + \text{OH}^- + \text{SO}_4^- \cdot \quad (3.4)
\]
\[
V^{3+} + \text{HSO}_5^- \rightarrow V^{4+} + \cdot \text{OH} + \text{SO}_4^{2-} \quad (3.5)
\]

The mechanism of peroxymonosulfate decomposition by Co(II) is well defined (see introduction) as well as that by Fe(II) (91,119,120) and the results of this study are in agreement
with literature information. However, there is no published information regarding the activation of peroxymonosulfate by Ru(III) or V(III). To our knowledge the coupling of Ru(III) (in the form of a simple salt) with KHSO$_5$ has not been tested before. As for vanadium, many studies have tested this metal but in all of them it was used at higher oxidation states (i.e. IV, V, and VII) (62,72,92,121). The interaction of Ce(III) with KHSO$_5$ leads to the formation of bound to the metal or caged sulfate radicals, judging from the % change in the transformation of the substrate due to the presence of TBA (+27%) and EtOH (-42%). This indicates that cerium participates differently than the previous four metals in the overall process and the rate-determining step of the Ce(III)/KHSO$_5$ interaction is suggested to be reaction 3.6:

$$\text{Ce}^{3+} + \text{HSO}_5^- \rightarrow [\text{Ce}^{IV}(\text{SO}_4\cdot^\bullet)]^{3+} + \text{OH}^- \quad (3.6)$$

All previous studies with cerium included the use of Ce(IV) and the generation of peroxymonosulfate radicals via reaction 3.7 has been reported by all of them (60,95,122).

$$\text{Ce}^{4+} + \text{HSO}_5^- \rightarrow \text{Ce}^{3+} + \text{SO}_5\cdot^- + \text{H}^+ \quad (3.7)$$

Unlike Ce(III) that was used in this study, Ce(IV) is an electron acceptor and decomposes potassium peroxymonosulfate by generating the peroxymonosulfate radical. From all the metals tested here only Fe(III) is an electron acceptor (oxidant) and similarly to Ce(IV) would decompose peroxymonosulfate as shown in reaction 3.8:

$$\text{Fe}^{3+} + \text{HSO}_5^- \rightarrow \text{Fe}^{2+} + \text{SO}_5\cdot^- + \text{H}^+ \quad (3.8)$$
Peroxymonosulfate radicals however react very slowly with phenols and are not expected to participate in the transformation of 2,4-DCP. In this case, Fe(III), as an oxidizing reagent, as well as sulfate radicals, formed via reaction 3.3, are the species responsible for the transformation of 2,4-DCP.

Finally, based on the results of the quenching experiments, it is suggested here that Mn(II) and Ni(II) activate KHSO₅ via the generation of caged sulfate radicals according to reactions 3.9 and 3.10 and this explains in part the low reactivity of these two couples.

\[
\text{Mn}^{2+} + \text{HSO}_5^- \rightarrow [\text{Mn}^{\text{III}}(\text{SO}_4\cdot')]^{2+} + \text{OH}^- \quad (3.9)
\]

\[
\text{Ni}^{2+} + \text{HSO}_5^- \rightarrow [\text{Ni}^{\text{III}}(\text{SO}_4\cdot')]^{2+} + \text{OH}^- \quad (3.10)
\]

Burrows and coworkers have previously reported the formation of caged or bound to the metal radical species via the Ni-mediated decomposition of peroxymonosulfate (63,70,71,96,115). They also reported that the simple nickel salt that was also used here is almost nonreactive compared with other Ni complexes coordinated with ligands such as peptides. This agrees with our results since Ni(II) in the form of NiSO₄.6H₂O is the second least reactive metal after Ag(I) toward activating peroxymonosulfate and transforming the substrate. The Mn(II)/KHSO₅ has also been investigated before but no other study has suggested the generation of caged sulfate radicals (60,120,123). An additional drawback that also contributes to the low reactivity of the latter couple is the fact that the Mn(III) ion, once formed from reaction 3.9, undergoes disproportionation according to the following reaction 3.11:
\[ 2\text{Mn}^{3+} + 2 \text{H}_2\text{O} \rightarrow \text{Mn}^{2+} + \text{MnO}_2 + 4\text{H}^+ \]  \hspace{1cm} (3.11)

MnO\textsubscript{2} that is formed as a product is nonreactive and thus Mn(III) cannot carry out sufficiently the redox cycling via reaction 3.12 (60,124).

\[ \text{Mn}^{3+} + \text{HSO}_5^- \rightarrow \text{Mn}^{2+} + \text{SO}_5^- + \text{H}^+ \]  \hspace{1cm} (3.12)

When Fe(II) was coupled with S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} (Table 1, line 10), the quenching results indicated that sulfate and hydroxyl radicals are formed at almost equal proportions. This finding is in agreement with the review study of Wilmarth and Haim who suggested that both radicals may form (118) but contradicts in part the results from more recent studies suggesting that only sulfate radicals are formed via this interaction (100,125). Our results though indicate that the couple may react according to general reaction 3.13, but also hydrogen peroxide may be formed from the hydrolysis of peroxydisulfate (reaction 3.14) (126) and hence hydroxyl radicals might be formed by a consecutive Fenton reaction (reaction 1.1).

\[ \text{Fe}^{2+} + \text{S}_2\text{O}_8\textsuperscript{2-} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{\cdot} + \text{SO}_4^{2-} \]  \hspace{1cm} (3.13)

\[ 2\text{H}_2\text{O} + \text{S}_2\text{O}_8\textsuperscript{2-} \rightarrow 2\text{HSO}_4^- + \text{H}_2\text{O}_2 \]  \hspace{1cm} (3.14)

The quenching results from the interaction of Fe(III) with S\textsubscript{2}O\textsubscript{8}\textsuperscript{2-} (line 11) are very different compared to all previous cases, since both the addition of TBA and EtOH facilitated the transformation of 2,4-DCP (77% and 47% increase in the transformation of 2,4-DCP,
respectively). This, combined with the very low reactivity of the Fe(III)/S$_2$O$_8^{2-}$ couple (7% transformation of the substrate in 30 min and 15% overall), suggests that Fe(III) species directly participated as oxidants in the transformation of the substrate. Finally, when Ru(III) was coupled with hydrogen peroxide the major species formed were hydroxyl radicals and thus the coupling is believed to proceed via reaction 3.15 (Table 3.1, line 14).

\[ \text{Ru}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Ru}^{4+} + \text{OH}^- + \cdot\text{OH} \]  

(3.15)

Reactions 3.16 and 3.17 are also included here to demonstrate the high rates of reactions between metals and radicals. The reaction rate between Ce(III) and \( \cdot\text{OH} \) has been reported to be 1.4x10$^8$ M$^{-1}$s$^{-1}$ (60) while the rate of reaction between Ag(I) and SO$_4^{•-}$ and between Fe(II) and \( \cdot\text{OH} \) have been reported to be 3x10$^9$ M$^{-1}$s$^{-1}$ (60) and 2.3-5.0 x10$^9$ M$^{-1}$s$^{-1}$ (119), respectively. These reactions strongly compete with the favorable reactions between the substrate and the radicals formed.

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

(3.16)

\[ M^{n+} + \cdot\text{OH} \rightarrow M^{(n+1)} + \text{OH}^- \]  

(3.17)

All the reactions between a metal and an oxidant are believed to proceed via one electron transfer from the reduced form of the metal to the oxidant and from the oxidized form of the metal back to the oxidant. The dual role of peroxymonosulfate and hydrogen peroxide as oxidizing and reducing agents is well documented but this has not been the case for persulfate that to our knowledge cannot act as a reducing agent. Based on the one electron transfer reaction mechanism along with literature information with respect to the occurrence of metals in solutions
(124,127,128) it was possible to depict the redox cycling of each metal in the overall process. The redox cycling for all metals was predicted almost with certainty, except for nickel that it is uncertain whether its (III) or (IV) oxidation state prevails after the oxidation of Ni(II). The knowledge of the metal speciation is very important since all these interactions may be explained to a certain extent by thermodynamic values (redox potentials). Moreover, the role of the transition metal at the higher oxidation state should not be excluded for participating as an oxidant in the overall process. Especially for the cases of Co(III), Ce(IV), Mn(III) and Ag(II) that their reduction potential from the (n+1) to the (n+) oxidation states are significantly high (> 1.5V). The last two columns of Table 3.1 show the oxidation states of the metals and their respective reduction potentials (41).

Theoretically, the higher the reduction potential of the oxidized form of the transition metal, the more efficient should the coupling be. This was proven true for the couples of Co, Ce and Mn with peroxymonosulfate but not for the other cases. The respective metal reduction reactions (general reaction 3.18), mediated by the oxidation of peroxymonosulfate and allowing the regeneration of the catalyst, are thermodynamically feasible for each couple since their respective overall redox potential is positive; 0.82V, 0.62V and 0.44V (103,108).

\[ M^{(n+1)^+} + HSO_5^- \rightarrow M^{n^+} + SO_5^- \cdot + H^+ \quad \text{where } M= \text{Co, Ce and Mn} \quad (3.18) \]

The decrease in the percent transformation of the chlorophenol induced by these three couples follows the decrease of the redox potentials of the above electron transfer reactions.
Obviously, the behavior of the dissolved metals in water would be a function of the charge, the ionic radius and the electronic structure (103,127). However, no pattern based on this assumption was found. Instead, it is suggested here that the combination of the reduction potential of the oxidized to the reduced form of the metal as well as hydrolysis and complexation reactions of the metals in both oxidation states with the counter ions present in solution plays the major role in the metal-mediated activation of the oxidants (especially peroxymonosulfate) and thus the radical generation and the transformation of the substrate. The particular strength of mono- or poly-nuclear hydrolysis products formed according to the generally slow reaction 3.19 (for simplicity only mononuclear species formation is reported in the general mechanism) as an initiation step greatly affects the behavior of the metals in the participation in the electron transfer reactions reported here.

\[
\text{M}^{n+} + \text{H}_2\text{O} \leftrightarrow \text{MOH}^{(n-1)} + \text{H}^+ \tag{3.19}
\]

For instance, Baes and Mesmer (124) suggest that Ce(IV) hydrolyzes extensively and V(III) also hydrolyzes partially to VO\(^+\) and V(OH)\(^{2+}\). It is also known based on reported stability constants (log\(\beta\)=11.8) that Fe(III) is another metal that hydrolyzes extensively to form FeOH\(^{2+}\) (129). The formation of the labile complexes of the form \([\text{M(H}_2\text{O})_x]^{n+}\) facilitates the electron transfer reactions while potential metal complexation with counter ions resulting from the addition of acidic and especially buffering species in solutions might inhibit the electron transfer reactions. All phosphate species, here in the form of H\(_2\)PO\(_4^-\)/HPO\(_4^{2-}\) (pH 7.0), are expected to form very strong complexes with all the metals tested at neutral pH. Stability constant values (log\(\beta\)) with such species have been reported for Co(II) and Ni(II); 15.5 for CoHPO\(_4^-\) and 15.4 NiHPO\(_4^-\) (129)
and are much greater than what is believed to be the lower limit ($\log \beta > 8$) for strong complexes (130). Although for Ni(II) the complexation with phosphates might account for its minimal reactivity toward activating the three oxidants tested here, this was not the case for Co(II) that its reactivity toward activating peroxymonosulfate was proven unaffected by the buffering species. In addition, the presence of the oxidants in solution might not always demonstrate a positive effect toward redox interactions. For instance, sulfate ions, here released from the addition of OXONE® (see chemical formula in the material section), have been reported to form stable complexes with Ce(IV) and Mn(III) (124). The interaction of cobalt(III) with hydrogen peroxide leading to the generation of a green cobalt (peroxy-acid) complex, which is then used for the chromatographic determination of hydrogen peroxide, is another typical example (131). Although it is not possible at the moment to pinpoint the particular factor responsible for all the nonreactive metal-oxidant couples, it is believed that stabilization of the metal due to hydrolysis or complexation and thus its resulting decreased oxidizing strength (represented by its reduction potential) should be accounted for the inefficiencies observed.
CHAPTER 4

Transition Metal/UV-based Advanced Oxidation Technologies for Water Decontamination

This Chapter explores the effect of ultraviolet (UV) light radiation and/or transition metals (M) for the activation of common oxidants (Ox) with the objective of treating recalcitrant organic contaminants in water. Hydrogen peroxide, potassium peroxymonosulfate and potassium persulfate were combined with iron, cobalt and silver, respectively, and/or with UV light (254 nm) and were tested for the treatment of 2,4-dichlorophenol (2,4-DCP). Results from the previous two Chapters indicated that these particular transition metals are the best catalysts for the activation of the respective oxidants. From the combined use of UV, the oxidants and the transition metals, four general categories of advanced oxidation technologies were evaluated and compared for the degradation and mineralization of 2,4-DCP. Those were (i) the dark conjunction of each oxidant with its favorable metal activator (M/Ox), (ii) the use of UV alone, (iii) the combination of UV with each oxidant (UV/Ox) and, (iv) the use of UV combined with each metal/oxidant systems (UV/M/Ox). In particular the systems UV/KHSO5, UV/Co(II)/KHSO5 and UV/Ag(I)/K2S2O8 and the sulfate radicals generated thereby have never been tested before for water decontamination, as opposed to the extensively investigated hydroxyl radicals generated by UV/H2O2 and the photo-Fenton. The comparison of the 2,4-DCP treatment results with respect to the transformation of the parent contaminant and the extent of organic carbon removal led to the construction of the following order of efficiencies: UV/K2S2O8 > UV/KHSO5 >
UV/H₂O₂ for the UV/Ox processes and UV/Fe(III)/H₂O₂ > UV/Fe(II)/H₂O₂ > UV/Co(II)/KHSO₅ > UV/Ag(I)/K₂S₂O₈ for the UV/M/Ox processes tested here. All experiments were homogeneous and conducted at ambient room temperature. The relative absorbance of the species participating in the reactions supports the former order of efficiency, since persulfate followed by peroxymonosulfate were proven more photosensitive than hydrogen peroxide. Among the metals tested, only iron species such as Fe(OH)²⁺ were found to absorb strongly at 254 nm and to this is attributed the higher efficiencies obtained with the photo-Fenton reagents.

4.1 Introduction

With the exception of the Fenton Reagent (Fe⁺⁺/H₂O₂), the potential of generating highly reactive radical species, by coupling transition metals with common electron acceptors and hence degrade organic contaminants in water, has not been adequately explored in the field of environmental chemistry. Following this approach, it was reported in Chapter 2 that the coupling of Co(II) with potassium peroxymonosulfate in a homogeneous system (Co⁺⁺/KHSO₅) leading to the generation of sulfate radicals demonstrates greater efficiencies and several operational advantages than the Fenton Reagent for the treatment of certain organic contaminants in water. In Chapter 3, several transition metals, such as Ag(I), Ce(III), Co(II), Fe(II), Fe(III), Mn(II), Ni(II), Ru(III) and V(III), were tested for the activation of the three common oxidants, hydrogen peroxide (H₂O₂), potassium peroxymonosulfate (KHSO₅), and potassium persulfate (K₂S₂O₈) with the objective of finding the favorable metal(s) for the decomposition of each oxidant and thus achieving high efficiencies in degrading organic contaminants in water. The study demonstrated that indeed Fe(III) and Fe(II) are the most efficient metals for the activation of H₂O₂, Co(II) for that of
KHSO₅ and Ag(I) for K₂S₂O₈. The primary radical species formed, when a metal is coupled with an oxidant in aqueous solution, were identified with quenching studies using specific alcohols and led to the postulation of the rate-determining steps of the redox reactions taking place. The proposed equations 1.1, 1.2, 2.1 and 3.1 are in accordance with previously published studies (14,61). It must be noted here that recent studies have suggested that the Fenton Reagent does not proceed universally via the generation of hydroxyl radicals and instead other species such as the ferryl ion (i.e., as Fe⁴⁺=O) might be responsible for the degradation of contaminants (132,133). Based on our previous investigations and the effective quenching of the Fenton Reagent with tert-BuOH, this study takes up the simplified Fenton chemistry as depicted in equations 1.1 and 1.2.

In continuation of our research on the activation of the three oxidants (H₂O₂, KHSO₅, K₂S₂O₈), this study explores the use of UV light radiation, alone or in combination with the favorable transition metals found previously. The objective was to further activate these inorganic electron acceptors and thus achieve even higher rates and efficiencies for the degradation and mineralization of a model organic contaminant such as 2,4-dichlorophenol (2,4-DCP, Scheme 4.1) at a concentration of 20 mg/L in water.

**Scheme 4.1. 2,4-dichlorophenol**
The use of UV light in general and especially at wavelengths lower than 240 nm leads to the generation of radical species through the photolysis of the oxidants according to the following reactions (117,134,135):

\[
\text{HO}_2 + \text{hv} \rightarrow 2 \cdot \text{OH}
\]  \hspace{1cm} (4.1)

\[
\begin{array}{c}
\text{O} \\
\text{S} \\
\text{O} \\
\text{O} \\
\cdot \\
\cdot \\
\text{O} \\
\text{O} \\
\cdot \\
\cdot \\
\end{array}
\quad \begin{array}{c}
\text{O} \\
\text{S} \\
\text{O} \\
\text{O} \\
\cdot \\
\cdot \\
\text{O} \\
\text{O} \\
\cdot \\
\cdot \\
\end{array}
\text{hv} \quad \begin{array}{c}
\text{O} \\
\text{S} \\
\text{O} \\
\text{O} \\
\cdot \\
\cdot \\
\text{O} \\
\text{O} \\
\cdot \\
\cdot \\
\end{array} + \cdot \text{OH}
\]  \hspace{1cm} (4.2)

\[
\begin{array}{c}
\text{O} \\
\text{S} \\
\text{O} \\
\text{O} \\
\cdot \\
\cdot \\
\text{O} \\
\text{O} \\
\cdot \\
\cdot \\
\end{array}
\quad \begin{array}{c}
\text{O} \\
\text{S} \\
\text{O} \\
\text{O} \\
\cdot \\
\cdot \\
\text{O} \\
\text{O} \\
\cdot \\
\cdot \\
\end{array}
\text{hv} \quad \begin{array}{c}
\text{O} \\
\text{S} \\
\text{O} \\
\text{O} \\
\cdot \\
\cdot \\
\text{O} \\
\text{O} \\
\cdot \\
\cdot \\
\end{array}
\end{array}
\]  \hspace{1cm} (4.3)

At the UV range, direct photolysis of the chlorophenol is also taking place regardless of the presence or not of oxidants or transition metals and is also reported here.

The Fenton Reagent demonstrates several limitations, one of which is the very slow catalyst regeneration via equation 1.2. Additional use of UV light, the photo-Fenton process (reactions 1.1 and 1.3), overcomes this limitation, since Fe(OH)$_2^+$, the major Fe(III) species in water, is photosensitive and absorbs light at wavelength up to 400 nm leading to the regeneration of Fe(II) according to equation 1.3 (22).

In addition to the comparison of the “dark” catalyzed reactions and the un-catalyzed photolytic reactions, this study also compares the photo-Fenton reagent with the UV/cobalt-catalyzed
activation of peroxymonosulfate and the UV/silver-catalyzed activation of persulfate for the treatment of 2,4-DCP.

Consequently, this study reports and compares the results from the degradation and mineralization of 2,4-DCP with the use of four different general categories of advanced oxidation technologies: (1) M/Ox (dark reaction) and in particular the systems Fe(II)/H$_2$O$_2$, Fe(III)/H$_2$O$_2$, Co(II)/KHSO$_5$ and Ag(I)/K$_2$S$_2$O$_8$; (2) UV alone; (3) UV/Ox and in particular the systems: UV/H$_2$O$_2$, UV/KHSO$_5$ and UV/K$_2$S$_2$O$_8$; (4) UV/M/Ox and in particular the systems UV/Fe(II)/H$_2$O$_2$, UV/Fe(III)/H$_2$O$_2$, UV/Co(II)/KHSO$_5$ and UV/Ag(I)/K$_2$S$_2$O$_8$.

Apart from the widely known use of UV/H$_2$O$_2$ (9,136,137) and photo-Fenton (16-18) for water decontamination and the very few studies reporting the use of UV/K$_2$S$_2$O$_8$ (138,139), all other reagents have never been tested before. Especially the use of peroxymonosulfate (without cobalt, other transition metal or under UV radiation) as an alternative electron acceptor, other than oxygen, chlorine or hydrogen peroxide, has not yet been fully explored for environmental applications. Only recently, the metal-mediated activation of peroxymonosulfate under visible light radiation has been investigated for the photobleaching of a dye (140,141). Consequently, the oxidizing reagents reported here significantly contribute to the development of new tools for water decontamination.

4.2 Experimental

The chemicals used in this study were listed in Chapter 3 (see Materials and Methods section).
4.2.1 Photoreactor

The rectangular reactor vessel (base: 10 cm x 10 cm, height: 25 cm), used here, was made of quartz glass and was placed on a magnetic stirrer allowing sufficient and constant mixing of the solution (total volume of 2 L). Four germicidal lamps (15W, Sankyo Denki G15T8), two at each side of the reactor, were emitting almost monochromatic radiation at 253.7 nm (low pressure mercury line sources, ~90% of energy output at 253.7 nm). The lamps were positioned in parallel to the longest dimension of the reactor at a distance of 6 cm from each side. From a port close to the bottom of the vessel, a syringe was adjusted and samples were withdrawn at specific time intervals for 4 h.

Using potassium ferrioxalate actinometry and following the procedure by Murov et al., the photon flux entering the reactor was measured to be 8.5x10^-6 E/s (142). This value corresponds to 4.01 W of photon flux power at 253.7 nm (1 Einstein at 253.7 nm equals to 471,528 J) and is much lower than the 60 W of electrical power consumed by the lamps. At this particular wavelength, it is not necessary to use concentrated ferrioxalate of 0.15 M (143-145). Instead ferrioxalate was prepared at the concentrations described in Murov et al. It must be noted here that the first step of complexation with EDTA was omitted since the pH of the ferric solution was almost zero in the first place. Problems were also encountered with potassium oxalate since the recommended 1.2 mol/L did not completely dissolve. This did not affect the analysis however, since potassium oxalate is used in excess to the concentration of ferric sulfate. All control values described in the procedure were met; all absorbance measurements were between
0.2 and 1.8 and the blank had an absorbance of 0.051 (<0.06). The UV lamps were on for 30 min prior to the analysis and the phenanthroline complex was left standing for 1 h to fully develop before measuring its absorbance at 510 nm (144).

### 4.2.2 Analysis

The initial concentration of the substrate (2,4-DCP) was approximately 20 mg/L (0.123 mM) and its transformation was monitored with an Agilent 1100 Series HPLC System with a QuatPump and a UV-vis diode array detector. The column used for the analysis was an Eclipse XDB-C8 column, obtained from Agilent and the mobile phase was 50%:50% of water:acetonitrile. The extent of mineralization of the chlorophenol (as non-purgeable organic carbon, NPOC) was also monitored with a Shimadzu VCSH-ASI TOC Analyzer. Absorbance and molar extinction coefficients of the species participating in the reactions were determined with an HP 8452A UV-vis spectrophotometer. The light path of the cuvette used was 1 cm.

### 4.2.3 Procedures

100 mM stock solution of each oxidant was prepared and a specific aliquot was diluted in the reaction vessel to achieve an initial concentration of 0.123 or 1.227 mM, corresponding to 1:1 and 10:1 mol ratios of the oxidant versus the contaminant, respectively. Stock solutions of the metal salts were prepared with concentrations varying from 5 mM to 100 mM depending upon the solubility of each salt. In the cases of silver and iron, the pH of the stock solution was adjusted in the acidic region (pH<3) with the corresponding acid of the metal counter ion to
facilitate complete dissolution of the salt. Specific aliquots of the stock solutions were added to the reactor in order to achieve a metal concentration of 1 to 50 ppm. In the cases that a transition metal was used for the catalytic activation of an oxidant, the reaction was quenched in the sample vial with excess of sodium nitrite solution. The latter does not interfere with the TOC analysis (no organic carbon content) and was preferred versus methanol, since it was found to demonstrate the same quenching efficiency in preliminary control experiments (not shown).

To avoid potential metal speciation and precipitation, the transition metals were added last in the reactor (after the oxidant addition), since it was found that each oxidant alone does not induce any transformation of the contaminant (control experiments not shown). All experiments were conducted in de-ionized water except from the cases where iron or silver was used. Those metals undergo speciation and precipitation at elevated pH, thus it was chosen to be tested at pH 3 adjusted with sulfuric or hydrochloric acid depending upon the counter ion of the metal.

All experiments were batch and were conducted at ambient room temperature. Most of the experiments were also performed in triplicate to assure accurate data acquisition and hence valid interpretation. As a result, error bars representing standard deviation are depicted in most Figures. In Figures 4.1-4.8, the y-axis represents the normalized concentrations of either 2,4-DCP (initially 20 mg/L) or NPOC (initially 8.84 mg/L) and the x-axis the reaction time.
4.3 Results and Discussion

First, the oxidants, activated by UV and with no addition of transition metals, were tested at 1:1 mol ratio versus the contaminant. It was found that under these conditions the rates and extent of 2,4-DCP degradation were almost identical with those obtained from the treatment of 2,4-DCP with just UV alone (the 1:1 mol ratio results are not shown). Consequently, when a 10-fold greater dose of each oxidant was tested, the results demonstrated significantly higher degradation rates as well as extent of mineralization of the contaminant. This particular dose of each oxidant was then tested in the dark with the use of the favorable transition metal (Fe$^{II}$/H$_2$O$_2$, Fe$^{III}$/H$_2$O$_2$, Co$^{II}$/KHSO$_5$, Ag$^{I}$/K$_2$S$_2$O$_8$) as well as under UV radiation combined with the presence of the favorable to each oxidant transition metal (i.e. UV/Fe$^{II}$/H$_2$O$_2$, UV/Fe$^{III}$/H$_2$O$_2$, UV/Co$^{II}$/KHSO$_5$, UV/Ag$^{I}$/K$_2$S$_2$O$_8$).

4.3.1 Activation of Hydrogen Peroxide

Figure 4.1 summarizes the degradation of 2,4-DCP from the activation of hydrogen peroxide with ferrous or ferric iron or UV light radiation. It is shown that complete transformation (undetectable amounts, greater than 99.9% conversion) of the contaminant is taking place with all the technologies tested within 4 h of reaction time. The only exception was the Fenton Reagent that demonstrated approximately 96% transformation of the contaminant in 4 h. The best results with respect to degradation reaction rates were obtained when the chlorophenol was treated with the combined UV/Fe(II) and UV/Fe(III) activation of hydrogen peroxide. The contaminant was completely transformed within 1 h of reaction time. The difference in the
reaction kinetics, when Fenton and Fenton-like reagents were used, is also depicted. Fenton Reagent is a fast reaction while the latter (Fe$^{III}$/H$_2$O$_2$) led to a slower degradation curve. It was also found that only 1 ppm of Fe(II) or Fe(III) is sufficient to achieve activation of hydrogen peroxide in the dark, since significant degradation of the parent contaminant was achieved at this metal concentration. In addition, the presence of iron combined with the UV/H$_2$O$_2$ system led to higher transformation rates and greater mineralization of the chlorophenol compared to the UV/H$_2$O$_2$ (see also Figure 4.2). This indicates that iron not only catalyzes the activation of hydrogen peroxide but also might directly participate in the transformation of the chlorophenol via photochemical or redox reactions from its ferric to ferrous form. The increased extent of mineralization due to the presence of iron might also be attributed to the formation of the highly photoactive ferrioxalate complex, since oxalic acid is expected to occur as a degradation intermediate of 2,4-DCP (see section 4.3.4).
Figure 4.1. Degradation of 2,4-DCP from the activation of hydrogen peroxide with iron and/or UV. Conditions: [2,4-DCP]₀=20 mg/L (0.123 mM); H₂O₂/2,4-DCP=10/1 mol; Fe(II) or Fe(III) at 1ppm; when iron was used: pH adjusted to 3 with either HCl or H₂SO₄, otherwise DI water at pH 5.5.

Figure 4.2 shows the organic carbon removal achieved from the treatment of the chlorophenol with the different peroxide activation techniques. As expected the combined UV/Fe processes demonstrated the best results with the Fe(III) being somewhat faster than the Fe(II) process. Figure 4.2 shows that the use of UV/Fe⁺⁺/H₂O₂ led to 87% organic carbon removal while that of UV/Fe⁺⁺/H₂O₂ led to 86% organic carbon removal, in 4 h of reaction time. The dark Fenton and Fenton-like reagents demonstrated limited mineralization, since the organic carbon removal was approximately 15% with both systems for the same treatment time.
Figure 4.2. Mineralization of 2,4-DCP from the activation of hydrogen peroxide with iron and/or UV. Conditions: \([2,4\text{-DCP}]_0=20\ \text{mg/L (0.123 mM); } \text{H}_2\text{O}_2/2,4\text{-DCP}=10/1\ \text{mol; } \text{Fe(II) or Fe(III) at 1ppm; when iron was used: pH adjusted to 3 with either HCl or H}_2\text{SO}_4, otherwise DI water at pH 5.5.}

4.3.2 Activation of Potassium Peroxymonosulfate

Figure 4.3 depicts the results from the degradation of the chlorophenol with the peroxymonosulfate activation reagents. From these, the combined UV/Co(II)/KHSO\(_5\) as well as the UV/KHSO\(_5\) led to complete transformation of the chlorophenol within 1 h of reaction. When UV alone was used, complete transformation of the chlorophenol was achieved only after 4 h of radiation time. The dark Co(II)/KHSO\(_5\) reagent degraded the chlorophenol in 2 h of reaction time and thus was proven slightly more efficient than the Fenton and faster than the Fenton-like reagents shown in Figure 4.1.
Figure 4.3. Degradation of 2,4-DCP from the activation of potassium peroxymonosulfate with cobalt and/or UV. Conditions: [2,4-DCP]₀=20 mg/L (0.123 mM); KHSO₅/2,4-DCP=10/1 mol; Co(II) at 1 ppm; DI water at pH 5.5.

With respect to organic carbon removal from the destruction of the chlorophenol and its intermediates, the combined UV/Co(II)/KHSO₅ and the UV/KHSO₅ reagents demonstrated almost identical results, since the extent of mineralization was approximately 75% in both cases, as shown in Figure 4.4. The UV/Co(II)/KHSO₅ demonstrated a slightly faster rate of mineralization than UV/KHSO₅ between the 30th and 120th min most probably due to the additional presence of cobalt. The dark cobalt/peroxymonosulfate reagent demonstrated 19% mineralization of the organic content, which is slightly higher than what was achieved with the Fenton and Fenton-like reagents shown in Figure 4.2. As in the case of iron for the activation of hydrogen peroxide, 1 ppm of cobalt was sufficient to catalyze the activation of
peroxymonosulfate in the dark. The difference however with the two metals is that cobalt does not appear to participate directly in the transformation or mineralization of the contaminant through photochemical or redox reactions as in the case of iron. Figure 4.4 shows that greater mineralization rates are achieved with the cobalt-mediated UV/KHSO$_5$ system compared to the uncatalyzed UV/KHSO$_5$ for the first 120 min of reaction time. Overall however and after the 120$^{th}$ min, the extent of mineralization achieved with the UV/Co(II)/KHSO$_5$ was identical to that obtained with the UV/KHSO$_5$ reagent, indicating that cobalt just facilitates the mineralization of 2,4-DCP as a catalyst and Co(III) does not participate as an oxidizing agent in the overall process.

**Figure 4.4.** Mineralization of 2,4-DCP from the activation of potassium peroxymonosulfate with cobalt and/or UV. Conditions: [2,4-DCP]$_0$=20 mg/L (0.123 mM); KHSO$_5$/2,4-DCP=10/1 mol; Co(II) at 1ppm; DI water at pH 5.5.
4.3.3 Activation of Potassium Persulfate

The results from the treatment of the chlorophenol with persulfate were proven different than the other two series of reagents. In this case, the use of UV with persulfate was proven slightly more efficient that the combined with silver as shown in both Figures 4.5 and 4.6. Figure 4.5 shows that the use of UV/K₂S₂O₈ and UV/Ag(I)/K₂S₂O₈ leads to complete degradation of 2,4-DCP within 30 and 60 min, respectively. Figure 4.5 also shows that 1 ppm of Ag(I) is not sufficient to activate potassium persulfate in the dark and as high as 50 ppm of Ag(I) are needed for transforming significantly the chlorophenol. Even in this case, the degradation curve of the chlorophenol is greatly different than those obtained from the use of Fenton, Fenton-like and cobalt/ peroxymonosulfate reagents. The former appears to be zero order while the others demonstrated pseudo-first order reaction kinetics. However, at high concentrations of Ag(I), color development is observed in solution, probably from the complexation of Ag(II), formed from reaction 3.1, with sulfates. For this, the combination of UV with silver at such conditions for the activation of potassium persulfate will be inefficient, due to the limited absorbance of the solution. In fact, the results especially from the extent of mineralization achieved with the persulfate activation reagents, shown in Figure 4.6, suggest that Ag(I) at 1 ppm has a detrimental effect on the degradation of the contaminant when it is combined with UV/K₂S₂O₈ compared to the UV/K₂S₂O₈ system. The combined UV/Ag(I)/K₂S₂O₈ system led to 71% removal of the organic carbon present in solution while the UV/K₂S₂O₈ reagent demonstrated more than 10% percent greater mineralization efficiency (82%). The dark Ag(I)/K₂S₂O₈, even with the addition of 50 ppm of silver, demonstrated limited mineralization of the chlorophenol (12%) and was
proven less efficient than the other three dark reagents reported here: the Fenton, Fenton-like and cobalt/peroxymonosulfate.

**Figure 4.5.** Degradation of 2,4-DCP from the activation of potassium persulfate with silver and/or UV. Conditions: $[2,4\text{-DCP}]_0=20$ mg/L (0.123 mM); $\text{K}_2\text{S}_2\text{O}_8/2,4\text{-DCP}=10/1$ mol; when silver was used: pH adjusted to 3 with $\text{H}_2\text{SO}_4$, otherwise DI water at pH 5.5.
Figure 4.6. Mineralization of 2,4-DCP from the activation of potassium persulfate with silver and/or UV. Conditions: [2,4-DCP]₀=20 mg/L (0.123 mM); K₂S₂O₈/2,4-DCP=10/1 mol; when silver was used: pH adjusted to 3 with H₂SO₄, otherwise DI water at pH 5.5.

4.3.4 Comparison of the Reagents

Before dealing with the UV/Ox and UV/M/Ox reagents, it is interesting to compare the dark M/Ox systems. Here, the metals were tested at the same mass concentration of 1 mg/L, although to obtain significant 2,4-DCP oxidation with Ag(I)/K₂S₂O₈, up to 50 mg/L of Ag(I) were necessary. The oxidant concentration was 10-fold higher than that of 2,4-DCP. The pH was also adjusted to 3.0 to minimize speciation of Ag(I), Fe(II) and Fe(III) in the respective Ag(I)/K₂S₂O₈, Fe(II)/H₂O₂ and Fe(III)/H₂O₂ reagents. In the case of Co(II)/KHSO₅ the pH was not controlled, since Co(II) does not demonstrate any speciation limitations. Figure 4.7a illustrates the degradation of 2,4-DCP with the different M/Ox reagents utilized in this study. It
is shown again that the Co(II)/KHSO₅ demonstrates the highest kinetics among all reagents and its overall efficiency of completely transforming 2,4-DCP within 2h is matched only by the Fenton-like Reagent but in 4h of reaction time instead.

![Graph showing degradation of 2,4-DCP](image)

**Figure 4.7a.** Comparative degradation of 2,4-DCP with the dark M/Ox systems. Conditions: [2,4-DCP]₀ = 20 mg/L (0.123 mM, normalized); [M] = 1 ppm, unless otherwise indicated; [Ox]:[2,4-DCP] = 10:1 molar.

In the previous Chapter, the same metals (among others) were tested at much more elevated concentrations at 1.244 mM molar, which was also the concentration of the oxidants, corresponding to a 4-fold higher molar concentration than that of 2,4-DCP. Again all systems involving the use of Ag(I), Fe(II) and Fe(III) were adjusted to pH 3.0, while Co(II)/KHSO₅ was buffered at pH 7.0. Figure 4.7b illustrates the comparative degradation of 2,4-DCP with the same dark reagents as before but under the different now conditions. Again, the fastest degradation
kinetics were achieved with the Co(II)/KHSO$_5$ and the Fenton Reagent, and the highest overall transformation with the Co(II)/KHSO$_5$ followed by the Fenton-like reagent, Fe(III)/H$_2$O$_2$.

![Graph](image)

**Figure 4.7b.** Comparative degradation of 2,4-DCP with the dark M/Ox systems. Conditions: $[2,4$-DCP]$_{0} = 50.7$ mg/L (0.311 mM, normalized); [M]:[Ox] = 1:1, [Ox]:[2,4-DCP] = 4:1 molar.

The efficiency of advanced oxidation technologies that utilize UV light for contaminant degradation is measured with the *electrical energy per order (EE/O)*, a Figure-of-Merit recommended by the Photochemistry Commission of International Union of Pure and Applied Chemistry (IUPAC) and is defined as “the electrical energy in kilowatt hours (kWh) required to bring about the degradation of a contaminant C by one order of magnitude in 1 m$^3$ (1000 L) of contaminated water or air” (22,86). EE/O in a batch reactor is calculated from the expression:

$$EE/O = \frac{P \cdot t}{60 \cdot V}$$
where $P$ is the total electrical power or flux entering the reactor (W), $t$ is the time (min) and $V$ is the volume (L) of water treated.

EE/O values, for every UV-reagent tested here, were calculated by plotting in semi-logarithmic scale the kinetic results of the degradation of the chlorophenol shown in Figures 4.1, 4.3 and 4.5. The two different EE/O values for each process reported in Table 4.1 correspond to two different $P$ values; one corresponding to the flux entering the reactor equal to 4.01 W and the other to the electrical power consumed equal to 60 W. The water volume treated was 2 L.

Table 4.1. Comparison of UV/Ox and UV/M/Ox technologies with respect to their energy requirements for the degradation of 2,4-DCP.

<table>
<thead>
<tr>
<th>UV/Ox Process</th>
<th>EE/O (kWh/m$^3$)</th>
<th>UV/M/Ox Process</th>
<th>EE/O (kWh/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV/H$_2$O$_2$</td>
<td>1.00</td>
<td>UV/Fe(II)/H$_2$O$_2$</td>
<td>0.27</td>
</tr>
<tr>
<td>UV/KHSO$_5$</td>
<td>0.73</td>
<td>UV/Fe(III)/H$_2$O$_2$</td>
<td>4.02</td>
</tr>
<tr>
<td>UV/K$_2$S$_2$O$_8$</td>
<td>0.50</td>
<td>UV/Co(II)/KHSO$_5$</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td>7.50</td>
<td>UV/Ag(I)/K$_2$S$_2$O$_8$</td>
<td>0.77</td>
</tr>
</tbody>
</table>

UV-utilizing technologies generally demonstrate high energy losses, since the electrical energy consumed is always much higher than the photochemical energy entering and utilized by the reaction system. The configuration used in this study was not optimized (i.e., relatively long distance between the lamps and the reactor wall) so the energy losses were even higher than what expected, with the flux entering the reactor equal to 4.01 W whereas the electrical power consumed was equal to 60 W (93% lost). It must be noted here that the smaller the EE/O value the more efficient and economical the process is. In any case and despite the big difference in the EE/O values, depending upon the $P$ value taken into account, the general trend of efficiency
among the reagents tested was the same. The results of the Table led to the following order of efficiency of the UV/Ox technologies tested here: \( \text{UV/K}_2\text{S}_2\text{O}_8 > \text{UV/KHSO}_5 > \text{UV/H}_2\text{O}_2 \). The same was performed for the UV/M/Ox technologies and the following order of efficiency was constructed: \( \text{UV/Fe(III)/H}_2\text{O}_2 > \text{UV/Fe(II)/H}_2\text{O}_2 > \text{UV/Co(II)/KHSO}_5 > \text{UV/Ag(I)/K}_2\text{S}_2\text{O}_8 \).

Another important parameter of the overall efficiency of an advanced oxidation technology is the organic carbon removal achieved from the degradation of a particular contaminant. As shown in Figures 4.1, 4.3 and 4.5, complete transformation of the parent contaminant is achieved with almost all systems within 4 h. In addition to the kinetics of the 2,4-DCP decay, the organic carbon removal also provides an overall evaluation of the efficiency of each process. The mineralization cannot be approximated with first order kinetics similarly to the degradation of the parent contaminant and therefore EE/O values cannot be calculated similarly to those of Table 4.1. Figures 4.8 and 4.9 depict the comparative results from the mineralization of the contaminated water achieved with the UV/Ox and UV/M/Ox reagents, tested here. The results from the monitoring of the organic carbon removal with the different oxidation technologies demonstrated the same order of efficiency compared to the EE/O values of Table 4.1. Figure 4.8 shows that in 4 h the organic carbon removed from the treatment of the chlorophenol was 82, 74 and 67\% when UV/K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}, UV/KHSO\textsubscript{5} and UV/H\textsubscript{2}O\textsubscript{2} were applied, respectively. Figure 4.9 shows that in 4 h the organic carbon removed from the treatment of the chlorophenol was 87, 86, 74, and 71\% when UV/Fe(III)/H\textsubscript{2}O\textsubscript{2}, UV/Fe(II)/H\textsubscript{2}O\textsubscript{2}, UV/Co(II)/KHSO\textsubscript{5} and UV/Ag(I)/K\textsubscript{2}S\textsubscript{2}O\textsubscript{8} were used, respectively.
Figure 4.8. Mineralization of 2,4-DCP with the UV/Ox systems. Conditions: [2,4-DCP]₀=20 mg/L (0.123 mM); Ox/2,4-DCP=10/1 mol; DI water at pH 5.5.
Figure 4.9. Mineralization of 2,4-DCP with the UV/M/Ox systems. Conditions: $[\text{2,4-DCP}]_0=20$ mg/L (0.123 mM); Ox/2,4-DCP=10/1 mol; metal concentration: 1 ppm; when iron and silver were used: pH adjusted to 3 with either HCl or H$_2$SO$_4$, otherwise DI water at pH 5.5.

According to reactions 4.1-4.3, the photolysis of hydrogen peroxide leads to the generation of hydroxyl radicals, that of potassium peroxymonosulfate to sulfate radicals and hydroxyl radicals and that of persulfate to sulfate radicals. These species are mainly responsible for the degradation of the organic contaminants in water. Table 2.3 (see Chapter 2) summarizes the standard redox potentials of the radical species formed here. It is shown that sulfate radicals are stronger oxidants than hydroxyl radicals, especially at elevated pH, and this might explain in part the higher mineralization of the chlorophenol achieved with the UV/K$_2$S$_2$O$_8$ and UV/KHSO$_5$ as compared to that with UV/H$_2$O$_2$. Hydroxyl radicals are less selective for oxidation than sulfate radicals. The former also demonstrate higher rates of hydrogen abstraction and addition reactions.
than sulfate radicals (106). The UV/Ox experiments were conducted at initial pH 5.5 and at this pH sulfate radicals might demonstrate greater redox potential than hydroxyl radicals.

Another important property of the oxidants tested here is the energy of their O-O bond. This bond in potassium persulfate has been estimated to be 33.5 kcal/mol (107) whereas in hydrogen peroxide is 51 kcal/mol (111). No values are available for potassium peroxymonosulfate but Flanagan et al. (113) have reported the distance of the O-O bonds of all oxidants tested here; 1.453 Å in solid H₂O₂, 1.460 Å in KHSO₅ and 1.497 Å in (NH₄)₂S₂O₈. This suggests that persulfate followed by peroxymonosulfate are cleaved more easily than hydrogen peroxide and thus the resulting sulfate radicals might be formed more readily than hydroxyl radicals. Meunier (114) also suggested that peroxymonosulfate, due to its non-symmetrical molecule, might be more easily activated than the other two oxidants tested here (see the structure of the oxidants in reactions 4.1-4.3).

The energy requirements alone cannot though predict the behavior of the oxidants under UV radiation, since the molecule of the oxidant must also be able to absorb this energy. The latter depends upon the absorption coefficient of the particular species. The molar extinction coefficients in the range 190-320 nm of the oxidants tested here in deionized water were measured with UV-vis spectrophotometer and are shown in Figure 4.10. It is shown that the lower the wavelength of emission the higher the molar extinction coefficient of all oxidants, with potassium persulfate and OXONE® absorbing the most compared to hydrogen peroxide. Since 1 mole of OXONE® (2KHSO₅·KH₂SO₄·K₂SO₄) contains 2 moles of potassium peroxymonosulfate,
the molar extinction coefficient of peroxymonosulfate was calculated to be half of that of the triple salt.

Figure 4.11a shows the absorbance, at the range 190-320 nm, of all species at the initial concentrations used here. Among all species, 2,4-DCP appears to absorb the most even though its concentration is 10-fold lower than that of the oxidants. The extinction coefficient of this organic compound (not shown) is far greater than that of the oxidants shown in Figure 4.10. Fe(III), presumably in the form of Fe(OH)$_{2+}$, is the only metal appearing to absorb appreciably at a concentration of 1 ppm. All other metals used initially (Fe$^{II}$ as FeOH$^+$ in water, Co$^{II}$ as CoOH$^+$, Ag$^{I}$ as AgOH) were at lower oxidation states and did not demonstrate any significant absorbance. From Figure 4.11a, it is also clear that a light source emitting at wavelengths less than 250 nm would be more appropriate and effective for the activation of the peroxides tested here as well as the photolysis of the organic material, since all species demonstrate maximum absorbance at wavelengths < 250 nm.
Figure 4.10. Extinction coefficients in deionized water of the oxidants used here at the range 190-320 nm. The extinction coefficient of KHSO₅ was calculated from that of OXONE®, since 1 mole of OXONE® contains 2 moles of KHSO₅.
Figure 4.11a. Absorbance in deionized water of all initial reactive species at the concentrations used in this study and at the range 190-320 nm. OXONE® at 0.615 mM is equivalent to 1.23 mM of KHSO5.

The absorbance of all initial reactive species at 254 nm, where the light sources used here are emitting, is shown in Figure 4.11b. At that particular wavelength, the following order of absorbance is derived: 2,4-DCP > K2S2O8 > Fe(OH)2+ > KHSO5 > H2O2. This particular order supports the order of efficiency constructed from the EE/O values and the mineralization results of the UV/OX systems reported above, since K2S2O8 followed by KHSO5 are more photosensitive than H2O2.
Figure 4.11b. Absorbance in deionized water of all initial reactive species at the concentrations used in this study and at the range 250-258 nm. OXONE® at 0.615 mM is equivalent to 1.23 mM of KHSO$_5$.

In the case of the catalyzed-UV-oxidant reagents, the additional presence of a transition metal makes very complicated our efforts to rationalize the results from the EE/O analysis and those shown in Figure 4.9. The interaction of the transition metals with the oxidants, the photolysis of the oxidants, the interaction of the transition metals with other species in solution and the effect of UV on all species in solution might explain the particular order of efficiency obtained. From all metal species used initially, only Fe(III), as FeOH$_2^+$, appeared to be appreciably photosensitive at 254 nm.

The dark step of cobalt regeneration via peroxymonosulfate (reaction 1.11 of the postulated in Chapter 1, section 1.2.4 mechanism) has been reported to be very fast (62) and Co(III) species
have not be reported to be photosensitive similarly to Fe(III) as shown in reaction 1.3 of the photo-Fenton. Moreover, Co(III) is believed to appear as CoO$^+$ in water (reaction 1.9) and even if photosensitive it would not give the highly reactive hydroxyl radicals. In the Ag(I)/K$_2$S$_2$O$_8$ reagent, silver cannot be regenerated, since, unlike hydrogen peroxide and peroxymonosulfate, persulfate is strictly an oxidizing agent and cannot induce the reduction of Ag(II) to Ag(I), similarly to equations 1.2 and 1.11 of the Fenton and the Co(II)/KHSO$_5$ reagents, respectively. This also explains the zero order kinetics obtained with the dark Ag(I)/K$_2$S$_2$O$_8$, by varying Ag(I) concentration. It was found that the higher the silver concentration the greater destruction of 2,4-DCP is achieved with time, indicating that silver is not regenerated in the process.

It must be noted here that oxalic acid has been identified as one of the major degradation intermediates of 2,4-DCP with advanced oxidation technologies and is formed before complete mineralization (formation of CO$_2$ and water) occurs (74-77). It is also well-known that Fe(III) forms complexes with organic acids, especially with oxalic acid (18). The resulting trioxalate complex demonstrates high quantum yield ($\Phi=1.25$, fraction of the absorbed photons that result in a photochemical reaction) and facilitates the regeneration of iron as shown in reaction 4.4, which in turn might be occurring in parallel to reaction 1.3.

\[
\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)_3^{3-} + h\nu \rightarrow \text{Fe}^{2+} + 2.5\text{C}_2\text{O}_4^{2-} + \text{CO}_2
\]  

(4.4)

Similar properties have not been reported for cobalt and silver and this combined with the previous discussion, might explain the better results obtained with the use of photo-Fenton (UV/Fe/H$_2$O$_2$) as compared with those of the other two reagents (UV/Co$^{\text{II}}$/KHSO$_5$ and
UV/Ag\(^{1}/\text{K}_{2}\text{S}_{2}\text{O}_{8}\)). We are currently investigating the degradation pathways (intermediates) of the chlorophenol tested here with the sulfate radical generating technologies and the potential complexation of Co(III) and Ag(II) with oxalate.

As a final remark, it should be noted that any concerns of further contaminating the treated water with metals and sulfates, released from the catalysts and oxidants used here, are certainly valid. In this study, the catalysts were added at relatively low concentrations (1 ppm). It was previously shown in Chapter 2, for the case of Co(II)/KHSO\(_{5}\) for example, that even less than 100 ppb of cobalt are sufficient for the activation of KHSO\(_{5}\) and the generation of sulfate radicals. This has not been the case for the dark Ag(I)/K\(_{2}\)S\(_{2}\)O\(_{8}\) however, since high Ag(I) concentrations are needed for the activation of persulfate. As for the Fenton Reagent and its modifications, there are already several field applications that employ this reagent for water decontamination. In addition, the (un-catalyzed) oxidants tested here are also widely used in different applications. Persulfate is activated thermally in a process called direct chemical oxidation, which is currently tested for water treatment, and the chemical has also been used in TOC analyzers. OXONE\textsuperscript{®} has been applied as an alternative non-chlorine agent for the treatment of water in pools and spas as well as a bleaching agent in the paper and pulp industry. It is believed that the technologies reported here would provide new alternatives to scientists and engineers working on the field of water treatment. Certainly to make these processes even more acceptable for environmental applications, we are currently investigating the use of immobilized catalysts.
4.4 Conclusions

This study compares the efficiency of several newly tested advanced oxidation technologies with established ones for the treatment of a model organic contaminant under certain conditions. More specifically, this study reports the extent and kinetics of degradation and mineralization of 2,4-dichlorophenol with the following reagents: Fe(III)/H₂O₂, Fe(II)/H₂O₂, Co(II)/KHSO₅, Ag(I)/K₂S₂O₈, UV alone, UV/H₂O₂, UV/KHSO₅, UV/K₂S₂O₈, UV/Fe(III)/H₂O₂, UV/Fe(II)/H₂O₂, UV/Co(II)/KHSO₅ and UV/Ag(I)/K₂S₂O₈. To assure valid comparison, several critical parameters when evaluating advanced oxidation technologies were investigated (146).

Thus, in addition to kinetics and extent of degradation and mineralization, the UV technologies tested here were also compared with respect to electrical energy consumption. From the results of this study the following order of efficiency was constructed for the UV/Ox technologies: UV/K₂S₂O₈ > UV/KHSO₅ > UV/H₂O₂. Comparison of the absorbance of the oxidants at 254 nm supports the above order, since persulfate followed by peroxymonosulfate are more photosensitive than hydrogen peroxide. The order of efficiency for the UV/M/Ox technologies tested here was: UV/Fe(III)/H₂O₂ > UV/Fe(II)/H₂O₂ > UV/Co(II)/KHSO₅ > UV/Ag(I)/K₂S₂O₈. This particular order of efficiency is believed to be due to the higher photosensitivity of the Fe(III) species in water as compared to those of Co(III) and Ag(II), and which appears to be more critical than the photolysis of the oxidants.
CHAPTER 5

Cobalt-mediated Activation of Peroxymonosulfate and Sulfate Radical Attack on Phenolic Compounds. Implications of Chloride Ions

This study reports the sulfate radical pathway for the room temperature degradation of two phenolic compounds in water. The sulfate radicals were produced by the cobalt-mediated decomposition of peroxymonosulfate (Oxone) in an aqueous homogeneous system. The major intermediates formed from the transformation of 2,4-dichlorophenol (2,4-DCP) were 2,4,6-trichlorophenol, 2,3,5,6-tetrachloro-1,4-benzenediol, 1,1,3,3-tetrachloroacetone, pentachloroacetone and carbon tetrachloride. Those resulting from the transformation of phenol in the presence of chloride ion were 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol, 1,1,3,3-tetrachloroacetone and pentachloroacetone. In the absence of chloride ion, phenol transformed into 2,5-cyclohexadiene-1,4-dione (quinone), 1,2-benzenediol (catechol) and 1,4-benzenediol (hydroquinone). Several parameters were varied and their impact on the transformation of the organic compounds is also discussed. The parameters varied were the initial concentration of the organic-substrate, the dose of Oxone used, the cobalt counter anion and in particular the impact of chloride ions and the quenching agent utilized for terminating the reaction. This is one of the very few studies dealing with intermediates formed via sulfate radical attack (SRA) on phenolic compounds. It is also the first study that explores the sulfate radical mechanism of oxidation, when sulfate radicals are generated via the Co/Oxone reagent.
Furthermore, it provides strong evidence on the interaction of chloride ions with sulfate radicals leading to halogenation of organic compounds in water.

5.1 Introduction

There have been a number of studies dealing with the mechanism under which sulfate radicals attack organic compounds (48,90,91,94,100,112,147-156), but compared to hydroxyl radicals, sulfate radicals have not been as extensively explored or understood. In these studies, sulfate radicals were generated via scission of the peroxide bond by radiolytic (106,147,153,154), photolytic (48,106,151,152,155-159) or thermal activation of persulfate (48,100). Alternatively and similarly to hydroxyl radicals formed via the Fenton Reagent, sulfate radicals were also formed via electron transfer by transition metal activation of persulfate (94,100,148-150,152) or peroxymonosulfate (90,91,94). Radiolysis, photolysis or thermal activation of peroxymonosulfate leads to the formation of both sulfate and hydroxyl radicals, as shown in Chapter 4, and only via transition metal catalysis it is possible to form sulfate radicals as the major oxidizing species, without using hydroxyl radical trapping reagents. In this study, sulfate radicals were generated by the cobalt-mediated activation of peroxymonosulfate, which to our knowledge is the most efficient catalytic activation of this peroxide.

Similar to hydroxyl radicals, sulfate radicals may react with organic compounds by electron transfer, hydrogen abstraction or addition (48,106,147). It is generally accepted, however, that sulfate radicals react more selectively via electron transfer (106,147). Although more selective towards oxidation, the majority of the products formed by sulfate radical attack on aromatics are
hydroxylation products, which are also intermediates of hydroxyl radical attack (93,106,112,147-149,152,153,156). There are a few but quite similar mechanisms proposed for the sulfate radical attack on aromatics. A sulfate radical may react via addition to the ring followed by hydrolysis (147). This would involve the elimination of sulfate after the addition and then hydrolysis of the radical cation to a OH-adduct radical via an $S_N1$ type mechanism (112,148,151,153,154) or nucleophilic attack by water on the $SO_4^{*-}$-adduct radical to give rise to the OH-adduct radical via an $S_N2$ type (151,154). Electron transfer from the ring to $SO_4^{*-}$ may also take place followed by hydroxylation with water or OH (48,147). Sulfate radicals react also by electron transfer with methoxy derivatives to give radical cations (147), carboxy derivatives to give decarboxylated radicals (48,147,156), amines to give N-centered radicals (48,154) and by addition to unsaturated bonds of alkenes (48,90,91,94). In all cases, the organic radicals formed can then undergo a series of propagation reactions to form other radical species and/or termination reactions towards more stable intermediates (48). Typical propagation reactions, besides nucleophilic addition such as hydroxylation, include oxidation (148,150), deprotonation (48,149,153,154), reduction (149,150), C-C bond cleavage (148,149,153) and reaction with $O_2$ (48,94,154,155) to form peroxyl radicals.

This study reports on the sulfate radical pathway of degradation of two phenolic compounds in water. The radicals were produced by the cobalt-mediated decomposition of OXONE® (peroxymonosulfate) in an aqueous homogeneous system (reaction 2.1) and their reaction with the substrate eventually leads to the mineralization of the organic material (reaction 5.1). The mechanism and the fact that sulfate radicals are the major species formed from such interaction were demonstrated in Chapters 2 and 3:
SO$_4^\cdot$ + Organics $\rightarrow$ [...many steps...] $\rightarrow$ CO$_2$ + H$_2$O  \hspace{1cm} (5.1)

Here, major intermediates formed from the sulfate radical attack on phenol and 2,4-dichlorophenol were identified and used for the elucidation of the sulfate radical attack mechanism on aromatics in water. Several parameters were varied and their impact on the transformation of the organic compounds is discussed. More specifically, the initial concentration of the organic-substrate was substantially increased even up to saturation to increase the sensitivity of the detection of intermediates. The dose of OXONE® was also varied significantly in order to identify intermediates at different stages of the reaction. Three different cobalt salts were tested as the source of the catalyst to determine whether the cobalt counter ion plays a role in the process. In particular the presence of chloride, either from the substrate itself, or from cobalt chloride, was found to significantly affect the overall transformation mechanism. It was observed the chloride ions react with sulfate radicals to form chlorine radicals. The latter, either react directly with the organic compounds or may form free available chlorine species that also participate in substrate transformation reactions. Finally, the quenching agent utilized to stop the reaction at specific time intervals was found to play a minor role in the formation of intermediates and such implications are also discussed here.
5.2 Experimental

The following chemicals were used as received with no further purification: 2,4-dichlorophenol (99%, Acros Organics), phenol (99%, Fisher), 4-nitrophenol (99+%, Aldrich), CoCl₂·6H₂O (98%, Aldrich), CoSO₄·xH₂O (Aldrich), Co(NO₃)₂·6H₂O (99.3%, Sigma), Oxone® (95%, Aldrich, manufactured by DuPont), NaNO₂ (99.99+%, Aldrich), Na₂S₂O₃ (99.9%, Fisher). Stock solutions of all chemicals were prepared in advance. Prior to an experiment, specific aliquots were transferred to the reactor vessel in order to obtain the concentrations reported in the Figures.

Dichlorophenol (DCP) was tested at three different initial concentrations ranging from 0.5 to 5 g/L. Three different cobalt salts such as CoCl₂·6H₂O, CoSO₄·xH₂O and Co(NO₃)₂·6H₂O were also tested to investigate the effect of the cobalt counter ion on the transformation of 2,4-DCP and especially the implications of the chloride ion. The cobalt:peroxymonosulfate mol ratios used were 1:100 mainly, and 1:1000. Samples were quenched with excess methanol, sodium nitrite and occasionally with methylene chloride, which was also the extraction solvent. Oxone (2KHSO₅·KHSO₄·K₂SO₄) was also tested at several doses from 0.5:1 to 64:1 as mol ratio of peroxymonosulfate versus 2,4-DCP. In the case of 5 g/L (30.7 mM) initial 2,4-DCP concentration, Oxone powder was dissolved directly in the reaction vessel at amounts very close to its solubility limit (256 g/L): 12.41 g in 50 mL obtaining a concentration of 383.5 mM (or 235.8 g/L) as Oxone. This was performed to assure that significant transformation of the substrate would take place. The molar ratio of Oxone versus 2,4-DCP was then 12.5:1 corresponding to KHSO₅:2,4-DCP equal to 25:1.
Phenol (solubility 87 g/L) was initially tested at an initial concentration of 30.7 mM (2.9 g/L) by transferring the appropriate aliquot from a stock solution of 712.8 mM (67.1 g/L) in the 50 mL reaction vessel. As in the case of 2,4-DCP, Oxone powder was again dissolved directly in the reaction vessel to obtain a concentration of 383.5 mM (or 235.8 g/L) as Oxone. The molar ratio of Oxone versus phenol was then 12.5:1 or that of KHSO₅ vs. phenol 25:1. Another experiment at extremely high concentrations of phenol (655.8 mM, corresponding to a 1.2:1 mol ratio of KHSO₅ vs. phenol) was also performed to detect the very early intermediates from the transformation of phenol with the Co/Oxone reagent. Two different cobalt salts were tested to investigate the effect of chloride on the transformation of phenol. Those were CoCl₂.6H₂O and Co(NO₃)₂.6H₂O and were added at specific aliquots from stock solutions to obtain a concentration of 7.7 mM (454 mg/L as Co), which corresponds to a 100:1 mol ratio of KHSO₅ vs. Co. An eight (8) mL sample was withdrawn at specific time intervals and quenched with 2 mL of 3 M Na₂S₂O₃. The quenched samples were then extracted via a liquid-liquid extraction process under vigorous agitation for a period of at least 2 min (Vortex mixer was also used in some cases) using 2 mL methylene chloride. Using a Pasteur pipette, samples (~1 mL) from the organic layer were transferred to appropriate vials for the GC-MS analysis.

All experiments were performed at room temperature and in de-ionized water without controlling the pH. Oxone contains peroxymonosulfate and bisulfate, thus Oxone addition led to a decrease in the solution pH, which was substantial in the cases that high Oxone doses were used. When buffering species were used for adjusting the pH₀ at 7.0 (0.1 M sodium bicarbonate and
adjustment with potassium bisulfate), higher transformation kinetics were generally observed compared to those under uncontrolled-acidic conditions.

After the initiation of some of the reactions, especially those utilizing concentrated reaction systems, some limited precipitation and also some oily like droplets were formed. In some cases and at the latest stages of the reaction, the reaction stirring bar was also coated with a yellowish/orange material resulting most probably from polymerization reactions, which are typical in advanced oxidation. After removing the majority of the aqueous phase for analysis, ethanol was utilized to both dissolve this material and quench the reaction. It was then further dissolved in methylene chloride for analysis and this portion is what is referred as hydrophobic in the results and discussion section.

Quantification of the transformation of 2,4-DCP and 4-nitrophenol (4-NP), which was tested as a model substrate in the quenching agent investigations, was performed with HPLC (Agilent 1100, UV-vis detector) and that of the organic carbon with a TOC (Shimadzu VCSH) Analyzer. 2,4-DCP and 4-NP samples were separated with an Eclipse XDB-C8 (4.6 x 150mm, 5µm, Agilent) column with their corresponding peaks detected at 205 and 316 nm, respectively.

For the analysis of 2,4-DCP, phenol and their transformation intermediates, liquid samples were also collected and analyzed using a Hewlett-Packard gas chromatograph (GC/6890) equipped with a mass selective detector (MSD/5973). This instrument (GC-MS) allowed for both qualitative and quantitative characterization. Samples were introduced by automatic injection into a heated split/splitless injection port and separated using a SUPELCO equity 5 capillary
column (30m x 0.32mm x 0.25mm). An injection size of 1.0 mL with two repetitive injections for reproducibility was performed. Quantification of the products was determined by using multipoint standard calibration curves.

Some phenol degradation samples were also injected to HPLC. The fractions of peaks were detected and separated with a Discovery RP Amide C16 (15cm x 4.6mm, 5µm, SUPELCO) column. They were then collected, concentrated and analyzed with a Micromass GC (Agilent 6890N) time-of-flight mass spectrometer (GC-TOF-MS). HPLC fractionation was performed by using initially 100% H₂O as the mobile phase and gradually introducing Acetonitrile (MeCN), eventually reaching a 50:50 ratio of H₂O:MeCN after 15 min of run time (1 mL/min). All inorganic compounds eluted early, and the peaks detected afterwards corresponded to the organic material only. Samples were introduced to the GC by injection into a heated splitless injection port and separated using an HP-5 (30m x 0.32mm x 0.25µm) column. Mass spectrometry was performed with an Electron Ionization Method.

5.3 Results and Discussion

5.3.1 2,4-Dichlorophenol Intermediates

Our initial objective was to investigate the formation of degradation intermediates of 2,4-DCP with the Co/Oxone reagent. The intermediates identified following a sulfate radical attack on 2,4-dichlorophenol were 2,4,6-trichlorophenol, 2,3,5,6-tetrachloro-1,4-benzenediol (tetrachlorohydroquinone, at early stages with excess chloride and in hydrophobic phase), pentachlorophenol
(traces, hydrophobic), 1,1,3,3-tetrachloroacetone, pentachloroacetone, carbon tetrachloride and are shown in Scheme 5.1. In the hydrophobic phase of the reaction system, 2,7-dichlorodibenzo[b,e][1,4]dioxin and 11-methoxybenz(A)anthracene-7,12-dione were also detected. When Co(NO₃)₂ was the catalyst source, 1,1’-sulfonylbis[4-chloro]benzene was detected and this is the only sulfur bearing organic intermediate detected. All investigations with 2,4-DCP gave chlorinated derivatives no matter whether CoCl₂ was used. This was due to the presence of chloride ions from CoCl₂ (when present) or the chlorophenol molecule itself. Treatment of 2,4-DCP in a chloride free solution led to the release of chloride atoms, which in turn reacted with sulfate radicals to produce chlorine radicals. The latter, either react directly with the organic compounds or may form free available chlorine species that also participate in substrate transformation reactions (see sections 5.3.4 and 5.3.5).
5.3.2 Phenol Intermediates, Chloride Present

Because of the presence of chloride in the molecule of 2,4-DCP and the detection of chlorinated intermediates when treated with Co/Oxone it was decided to test phenol in both chloride-free and chloride-present matrices. With this, our objective was first to identify any non-chlorine bearing intermediates in the absence of chloride in solution. Secondly, under a chloride-rich environment, we wanted to explore if intermediates similar to 2,4-DCP pathway are also formed following a SRA on chloride and phenol. Two complementary experiments using CoCl$_2$.6H$_2$O
and Co(NO$_3$)$_2$.6H$_2$O respectively as the cobalt source were performed at different sampling periods to assure representative intermediate detection. When CoCl$_2$.6H$_2$O was used, thus additional Cl$^-$ being present, the intermediates detected in order of appearance and peak area (see also Figures 5.1a and b and Scheme 5.2) were: 2-chlorophenol (2-CP), 4-chlorophenol (4-CP, almost as much and as early as 2-CP), 2,4-dichlorophenol (24-DCP), 2,6-dichlorophenol (2,6-DCP, limited, much less compared to 2,4-DCP), 2-(3,5-dichloro-2-methoxyphenyl) pyrrole, 1,1,3,3-tetrachloroacetone (TCA, seems to convert to pentachloroacetone) and pentachloroacetone (PCA). High amounts of octa-sulfur were also detected at the later stages of the reaction due to the interaction of OXONE$^{®}$ with the quenching agent (see Effect of Quenching section). It is noted here that 1,1,3,3-tetrachloroacetone and pentachloroacetone were also detected following the transformation of 2,4-DCP.

**Scheme 5.2: Phenol Products, Chloride Present**

![Scheme 5.2: Phenol Products, Chloride Present](image-url)
5.3.3 Phenol Intermediates, no Chloride

When there was no chloride present in the reacting solution, no strong or clear intermediate was detected with the liquid-liquid extraction and GC-MS analysis at an initial phenol concentration of 2.9 g/L. A small peak corresponding to 1,1'-sulfonylbis[4-chloro]benzene was again identified with chlorine in the molecule most likely coming from the extraction solvent. Again high amounts of octa-sulfur were detected at the later stages. Assuming detection limitations of the intermediates formed, due to their hydrophobicity or volatility, it was decided to dramatically increase the precursor concentration to 61.7 g/L. Under these conditions, the intermediates, which are also the very early ones, due to the low OXONE® dose used compared to that of phenol, were: 2,5-cyclohexadiene-1,4-dione (quinone), 1,2-benzenediol (catechol) and 1,4-benzenediol (hydroquinone, only in the hydrophobic phase) (see Scheme 5.3). The last sample collected after 2 h from the initiation of the reaction contained: phenol, catechol, molecular sulfur (octa-sulfur) and sulfur precipitated. The hydrophobic sample was analyzed and found to contain: phenol, catechol, hydroquinone, molecular sulfur (octa-sulfur) and sulfur precipitated. The GC-TOF-MS analysis (see experimental section) also showed the formation of several compounds, which were comprised of polycyclic, fully or partially, unsaturated rings such as C_{17}H_{12}O, C_{18}H_{16} (three species), C_{18}H_{18} (two species), C_{18}H_{20}, C_{19}H_{22} and C_{19}H_{24}. These may be compared with 11-methoxybenz(A)anthracene-7,12-dione (C_{19}H_{12}O_{3}), which was also detected in the transformation of 2,4-DCP. In fact, if we eliminate the methoxy group, which most probably is coming from the ethanol utilized to dissolve the hydrophobic phase of the reactor (see section below), 11-methoxybenz(A)anthracene-7,12-dione (C_{19}H_{12}O_{3}) becomes
benz(A)anthracene-7,12-dione (C$_{18}$H$_{20}$O$_{2}$), which is even closer to the ones detected with the TOF-MS.

**Scheme 5.3: Early Phenol Products, no Chloride**

5.3.4 Transformation of Chloride to Free Available Chlorine

So far there has been strong evidence on the formation of free chlorine from the reaction of chloride with sulfate radicals. To undoubtedly validate this, control experiments in de-ionized (DI) water were performed by using NaCl as the source of chloride and 12 ppm OXONE® activated by Co from CoSO$_{4}$. The following two Figures 5.1a and 5.1b depict the evolution of free chlorine in:

(a) DI at three chloride loadings (50, 100 and 200 ppm), using 0.1 ppm-Co and FC monitored with the DPD-FAS standard method

(b) DI and tap water at a chloride loading of 100 ppm using 1 ppm-Co and FC monitored with the HACH DPD-FEAS modified method.

In the first case shown in Figure 5.1a, the values of free chlorine obtained were between 1.5 and 2.5 ppm in DI water, with the free chlorine slightly increasing following the increase in chloride concentration.
**Figure 5.1a**: FC formation in DI water with the Co/Oxone reagent. Conditions: \([\text{Co}^{2+}]=0.1\) ppm (CoSO₄), \([\text{OXONE}^{®}]= 12\) ppm, values in the legend correspond to ppm, results obtained with the DPD-FAS standard method.

With the HACH DPD-FEAS modified method and using 1 ppm cobalt instead, similar results were obtained as shown in Figure 5.1b with FC values being again in the area of 2.0 ppm. In tap water, 0.76 ppm-FC were initially present, but still some additional was also formed from the reaction of sulfate radicals with chloride ions. It must be mentioned here that in both cases control experiments were initially performed that did not demonstrate any interference of OXONE® in the FC measurements. To further validate our findings and taking into account the redox equivalence of Cl₂ with OXONE® (1 ppm Cl₂ = 4.8 ppm OXONE®, calculated by equivalent weights for redox reactions), one can see that 2.2 ppm Cl₂, which was the maximum chlorine formed in DI water, are equal to 10.6 ppm of OXONE®. The latter value is very close to the 12 ppm of OXONE® used here.
**Figure 5.1b:** FC formation in DI and tap water with the Co/Oxone reagent. Conditions: [Cl$^{-}$]=100 ppm (NaCl), [Co$^{2+}$]=0.1 ppm (CoSO$_4$), [OXONE$^{\circledR}$]= 12 ppm, *in Tap water initial FC=0.76 mg/L, results obtained with the HACH DPD-FEAS modified method

This means that in DI water and having excess chloride almost all OXONE$^{\circledR}$, via the radical mechanism shown below, reacts to give free available chlorine. More specifically OXONE$^{\circledR}$ activation leads to the generation of sulfate radicals, which then oxidize chloride to chlorine radicals (reactions 5.2 and 5.3). The latter species either react directly with the organic material (reaction 5.13) or recombine forming free available chlorine (aqueous chlorine, hypochlorous acid, and hypochlorite, reactions 5.4-5.7). From a thermodynamic point of view, sulfate radicals demonstrate high enough redox potential (2.43 V) to oxidize chloride into chlorine radicals (-2.41 V). Peroxymonosulfate (1.75 V) can also oxidize chloride to free available chlorine species (1.36 V Cl$_2$/2Cl$^{-}$ and 1.48 V HOCl/Cl$^{-}$) as shown in reactions 5.8-5.11 (42,106,107,109,112).
There have been after all several other reports which have observed such interaction (48,49,109,162). In fact, several previous studies have shown the mechanism of choice to generate chlorine radicals is via the reaction of sulfate radicals with chloride (157-159,163-166) and the potential of generating active chlorine species from monosubstituted peroxides such as OXONE® has been known for quite some time (reactions 5.11 and 5.12) (167,168). When OXONE® is used without activation, no radical mechanism occurs and the rates of active chlorine formation are extremely slow (168,169), when compared to the rates obtained when a radical process is taking place. For reaction 5.11 for instance the rate was reported to be $1.4 \times 10^{-3}$ M$^{-1}$s$^{-1}$ (168). The termination reactions of chlorine radicals with organic radicals (reaction 5.13) or the reaction of free available chlorine species such as HOCl with the organic material (reaction 5.14) give rise to the chlorinated derivatives detected from the transformation of 2,4-dichlorophenol and phenol.

$$\text{SO}_4^{*-} + \text{Cl}^- \leftrightarrow \text{SO}_4^{2-} + \text{Cl}^*$$

Rates in M$^{-1}$s$^{-1}$

\begin{align*}
\text{SO}_4^{*-} + \text{Cl}^- & \leftrightarrow \text{SO}_4^{2-} + \text{Cl}^* \\
\text{Cl}^* + \text{Cl}^- & \rightarrow \text{Cl}_2^{*-} \\
\text{Cl}_2^{*-} + \text{Cl}_2^{*-} & \rightarrow \text{Cl}_2 + 2\text{Cl}^- \\
\text{Cl}^* + \text{Cl}^* & \rightarrow \text{Cl}_2 \\
\text{Cl}_2(\text{aq}) + \text{H}_2\text{O} & \rightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \\
\text{HOCl} & \rightarrow \text{OCl}^- + \text{H}^+ \\
\text{Cl}_2 + 2\text{e}^- & \rightarrow 2\text{Cl}^- \\
\text{HClO} + \text{H}^+ + 2\text{e}^- & \rightarrow \text{Cl}^- + \text{H}_2\text{O}
\end{align*}$

$pK_a = 7.5$

1.36 V (42)

1.48 V (42)
\[
\begin{align*}
\text{HSO}_5^- + \text{H}^+ + 2\text{e}^- & \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} & 1.75 \text{ V} \ (43) \\
\text{HSO}_5^- + \text{Cl}^- & \rightarrow \text{SO}_4^{2-} + \text{HOCl} & 0.27 \text{ V} / 1.4 \times 10^{-3} \ (168) \\
\text{HSO}_5^- + 2\text{Cl}^- + \text{H}^+ & \rightarrow \text{SO}_4^{2-} + \text{Cl}_2 + \text{H}_2\text{O} & 0.39 \text{ V} \\
\text{R}^* + \text{Cl}_2^* & \rightarrow \text{R-Cl} + \text{Cl}^- & (5.13) \\
\text{R-H} + \text{HOC}l & \rightarrow \text{R-Cl} + \text{H}_2\text{O} & (5.14)
\end{align*}
\]

5.3.5 Effect of Chloride

A profile of the major phenol degradation intermediates when chloride was present in solution is provided in Figures 5.2a and 5.2b. Phenol disappeared within 30 min of treatment time (see Figure 5.3). The resulting mono- and di-chlorophenols were also completely degraded within 60 min of treatment time. It is noted that chlorine addition to the ring took place mainly at ortho and para positions. 2- and 4-chlorophenol were the major early intermediates and were formed at almost equal proportions. Further addition of chlorine to both compounds led to the formation of 2,4-DCP. The late intermediates 1,1,3,3-tetrachloroacetone and pentachloroacetone were also detected when 2,4-DCP was the initial organic substrate. Side chain products are certainly expected to form contributing to parallel pathways of intermediates degradation and mineralization of the organic material.
Figure 5.2a and b: Evolution of intermediates from phenol transformation using CoCl₂/Oxone. Conditions: [phenol]₀ = 2.9 g/L (30.7 mM), mol ratios KHSO₅:phenol = 25:1; KHSO₅:Co = 100:1, no pH adjustment, samples quenched with Na₂S₂O₃. For comparison, all compounds in 1b are depicted with respect to area and 2,4-DCP and 2,6-DCP are also shown in concentrations.
Tetra- and penta-chloroacetone authentic samples were not available and hence not quantified. Some points are the average of duplicate experiments.

The data in Figures 5.3-5.5 demonstrate that faster degradation kinetics take place in the presence of chloride ion. Chlorinated derivatives are indeed formed but, due to the dual effect of chlorine and sulfate radicals, the parent compound is transformed faster only when sulfate radicals are present. This was observed with both phenol and 2,4-DCP as the initial substrate. The observed chlorination of the organic compounds due to the interaction of chloride with sulfate radicals and the fragmentation of the substrate eventually leads to the formation of trichloromethane and carbon tetrachloride. The latter was a final product detected from the transformation of 2,4-DCP and from an environmental point of view a compound that is highly undesirable. These species are very resistant to further oxidation, since the carbon atom in the molecule is fully oxidized (49).
**Figure 5.3:** Phenol transformation using Co/Oxone. Effect of cobalt counter ion. Conditions: \([\text{phenol}]_0 = 2.9 \text{ g/L (30.7 mM)}, \) mol ratios \(\text{KHSO}_5:\text{phenol} = 25:1; \) \(\text{KHSO}_5:\text{Co} = 100:1, \) no pH adjustment, samples quenched with \(\text{Na}_2\text{S}_2\text{O}_3\)

![Graph showing phenol transformation using Co/Oxone](image)

**Figure 5.4:** 2,4-Dichlorophenol (high concentration) transformation using Co/Oxone. Effect of cobalt counter ion. Conditions: \([2,4-\text{DCP}]_0 = 0.5 \text{ g/L (3.07 mM)}, \) mol ratios \(\text{KHSO}_5:2,4-\text{DCP} = 30:1 \) and \(\text{KHSO}_5:\text{Co} = 100:1, \) no pH adjustment, samples quenched with MeOH.
Figure 5.5: 2,4-Dichlorophenol (low concentration) transformation using Co/Oxone. Effect of cobalt counter ion. Conditions: [2,4-DCP]₀ = 50 mg/L (0.307 mM), KHSO₅:2,4-DCP = 3:1, [Co] = 1 mg/L or KHSO₅:Co = 54:1 mol, no pH adjustment, samples quenched with MeOH, error bars represent standard deviation from triplicate experiments.

Figure 5.6 shows it is difficult to achieve complete mineralization of the organic material, due to the presence of chloride, and a maximum of approximately 91% mineralization is reached. When we changed the counter anion on the cobalt salt, slightly higher values were reached as shown in Table 5.1: 96% with CoSO₄ and 98% with Co(NO₃)₂, but still the mineralization was incomplete, since most of chloride was coming from 2,4-DCP anyway. Carbon dioxide is certainly the main final product but in chloride rich environments species such as carbon tetrachloride might account for the remaining low levels of organic carbon. At very high concentrations of 2,4-DCP and in unbuffered (acidic) solution the results with respect to mineralization indicate a different trend as also shown in Table 5.1. In this case, it appears higher chloride concentrations, due to
the use of CoCl$_2$, facilitated the organic carbon removal compared to the case when CoSO$_4$ was used. The organic carbon removal efficiency seems to follow the trend of the transformation of 2,4-DCP shown in Figure 5.4: higher chloride concentrations gave higher 2,4-DCP transformation rates as well as higher organic carbon removal efficiency.

![Figure 5.6: Mineralization of 2,4-DCP with CoCl$_2$/Oxone. Effect of OXONE® dose as KHSO$_5$:2,4-DCP mol ratio. Conditions: [2,4-DCP]$_0$ = 50 mg/L (0.307 mM), KHSO$_5$:Co = 1000:1, pH$_0$ 7.0 with 0.1 M total phosphates.](image-url)
**Table 5.1.** Mineralization of 2,4-DCP with the Co/Oxone reagent. Effect of cobalt salt and OXONE® dose represented as KHSO₅:2,4-DCP mol ratio

<table>
<thead>
<tr>
<th>Cobalt Salt</th>
<th>% TOC Removal (4 h)</th>
<th>[2,4-DCP]₀ in mg/L</th>
<th>Molar KHSO₅:2,4-DCP</th>
<th>Molar KHSO₅:Co</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCl₂</td>
<td>91.3</td>
<td>50</td>
<td>100:1</td>
<td>1000:1</td>
<td>7.0 with 0.1 M total phosphates</td>
</tr>
<tr>
<td>CoSO₄</td>
<td>95.7</td>
<td>50</td>
<td>100:1</td>
<td>1000:1</td>
<td>7.0 with 0.1 M total phosphates</td>
</tr>
<tr>
<td>Co(NO₃)₂</td>
<td>98.4</td>
<td>50</td>
<td>100:1</td>
<td>1000:1</td>
<td>7.0 with 0.1 M total phosphates</td>
</tr>
<tr>
<td>CoCl₂</td>
<td>50.4</td>
<td>500</td>
<td>15:1</td>
<td>100:1</td>
<td>Acidic (no adjustment)</td>
</tr>
<tr>
<td>CoSO₄</td>
<td>52.3</td>
<td>500</td>
<td>30:1</td>
<td>100:1</td>
<td>Acidic (no adjustment)</td>
</tr>
<tr>
<td>CoSO₄</td>
<td>63.3</td>
<td>500</td>
<td>60:1</td>
<td>100:1</td>
<td>Acidic (no adjustment)</td>
</tr>
<tr>
<td>CoCl₂</td>
<td>70.0</td>
<td>500</td>
<td>60:1</td>
<td>100:1</td>
<td>Acidic (no adjustment)</td>
</tr>
</tbody>
</table>

**5.3.6 Effect of OXONE® dose**

Figure 5.7a illustrates upon increasing the OXONE® dose, a faster and more efficient transformation of 2,4-DCP occurs. It is also shown that doses of OXONE® corresponding to 15:1, 30:1 and 60:1 mol ratios of KHSO₅:2,4-DCP led to the complete transformation of 0.5 g/L 2,4-DCP within 2 h, 30 and 15 min of treatment time, respectively. These values correspond to OXONE® concentrations of 14, 28 and 56 g/L, respectively. The transformation of 2,4-DCP leads to the detection of 2,4,6-trichlorophenol, qualitative evolution of which at three different OXONE® doses is shown in Figure 5.7b. The Figure also shows that the higher the OXONE®
dose, the faster the evolution of 2,4,6-TCP takes place. At a 15:1 mol ratios of KHSO₅:2,4-DCP 2,4,6-TCP disappeared within 2h of treatment time as did 2,4-DCP as shown in Figure 5.6a.

Figure 5.7a: 2,4-Dichlorophenol transformation using CoCl₂/Oxone. Effect of KHSO₅ dose as KHSO₅:2,4-DCP mol ratio. Conditions: [2,4-DCP]₀ = 0.5 g/L (3.07 mM), KHSO₅:Co = 100:1 mol, no pH adjustment, samples quenched with MeOH.
Figure 5.7b: Evolution of 2,4,6-Trichlorophenol following the transformation of 2,4-DCP with CoCl₂/Oxone. Effect of KHSO₅ dose as KHSO₅:2,4-DCP mol ratio. Conditions as in 5.7a.

5.3.7 Mechanisms

A sulfate radical mediated attack on an aromatic leads to the formation of carbon-centered radicals via electron transfer from the organic compound to the sulfate radical. Electron transfer from 2,4-DCP to the sulfate radical gives rise to the formation of a 2,4-dichlorohydroxycyclodienyl radical. More mechanistic information on the electron transfer process is described in further details in the example of the transformation of phenol as explored in a chloride free environment.

In a chloride rich environment, chlorine radicals are also formed following a sulfate radical attack on chloride. A termination reaction of a chlorine radical with a 2,4-dichlorohydroxycyclodienyl radical leads to the formation of the chlorinated derivatives as
detected from the transformation of 2,4-dichlorophenol provided in Scheme 5.4. Also since both the ortho and para positions are occupied by chloride, chlorination occurs at position ortho to the phenol group (carbon number 6). It is noted when additional chloride was present from the anion of the cobalt salt, tetrachlorohydroquinone was formed in addition to 2,4,6-trichlorophenol. The intermediates detected in the hydrophobic phase of the reaction mixture suggest that recombination of radical ring intermediates is also occurring. Ring opening followed by cleavage is also taking place to allow for formation of the chloro-acetone species. Traces of carbon tetrachloride were detected in the final samples collected. However, carbon dioxide is the major final product of the process. In particular the detection of 2,7-dichloro-dibenzo[b,e][1,4]dioxin suggests another type of sulfate radical mechanism, which involves the formation of the chlorophenoxyl radical instead of the chlorohydroxycyclohexadienyl radical. Although 4-chlorophenol was not detected, it is assumed that was formed by dechlorination of 2,4-dichlorophenol. SRA on 4-chlorophenol may give rise to 4-chlorophenoxy radical, which reacts with another chlorohydroxycyclohexadienyl radical and cross-linking products, such as the dioxin detected, may eventually form.
Scheme 5.4: SRA on 2,4-DCP

Phenol reacts with a sulfate radical to form the hydroxycyclohexadienyl radical as shown in Scheme 5.5. The combination of a chlorine radical with the hydroxycyclohexadienyl radical leads to the formation of chlorinated organic products, with chlorination taking place mainly at ortho and para positions. 2- and 4-chlorophenol were the major initial intermediates following the transformation of phenol and were detected at almost equal proportions. Formation of 2,4-DCP occurs, upon further addition of chlorine to both compounds. The latter intermediates 1,1,3,3-tetrachloroacetone and pentachloroacetone were formed following the ring opening and
cleavage of the aromatic ring and were also detected when 2,4-DCP was the initial organic substrate.

**Scheme 5.5: SRA on phenol – presence of chloride**

Hydrolysis of the hydroxycyclohexadienyl radical leads to the formation of hydroxylated radical products and then further react with O₂ (either dissolved or mainly from the decomposition of peroxymonosulfate) to the form the stable intermediates of 1,2-benzenediol and 1,4-benzenediol (hydroquinone) as shown in Scheme 5.6. Quinone is then produced via hydrogen abstraction from hydroquinone, either via the reduction of Co(III) to Co(II), or by the decomposition of peroxymonosulfate. It is noted that the unstable peroxyl radicals formed might also decompose and give rise to ring-cleavage products via a Russell mechanism (24,172). Recombination of the organic radicals leads to the formation of coupling products containing several aromatic or saturated rings as detected by GC-TOF-MS or the 11-methoxybenz(A)anthracene-7,12-dione as detected by GC-MS. The observed hydroxylation products formed following SRA on phenol are obviously typical of hydroxyl radical generating reagents. In fact, the three major intermediates detected here, from the sulfate radical attack on phenol with no chloride present, have been
identified in hydroxyl radical oxidation processes such as the Fenton Reagent (24), sonolysis (173), ozonolysis (174) and photocatalysis (175).

**Scheme 5.6: SRA on phenol – formation of catechol, hydroquinone and quinone (chloride free)**

In the case of Co/Oxone, sulfate radicals are the predominant species formed. The first step in all cases is the addition of sulfate radical to the aromatic ring in an unstable form. Since sulfate is an excellent leaving group, the formation of the hydroxycyclohexadienyl radical is taking place via elimination of the sulfate group, followed by hydroxylation via hydrolysis, as shown in more detail in Scheme 5.7. As mentioned earlier, this might involve elimination of sulfate after the addition and then hydrolysis of the radical cation to a OH-adduct radical via an $S_{N1}$ type mechanism (112,148,151,153,154) or nucleophilic attack by water on the $SO_4^\cdot$-adduct radical to give rise to the OH-adduct radical via an $S_{N2}$ type (151,154).
5.3.8 Effect of Quenching Agent

To this point, NaNO₂ and MeOH were the only quenching agents tested, with the former being preferred in the cases that TOC analysis of the samples was required. It was determined the presence of nitrite and sulfate radical attack on 2,4-DCP leads to the formation of 2-nitro-4,6-dichlorophenol. Therefore, a more efficient quenching agent was required; one that will not interfere with the organic material. For this, sodium thiosulfate, a reducing agent utilized in dechlorination and OXONE® titrimetric quantification, was tested, as well as Ag(I) which has been reported to be an effective sulfate radical scavenger. Figure 5.8 demonstrates thiosulfate as effective a quenching agent as nitrite. It was also found that the only implication it had in the analysis was the formation of octa-sulfur via its acidic disproportionation (see reaction 5.20 further below), since after OXONE® addition, especially at high doses, the pH drops significantly. Ag(I) would be most probably the most efficient transition metal radical scavenger (61), since its reaction rate with sulfate radicals is the highest reported but here it is shown that is not as effective as the rest of the agents used. This is because OXONE® contains approximately
3% of persulfate as an impurity and Ag(I) is the best metal activator of persulfate leading to the formation of sulfate radicals, as shown in Chapter 3. Methanol reacting competitively to 4-nitrophenol with sulfate radicals performed almost as well as nitrite and thiosulfate but at extremely high concentrations, due most probably to solvent effect, showed to slightly facilitate the decomposition of 4-nitrophenol with Co/Oxone.

![Figure 5.8: 4-Nitrophenol transformation with CoCl₂/Oxone. Effect of quenching agent as mol ratio of quenching species versus KHSO₅. \([4\text{-NP}]_0 = 20 \text{ mg/L (0.144 mM)}\) KHSO₅:4-NP = 5:1, \([\text{Co}] = 0.05 \text{ mg/L, pH}_0\) adjusted to 7.0 with 2 mM H₂PO₄⁻ and 1 mM NaOH.](image)

Table 5.2 summarizes the implications the quenching agents demonstrated during the transformation of 2,4-dichlorophenol with Co/Oxone and specifically the intermediates detected from the interaction of the quenching agents with the radical species formed after the formation of the sulfate radicals.
Table 5.2. Intermediates formed from the SRA on the quenching agent (2,4-DCP present unless otherwise indicated)

<table>
<thead>
<tr>
<th>Quenching agent used</th>
<th>Compound detected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium nitrite</td>
<td>2-Nitro-4,6-dichlorophenol</td>
</tr>
<tr>
<td>Methanol</td>
<td>Trichloroacetaldehyde</td>
</tr>
<tr>
<td></td>
<td>2,3-Dichloro-2-methyl-butane</td>
</tr>
<tr>
<td></td>
<td>Dichloro-acetic acid methyl ester</td>
</tr>
<tr>
<td></td>
<td>Trichloro-acetic acid methyl ester</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1,1-Diethoxyethane</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>Trichloroacetaldehyde</td>
</tr>
<tr>
<td></td>
<td>2,3-Dichloro-2-methyl-butane</td>
</tr>
<tr>
<td>Sodium thiosulfate (phenol experiments)</td>
<td>Octa-sulfur, S₈</td>
</tr>
</tbody>
</table>
Reactions 5.15-5.23 depict the scavenging effect the reagents demonstrate against sulfate radicals (176):

\[
\text{SO}_4^{\bullet-} + \text{NO}_2^- \rightarrow \text{SO}_4^{2-} + \text{NO}_2^* \\
\text{HSO}_5^- + \text{NO}_2^- \rightarrow \text{HSO}_4^- + \text{NO}_3^- \quad 1.80 \text{ V} \quad (5.15)
\]

\[
\text{HSO}_5^- + \text{NO}_2^- + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \text{NO}_3^- + \text{H}_2\text{O} \quad 1.74 \text{ V} \quad (5.16)
\]

\[
\text{HSO}_5^- + 2\text{H}^+ + 2\text{S}_2\text{O}_3^{2-} \rightarrow \text{HSO}_4^- + \text{S}_4\text{O}_6^{2-} + \text{H}_2\text{O} \quad 1.73 \text{ V} \quad (5.17)
\]

\[
\text{HSO}_5^- + \text{H}^+ + 2\text{S}_2\text{O}_3^{2-} \rightarrow \text{SO}_4^{2-} + \text{S}_4\text{O}_6^{2-} + \text{H}_2\text{O} \quad 1.67 \text{ V} \quad (5.18)
\]

\[
\text{S}_2\text{O}_3^{2-} + 2\text{H}^+ \rightarrow \text{S} + \text{SO}_2 + \text{H}_2\text{O} \quad (5.19)
\]

\[
\text{SO}_4^{\bullet-} + \text{Ag}^+ \rightarrow \text{SO}_4^{2-} + \text{Ag}^{2+} \quad (5.20)
\]

\[
\text{SO}_4^{\bullet-} + \text{CH}_3\text{OH} \rightarrow \text{HSO}_4^- + {^\bullet}\text{CH}_3\text{OH} \quad (5.21)
\]

\[
\text{SO}_4^{\bullet-} + \text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{HSO}_4^- + \text{CH}_3{^\bullet}\text{CHOH} \quad (5.22)
\]

Taking into account these reactions, the interaction of chloride ions with sulfate radicals and the mechanism of sulfate radical attack on organic compounds, one can predict the mechanism of formation of the compounds reported in Table 5.2.

**Supporting Information**

Chromatographs and mass spectra of standards and unknown samples relevant to the mechanistic interpretations of Chapter 5 are included in the Appendix.
CHAPTER 6

Heterogeneous activation of OXONE® using Co₃O₄

This Chapter explores the potential of heterogeneous activation of OXONE® (peroxymonosulfate) in water using cobalt oxides. Two commercially available cobalt oxides, CoO and Co₃O₄ (CoO:Co₂O₃) were tested for the activation of peroxymonosulfate and the consequent oxidation of 2,4-dichlorophenol (2,4-DCP) via a sulfate radical mechanism. Both systems, CoO/Oxone and Co₃O₄/Oxone, were tested at acidic and neutral pH and compared with the homogeneous Co(NO₃)₂/Oxone system. The activity of these systems was evaluated on the basis of the induced transformation of 2,4-DCP as well as the dissolution of cobalt occurred after 2 h of reaction. It was observed that only Co₃O₄ activates peroxymonosulfate heterogeneously, with its heterogeneity being more pronounced at neutral pH. Both CoO and Co₂O₃ contained in Co₃O₄ might be responsible for the observed heterogeneity and the relative mechanisms are further discussed here. To our knowledge, this is perhaps the first study that documents the heterogeneous activation of peroxymonosulfate with cobalt, the best-known catalyst-activator for this inorganic peroxide.

6.1 Introduction

The catalytic decomposition of OXONE® using cobalt, first reported in 1958 (58), was shown to proceed via a radical mechanism (61,64,177). Since then, there have been a few studies
exploring the transition metal activation of peroxymonosulfate for the oxidation of organic compounds (90,91,94,178), but to our knowledge and as shown in Chapter 3, cobalt is the best catalyst-activator of this versatile inorganic peroxide. The cobalt-mediated activation of peroxymonosulfate leads mainly to the formation of sulfate radicals as shown in Scheme 6.1 (60-62,64). These species are very effective in oxidizing and transforming several organic compounds (48,87,88,90,91,94,100,112,147-156). Photolytic activation of OXONE® under visible (179) or UV light (Chapter 4), with or without cobalt, has also been investigated for environmental purposes. The enhanced reactivity of this novel oxidizing reagent has also been applied for graft copolymerization (180), the specific cleavage of DNA (64), the initiation of chemiluminescent reactions(66) and is of interest in the paper and pulp industry (45). Previous investigations on the metal activation of peroxymonosulfate are limited to homogeneous systems. Although very low catalyst concentrations were proven sufficient for the effective activation of OXONE® and cobalt has not been regulated for water applications, there is always the possibility of adverse health effects in cases that high metal concentrations are released in water. Besides the obvious environmental benefits and given the broad interest of the reagent in several areas, the heterogeneous activation of OXONE® using commercially available Co₃O₄ discussed here is a significant advancement in the field of catalysis. As with the homogeneous Co/Oxone reagent shown in Chapters 2 and 3, the heterogeneous system was very efficient in degrading 2,4-dichlorophenol (2,4-DCP), a model organic contaminant at neutral pH (7-8), buffered with bicarbonate species. Under these conditions, the dissolution of cobalt ions from Co₃O₄ was very limited. Dissolved cobalt concentrations up to 70 μg/L were measured. These values are one order of magnitude below those reported in a study where heterogeneous cobalt catalyst was used for ozonation (181). Average cobalt levels in drinking water generally do not exceed 2 μg/L but in some cases concentrations up to 107 μg/L have been reported (182).
Following the proof of heterogeneous activation of OXONE\textsuperscript{®} discussed here, future research should now focus on the preparation of immobilized Co\textsubscript{3}O\textsubscript{4} on solid surfaces.

Scheme 6.1. Cobalt-mediated activation of peroxymonosulfate

6.2 Materials and Methods

Two commercially available cobalt oxide forms, CoO (Aldrich) and Co\textsubscript{3}O\textsubscript{4} (CoO,Co\textsubscript{2}O\textsubscript{3}, Fisher) were screened for the heterogeneous activation of OXONE\textsuperscript{®} and the destruction of 20 mg/L of 2,4-dichlorophenol (2,4-DCP) in water. OXONE\textsuperscript{®} is the commercial name of the triple salt (2KHSO\textsubscript{5},KHSO\textsubscript{4},K\textsubscript{2}SO\textsubscript{4}, DuPont), with potassium peroxymonosulfate (KHSO\textsubscript{5}) being its active component. Both oxides (powders) were tested at the same cobalt mass of 23.6 mg-Co (32.1 mg Co\textsubscript{3}O\textsubscript{4}; 30 mg CoO) in 150 mL MilliQ water, obtaining a total cobalt concentration of 157 mg/L or 2.67 mM. OXONE\textsuperscript{®} was then added from a stock solution at specific aliquots to obtain 1.33 or 2.67 mM as KHSO\textsubscript{5} (11/1 or 22/1 molar ratio versus 2,4-DCP, respectively). It must be noted here that OXONE\textsuperscript{®} addition in unbuffered water led to a significant decrease in the pH; from 6.4 to 2.8 when 2.67 mM KHSO\textsubscript{5} were used and from 6.4 to 2.9 when 1.33 mM KHSO\textsubscript{5} were used. Experiments were resumed at neutral pH, adjusted initially at 7.0 with 0.1 M NaHCO\textsubscript{3} and
Following OXONE addition and after 2 h of reaction, the pH increased to 8.3 when 1.33 mM KHSO₄ were used and 8.0 when 2.67 mM KHSO₄ were used. These final pH values are attributed to the equilibration of the system with the ambient CO₂. Samples were withdrawn at specific time intervals and quenched with excess ethanol. The activity of the system was evaluated by monitoring the transformation of 2,4-DCP with HPLC (Agilent 1100). Samples were also withdrawn, filtered with 0.1 µm filters, and analyzed for dissolved cobalt with Atomic Absorption (PerkinElmer AA-300).

6.3 Results and Discussion

The first two rows of Table 6.1 show the results from the screening experiments and in particular those from the transformation of 2,4-DCP with CoO/Oxone and Co₃O₄/Oxone as well as the dissolution of cobalt from the two oxides. Although with CoO almost complete destruction of 2,4-DCP took place within 30 min of reaction while the respective 2,4-DCP transformation using Co₃O₄ was 74%, significantly higher amounts of cobalt from CoO leached in solution compared to Co₃O₄; 3.01 mg/L versus 0.59 mg/L, respectively. CoO at acidic pH leads to significant dissolution of Co and the CoO/Oxone system is homogeneous. As with pure CoO, the cobalt leached from Co₃O₄ must have resulted from the CoO component of Co₃O₄ (CoO·Co₂O₃).
Table 6.1. Comparative results from the transformation of 2,4-DCP using different cobalt forms.

Conditions: \([2,4-\text{DCP}]_0 = 20 \ \text{mg/L}, [\text{CoO}] = [\text{Co}_3\text{O}_4] = 157 \ \text{mg/L} \) as Co, unless otherwise indicated.

<table>
<thead>
<tr>
<th>Cobalt Source</th>
<th>( \text{Co}^a ) (mg/L)</th>
<th>% tran. DCP (30 min)</th>
<th>pH</th>
<th>KHSO(_5) (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoO</td>
<td>3.01</td>
<td>100</td>
<td>Acidic</td>
<td>2.67</td>
</tr>
<tr>
<td>Co(_3)O(_4)</td>
<td>0.59</td>
<td>73.8</td>
<td>Acidic</td>
<td>2.67</td>
</tr>
<tr>
<td>Co(_3)O(_4)</td>
<td>0.73</td>
<td>85.2</td>
<td>Acidic</td>
<td>2.67 (Fig. 6.1)</td>
</tr>
<tr>
<td>Co(_3)O(_4)</td>
<td>0.03</td>
<td>99.9</td>
<td>Neutral</td>
<td>2.67 (Fig. 6.1)</td>
</tr>
<tr>
<td>CoO</td>
<td>2.75</td>
<td>99.9</td>
<td>Acidic</td>
<td>1.33</td>
</tr>
<tr>
<td>CoO(^\beta)</td>
<td>1.01</td>
<td>83.3</td>
<td>Acidic</td>
<td>1.33</td>
</tr>
<tr>
<td>CoCl(_2)</td>
<td>1.00</td>
<td>77.2±4.2</td>
<td>Acidic</td>
<td>1.23 (Chapter 4)</td>
</tr>
<tr>
<td>Co(_3)O(_4)</td>
<td>0.75 ± 0.06</td>
<td>71.7±1.9</td>
<td>Acidic</td>
<td>1.33 (Fig. 6.2)</td>
</tr>
<tr>
<td>Co(NO(_3))(_2)</td>
<td>0.80 ± 0.08</td>
<td>50.9±9.5</td>
<td>Acidic</td>
<td>1.33 (Fig. 6.2)</td>
</tr>
<tr>
<td>CoO</td>
<td>0.77</td>
<td>99.1</td>
<td>Neutral</td>
<td>1.33</td>
</tr>
<tr>
<td>CoO(^\beta)</td>
<td>0.39</td>
<td>96.7</td>
<td>Neutral</td>
<td>1.33</td>
</tr>
<tr>
<td>Co(_3)O(_4)</td>
<td>0.07 ± 0.02</td>
<td>91.0±5.9</td>
<td>Neutral</td>
<td>1.33 (Fig. 6.3)</td>
</tr>
<tr>
<td>Co(NO(_3))(_2)</td>
<td>0.07 ± 0.01</td>
<td>36.7±1.6</td>
<td>Neutral</td>
<td>1.33 (Fig. 6.3)</td>
</tr>
</tbody>
</table>

\(^a\) Leached or homogeneous.

\(^\beta\) \([\text{CoO}] = 66.7 \ \text{mg/L equal to CoO contained in 157 mg-Co/L Co}_3\text{O}_4\)

Given these comparative results and the fact that CoO is the most soluble cobalt oxide form, it was decided to further explore the use of Co\(_3\)O\(_4\) under both acidic (OXONE\(^\text{®}\) addition) and neutral (0.1 M NaHCO\(_3\), pH\(_0\)=7.0) conditions. Our objective was to determine whether heterogeneous activation of OXONE\(^\text{®}\) could take place and, at the same time, achieve as limited as possible cobalt dissolution from Co\(_3\)O\(_4\). For this, Co\(_3\)O\(_4\) at 157 mg-Co/L was tested and the induced transformation of 2,4-DCP as well as the dissolution of cobalt both in buffered and
unbuffered solution were monitored. Figure 6.1 shows the transformation of 2,4-DCP with the Co$_3$O$_4$/Oxone reagent under these two conditions as well as the soluble Co evolution versus the reaction time. It is shown that at acidic conditions, Co from Co$_3$O$_4$ is slowly dissolved in solution, reaching a value of 0.73 mg/L after 2 h of reaction. At neutral pH, dissolved Co was always below 0.07 mg/L. The initial slight increase in Co concentration followed by a gradual drop is most probably due to the increase of the pH. From an initial value of 7.0, the pH increased to 8.0 after 2 h of reaction and some co-adsorption of Co$^{2+}$ ions might have taken place. In addition, the transformation of 2,4-DCP at neutral pH was faster compared to that at acidic pH.

![Graph showing 2,4-DCP transformation and dissolved cobalt evolution under acidic and neutral conditions using Co$_3$O$_4$/Oxone. Conditions: 2,4-DCP 20 mg/L, OXONE® 2.67 mM as KHSO$_5$, Co$_3$O$_4$ 157 mg/L as Co.]()

**Figure 6.1.** 2,4-DCP transformation and dissolved cobalt evolution under acidic and neutral conditions using Co$_3$O$_4$/Oxone. Conditions: 2,4-DCP 20 mg/L, OXONE® 2.67 mM as KHSO$_5$, Co$_3$O$_4$ 157 mg/L as Co.
Based on the results from the dissolution of Co from Co$_3$O$_4$ and using instead Co(NO$_3$_2$\cdot$6H$_2$O, homogeneous experiments at dissolved cobalt concentrations equal to those leached from Co$_3$O$_4$ were performed. Our objective was to compare the homogeneous Co/Oxone reagent with the Co$_3$O$_4$/Oxone and explore whether heterogeneity with the latter is achieved. Figures 6.2 and 6.3 show the transformation of 2,4-DCP using the homogeneous Co/Oxone and the Co$_3$O$_4$/Oxone reagents under acidic and neutral pH conditions, respectively. Figure 6.2 shows that, under acidic conditions, Co$_3$O$_4$/Oxone demonstrated some heterogeneity as compared to the homogeneous Co/Oxone reagent but again the Co leached in solution, most probably from the CoO component of Co$_3$O$_4$, was rather elevated at 0.75 ± 0.06 mg/L. Figure 6.3 shows that, at neutral pH, the heterogeneous character of Oxone® activation with Co$_3$O$_4$ was much more pronounced and the amount of Co leached in solution was approximately 10-fold less than the previous case; at 0.07 ± 0.02 mg/L. Error bars correspond to standard deviation from replicate experiments. Several control experiments were performed and showed that no significant adsorption of 2,4-DCP is taking place on the oxide surface and OXONE® alone does not induce any significant transformation of 2,4-DCP within the 2 h of reaction time. Some limited 2,4-DCP transformation was observed when OXONE® alone (no cobalt catalyst) was used in buffered water due to the interaction with bicarbonate species (0.1 M) and probably the generation of percarbonate, but still it was much less than the homogeneous cobalt-mediated activation of OXONE® shown in Figure 6.3.
Figure 6.2. 2,4-DCP transformation with Co$_3$O$_4$/Oxone and homogeneous Co/Oxone at acidic pH (both in triplicates). Conditions: 2,4-DCP 20 mg/L, OXONE$^\text{®}$ 1.33 mM as KHSO$_5$, Co$_3$O$_4$ 157 mg/L as Co, Co leached from Co$_3$O$_4$ 0.75 ± 0.06 mg/L, homogeneous Co from Co(NO$_3$)$_2$ 0.80 ± 0.08 mg/L.
Figure 6.3. 2,4-DCP transformation with Co₃O₄/Oxone (4 replicates) and homogeneous Co/Oxone (average of duplicate) at neutral pH. Conditions: 2,4-DCP 20 mg/L, OXONE® 1.33 mM as KHSO₅, 0.1 M HCO₃⁻, pH initially adjusted to 7.0 with KHSO₄, Co₃O₄ 157 mg/L as Co, Co leached from Co₃O₄ 0.07 ± 0.02 mg/L, homogeneous Co from Co(NO₃)₂ 0.07 ± 0.01 mg/L.

For comparison purposes and under the same conditions, CoO was also tested at 157 mg-Co/L and 66.7 mg-CoO/L, with the latter being equivalent to CoO contained in 157 mg-Co/L Co₃O₄ (Co₃O₄ contains equimolar amounts of CoO and Co₂O₃). All results with respect to cobalt dissolution and the transformation of 2,4-DCP are summarized in Table 6.1. At acidic conditions significant cobalt dissolution from CoO was observed. At neutral pH, as expected, the amount of cobalt dissolved was much less, but still significantly higher compared to Co₃O₄. In particular for the case that CoO was used at the same amount as it is contained in 157 mg-Co/L Co₃O₄, the amount of cobalt dissolved was 1.01 mg/L from pure CoO and 0.75 mg/L from Co₃O₄. The values are close and rather elevated, but still the dissolution of CoO appears to be somewhat
suppressed when it is contained in Co$_3$O$_4$ as opposed to its pure form. At neutral pH, the overall cobalt dissolution either from CoO or Co$_3$O$_4$ was more limited. The respective values were 0.39 mg/L from pure CoO and 0.07 mg/L from Co$_3$O$_4$. Due to this relatively high solubility, there was no evidence of pure CoO participating heterogeneously in the activation of OXONE®. We have previously reported in Chapter 4 almost the same percent transformation of 2,4-DCP in an unbuffered homogeneous system where CoCl$_2$ at 1.00 mg/L as Co$^{2+}$ was mixed with OXONE® at 1.23 mM as KHSO$_5$. The slight difference in the 2,4-DCP as shown in Table 6.1 is due to the OXONE® dose used; a 10/1 molar ratio of KHSO$_5$ versus 2,4-DCP was used in Chapter 4 while 11/1 was used here. Even at neutral pH, dissolved cobalt concentrations as high as 0.39 mg/L, either coming from dissolution of CoO or a simple cobalt salt would induce the same 2,4-DCP transformation and pure CoO appears to react homogeneously with OXONE®.

In Co$_3$O$_4$, Co appears in two redox states; as Co(II) in CoO and Co(III) in Co$_2$O$_3$. As with the homogeneous system, it is believed that the mechanism of the heterogeneous catalysis, shown in Scheme 6.1, involves an one electron transfer process: the oxidation of Co$^{II}$ to Co$^{III}$ with peroxymonosulfate and the generation of sulfate radicals as well as the reduction of Co$^{III}$ to Co$^{II}$ and the generation of the peroxymonosulfate radical. It was already demonstrated in Chapter 3 that the latter transient species are too weak compared to sulfate radicals to induce any transformation on 2,4-DCP. Based on the results presented and the cobalt species tested here, there are two main hypotheses with respect to the species responsible for the heterogeneous catalysis observed with Co$_3$O$_4$. These hypotheses are associated with the two oxides bound together and contained in Co$_3$O$_4$ (CoO,Co$_2$O$_3$).
The first suggests that cobalt redox cycling is taking place mainly in Co$_2$O$_3$ (contained in Co$_3$O$_4$), which is an unstable oxide, given also the fact that pure CoO is soluble and did not appear to react heterogeneously. CoO is the most stable cobalt oxide and presumably, Co from CoO needs to be in ionic form (dissolved) to participate in redox reactions.

The second hypothesis indicates that CoO (contained in Co$_3$O$_4$) might also be the species responsible for the heterogeneous decomposition of OXONE$^\text{®}$. The results of Table 6.1 show that pure CoO released relatively high amounts of cobalt in solution and was shown not to react heterogeneously. CoO contained in Co$_3$O$_4$, on the other hand, might be the species contributing to the catalysis and, being bound to Co$_2$O$_3$, released minimal amounts of cobalt in solution as opposed to the case of pure CoO where there was no such inhibition. The difference in the reactivity observed might thus be due to the difference in the availability of CoO in the two oxides used; pure CoO and Co$_3$O$_4$.

Further insights on the mechanism of the heterogeneous catalysis, including exact cobalt speciation when cobalt transits from one oxidation state to the other and clear proof of the species responsible for the heterogeneity observed are currently under way.
CHAPTER 7

Recommendations and Potential Applications

7.1 Recommendations

This study deals with the development and fundamental mechanism of novel chemical reagents for water decontamination such as the Co(II)/KHSO₅, Ag(I)/K₂S₂O₈ reagents and the systems involving the use of UV light radiation coupled with Oxidants or Metal/Oxidants. Since these new chemical systems may ultimately be applied for the treatment of real wastewater and natural water, the influence of important water quality characteristics is of great concern. Consequently, any future work should examine the effect of some other critical parameters that would greatly affect the effectiveness of these newly developed AOTs and were not included here. In addition, certain modifications that will enhance the environmental friendliness of the new reagents and make the newly developed processes more competitive commercially should also be explored. Under these guidelines the following tasks should be considered in future research projects:

7.1.1 Dissolved Oxygen

The presence of dissolved oxygen (DO) is a significant parameter since insoluble hydroxo complexes might be formed at elevated pH and the catalytic activity of a transition metal may be minimized. Our investigations showed that the Co(II)/KHSO₅ does not lie in this category but, if
one chooses to proceed with other transition metals such as Fe and Ag, such investigation is critical. In addition as discussed in Chapter 5, the presence of oxygen is very important in all oxidation reaction pathways. It might not significantly affect the destruction of a parent contaminant but plays a significant role in the overall TOC removal or else the mineralization of the organic material including all intermediates formed. Simulating the oxic conditions of surface waters and the anoxic conditions of groundwater aquifers, comparative results by varying the oxygen concentration should be collected. These conditions may be simulated by purging completely closed reactors, before and during the reaction, with oxygen, air, nitrogen or argon gases.

7.1.2 Common Cations and Anions

The presence of common ions in water should be examined at concentrations found in natural waters. Candidate species include Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Al\(^{3+}\), NO\(_3^-\), Cl\(^-\), Br\(^-\), and SO\(_4^{2-}\). The possibility of the cations competing with the transition metal used as the catalyst and the anions scavenging the radicals generated (sulfate) should be investigated.

7.1.3 Natural Organic Matter

The presence of humic and fulvic acids should also be examined at typical concentrations found in natural water (0-10 mg/L). Experiments may be performed at at three concentration levels: 0, 5 and 10 mg/L. Enhanced concentrations may also be used to study the effect of natural organic matter as humic or fulvic acids at concentrations 0-10 mg/L as total organic carbon. In a first
approach, commercially available humic and fulvic acids may be used (i.e., samples from the International Humic Substances Society and Humin-P 775, Humintech, Germany). Control experiments to test the reactivity of sulfate radicals with natural organic matter should also be performed. To the best of my knowledge, this will be the first investigation on the effect of natural organic matter on the sulfate radical attack on organic contaminants.

7.1.4 Testing Real Wastewater

Future work should also include evaluation of the Co(II)/KHSO₅ for the treatment of real wastewater. Wastewater from the pulp and paper industry may be a potential candidate as test water. A typical pulp and paper facility discharges wastewater with the following characteristics: BOD 420 mg/L, AOX (adsorbable organic halides) 100 mg/L, suspended solids 1,300 mg/L, lignin and its derivatives 5-8 mg/L, conductivity 2,000 μS/cm, pH 6-8, chloride 320 mg-Cl/L, sulfate 430 mg-S/L, calcium 360 mg-Ca/L, total Kjeldahl nitrogen 2-5 mg-N/L, NH₃ 4 mg-N/L, and phosphorous 1.2 mg-P/L. Aiming at evaluating the Co(II)/KHSO₅ system in the treatment of wastewater containing polychlorinated phenolic compounds, future work should investigate the role of: (a) natural organic suspended solids such as lignin, and b) insoluble, inorganic compounds including precipitates present in the wastewater. In order to be able to determine the influence of these factors on the Co(II)/KHSO₅ system, tests should be conducted using: a) a synthetic wastewater containing limited amounts of nutrients, lignin, and some chlorinated phenolic compounds within the range of a typical wastewater stream from paper mill industries (<100 mg of total chlorinated phenols/liter); (b) a simulated wastewater that contains limited amounts of nutrients, lignin, some chlorinated phenols and inorganic salts; and (c) a wastewater
that is obtained from the plant. The characteristics of wastewater reported above will be used to simulate a synthetic pulp and paper wastewater. The same approach and methodology may be followed for testing other kinds of wastewater (also see section 7.2).

7.1.5 Silver-impregnated Activated Carbon (AC) with Persulfate

Following our discovery that Ag(I) is the best metal-activator of potassium persulfate, it would be interesting to examine the integration of this reagent with activated carbon adsorption, a well-known best available technology (BAT) for the treatment of several contaminants. Silver impregnated activated carbon is available commercially and has demonstrated significantly high adsorption capacities for the removal of both organic and inorganic contaminants in water, while simultaneously providing the disinfection and biocidal effect of the silver (183-185). Presence of potassium persulfate in solution will lead to the generation of sulfate radicals, since silver activates the decomposition of persulfate. As a result, in addition to adsorption onto the activated carbon surface, degradation of the contaminants and perhaps enhanced biocidal effect will take place from the sulfate radical attack on substances and microorganisms present. Leaching proof of silver should be given special consideration. Successful proof of this hypothesis will have a significant impact in the field of water treatment, since activated carbon is already used in numerous water treatment plants throughout the country. The potential of initiating oxidation phenomena that will lead to destruction of harmful substances in water and enhanced biocidal efficiency of activated carbon columns, in addition to the contaminant removal with adsorption, has never been explored before.
7.1.6 Immobilization of the Catalyst

In Chapter 6, we showed that Co oxides could heterogeneously activate potassium peroxymonosulfate while leaching of cobalt from the oxide form remains minimal. In particular Co$_3$O$_4$ was the oxide form that demonstrated heterogeneity. Perhaps the most important future study in continuation of this project is the preparation of solid surfaces (i.e., glass, ceramic, stainless steel) impregnated with cobalt. There are several alternative techniques for immobilizing transition metals on a solid support. The first and the simplest one is the so-called incipient wetness (IW) method where a cobalt salt solution is added on commercially available solid supports such as silica, titania, alumina, zirconia or ceria nanoparticles. After obvious wetness is achieved the mixture is heated at 100-130 C for 3-4 h. This process is repeated several times until the required %wt of cobalt is impregnated in the solid support (186,187). The second alternative is to impregnate the transition metal during the preparation of titania or silica coatings using the sol-gel technique (188,189). The sol-gel technique we are currently using will be modified in order to successfully impregnate the transition metal and obtain leaching-proof heterogeneous catalysts (190). The modifications will include:

- Dissolution of the cobalt salt in the water used initially for the sol preparation.
- Addition of the cobalt salt after the preparation of the sol, at the step of the P-25 powder addition.
- Addition of the cobalt salt after the preparation of the sol, without addition of P-25 powder.

Critical parameters that will require further investigation and will contribute to the maximum performance of the catalysts prepared are:

- Appropriate selection of the catalyst precursor; organic or inorganic salt
• Effect of pH; buffering species during immobilization

At the final stage of the project, the prepared immobilized catalysts will be compared with the currently used homogeneous systems for the treatment of several environmentally important organic and inorganic contaminants.

7.1.7 Optimization of UV Technologies

Chapter 4 showed that oxidant activation with UV light is more efficient at wavelength below 254 nm. That particular wavelength however is optimum for disinfection and it is expected that biocidal efficacy will decrease at wavelengths away from 254 nm. The lower the wavelength utilized, the higher the absorbance the inorganic oxidants demonstrate, and hence the radical generation reactions become more efficient. There are commercially available lamps emitting at wavelengths close to 190 nm but it is suggested not to be utilized in a lab environment since radiation at that wavelength leads to the transformation of O₂ to O₃. The latter is a hazardous gas that might affect human health if not handled properly. Given these drawbacks, it is suggested a combination of lamps emitting at both 222 nm and 254 nm to be tested. That way, not only we can maximize the absorbance of the oxidants and increase the efficiencies of chemical oxidation but also sustain the germicidal properties of the radiation emitted and achieve simultaneous disinfection. Finally, the energy losses described in Chapter 4 from the use of the specific reactor configuration may be minimized with an engineered reactor (i.e, annular reactor) where the distance between the treated solution and the UV sources is minimized.
7.1.8 Thermal Activation

This study involved the activation of inorganic peroxides with the use of transition metals and/or UV radiation. Another way of activation includes the use of heating, which may be more economical and more beneficial than UV light in certain cases. Thermal activation of peroxymonosulfate may become a viable decontamination or even analytical technology given the uses a similar technology such as heating/persulfate has found in recent years; both for water remediation (191) and TOC analysis (49).

7.1.9 Halogen Regeneration

Chapter 5 describes the generation of free available chlorine via the reaction of chloride ions with sulfate radicals, released from the decomposition of peroxymonosulfate. Such regeneration may be beneficial from a disinfection point of view, given the sanitizing strength of chlorine but also unfavorable, since chlorine might then react with organic compounds to form carcinogenic chlorinated organic compounds. From an economical point of view, the use of peroxymonosulfate with the sole objective of regenerating chlorine cannot be supported, since peroxymonosulfate is more expensive than chlorine. Regeneration of bromine, another known antimicrobial agent however, might be economically advantageous since bromine is more expensive than chlorine. It remains therefore to explore whether peroxymonosulfate and a sulfate radical mechanism in general might also lead to bromine regeneration and if so, what are the economics associated with such process.
7.1.10 Process Universality

Finally all these novel chemical reagents and the different formulations discussed here will prove their future viability by demonstrating high efficiencies in degrading several other than those tested here water contaminants; contaminants that also exhibit high toxicity or show diversity in properties and structure. Such study should include both organic chemicals that are currently regulated, chemicals that are in the Drinking Water Candidate Contaminant List (CCL), special compounds found in industrial effluents and inorganic species.

7.2 Potential Uses of M/Ox Chemical Oxidation

In Chapter 2, we showed that the coupling of Co(II) with potassium peroxymonosulfate in a homogeneous system (Co\textsuperscript{II}/KHSO\textsubscript{5}) leading to the generation of sulfate radicals demonstrates greater efficiencies and several operational advantages than the Fenton Reagent for the treatment of several organic contaminants in water. In Chapter 3, several transition metals, such as Ag(I), Ce(III), Co(II), Fe(II), Fe(III), Mn(II), Ni(II), Ru(III) and V(III), were tested for the activation of the three common oxidants, hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), potassium peroxymonosulfate (KHSO\textsubscript{5}), and potassium persulfate (K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}) with the objective of finding the favorable metal(s) for the decomposition of each oxidant and thus achieving high efficiencies in degrading organic contaminants in water. Our study demonstrated that indeed Fe(III) and Fe(II) are the most efficient metals for the activation of H\textsubscript{2}O\textsubscript{2}, Co(II) for that of KHSO\textsubscript{5} and Ag(I) for K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}. In addition to these couples, it was recently reported that Mn(II) catalyzes the decomposition of
ozone and very low concentrations of Mn(II) significantly enhanced the destruction of atrazine with ozone (192).

There are numerous cases especially in industrial wastewater where transition metals and organic contaminants are co-present. The novel oxidation technologies reported here are expected to provide new tools for the treatment of specialty wastewater (i.e, paper and pulp, photographic, automotive, nuclear) where the presence of metals (i.e, Mn, Fe, Cu, Ag, Ni, Co) can be exploited for the treatment of other refractory organic compounds that are co-present. Furthermore after substantial optimization, it is believed that some of these technologies have the potential to even become “stand-alone” treatment processes for water decontamination and disinfection.

7.2.1 Paper & Pulp

Wastewater effluents from paper and pulp industries are highly contaminated with organic matter, suspended solids and dissolved salts. Several transition metals such as Mn, Fe Cu, V and Co are also present at low concentrations. During kraft pulp bleaching the presence of metals is detrimental since they induce decomposition of the peroxides used for bleaching into radicals that attack not only lignin but also cellulose (44-46).

There is an increasing trend in replacing the use of chlorine for bleaching by chlorine dioxide, avoiding thus the generation of chlorinated organic compounds but still organochlorine products measured as AOX (adsorbable organic halides) are found in high concentrations and are the most toxic and persistent contaminants of such wastewater. Typical chlorinated compounds include
chlorophenols such as pentachlorophenol and trichlorophenols, chloroform, carbon tetrachloride, 1,2-dichloroethane, 1,1,1-trichloroethane, tri- and tetra-chloroethylene chlorobenzene, spent solvents such as dichloromethane, benzene and methyl ethyl ketone. Dioxins and furans are also found as well as chelating agents used to bind the metals, thus avoiding the degradation of the peroxides during bleaching. As a result, such heavily polluted wastewater contains high values of COD, BOD, TSS and AOX (see also section 7.1.4) (193-195).

On the basis of this study where it was found that peroxymonosulfate could be activated by almost all transition metals present in such wastewater, addition of this oxidant for destroying the organic compounds may be a viable and effective choice of treatment.

7.2.2 Textile

Textile wastewater contains solids, oil and grease, solvents, phenols from dyeing and finishing as well as halogenated organic compounds from bleaching. It is also contaminated with metals such as copper, chromium and cobalt. Typical values of such wastewater include BOD 700-2000 mg/L and COD 2-5 times BOD (195). For wastewater where the COD is significantly higher than the BOD values there is no other option than chemical oxidation.

7.2.3 Electroplating

Another typical example of wastewater where organic compounds are present at high concentrations along with metals is that of the electroplating industry where high concentrations
of trichloroethylene, trichloroethane along with copper, nickel, silver, zinc, lead and other metals are detected in the liquid effluents (195).

7.2.4 Photographic

Photographic wastewater contains solvents, hydroquinone, ammonia as well as silver at high concentrations (196,197). The silver/persulfate technology would have a great impact in treating the organic material of such wastewater.

7.2.5 Nuclear

Choo et al. 2002 simulated nuclear wastewater using Co(NO$_3$)$_2$, H$_3$BO$_3$ and NaCl (198). Cobalt nitrate was used instead of the radioactive Co-60, a beta and gamma emitter used extensively in nuclear power stations. Such wastewater contains also organic compounds such as hydrazine, a corrosion controller, as well as spent cleaning solvents that require treatment before being discharged.

7.2.6 Cobalt Catalysis

Especially the cobalt/peroxymonosulfate reagent has a tremendous potential in water treatment due to the operational advantages of the system, considering also the wide use of cobalt as a catalyst in organic synthesis, as a radioactive isotope in nuclear reactors and as a painting agent.
According to the Cobalt Development Institute there are three major uses of cobalt in catalysis both in homogeneous and heterogeneous systems (199). Those include:

- Hydrodesulfurization process in refineries where Co/Mo catalysts are supported on alumina.
- Production of terephthalic acid where cobalt is used homogeneously along with manganese to catalyze the process.
- Hydroformylation reactions where cobalt is used to catalyze the addition reactions to the double bond of alkenes

There are several cases where industries, due to economical reasons, do not choose to regenerate and reuse spent catalysts. In such cases effluents are polluted with transition metals that before being removed can be used for the activation of oxidants-additives and thus destroy any toxic and persistent organic compounds also present. This will also lead to a dramatic reduction of COD and BOD values.

Wastewater from the production of terephthalic acid contains high concentrations of cobalt and phthalic acid. Just recently the use of photocatalysis has been reported as a very effective treatment alternative (200) but the degradation rates of the organic material were slowed down due to the presence of cobalt. In such a case, the use of peroxymonosulfate as an oxidant would be ideal, since its optimum catalyst-activator is already present in the wastewater without the use of a photocatalyst.
The following Table 7.1 summarizes the metals and the organic compounds found in industrial wastewater and can serve as a reference along with the study of Chapter 3 for selecting the best inorganic peroxide for water treatment.

**Table 7.1. Metals and Organic compounds in Industrial Wastewater**

<table>
<thead>
<tr>
<th>Wastewater</th>
<th>Metals</th>
<th>Organic compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper &amp; Pulp</td>
<td>Mn, Fe, Cu, V, Co</td>
<td>Chlorinated organic compounds, solvents, dioxins, furans, chelating agents</td>
</tr>
<tr>
<td>Terephthalic acid</td>
<td>Co</td>
<td>Phthalic Acid</td>
</tr>
<tr>
<td>Textile</td>
<td>Cu, Cr, Co</td>
<td>Oil, grease, solvents, phenols, halogenated organic compounds</td>
</tr>
<tr>
<td>Nuclear</td>
<td>Co</td>
<td>Hydrazine, spent cleaning solvents</td>
</tr>
<tr>
<td>Photographic</td>
<td>Ag</td>
<td>Solvents, hydroquinone, ammonia</td>
</tr>
<tr>
<td>Electroplating</td>
<td>Cu, Ni, Ag, Zn, Pb</td>
<td>Trichloroethylene, trichloroethane</td>
</tr>
</tbody>
</table>

### 7.3 Green Engineering Considerations

One may argue that further release of sulfates in water from using oxidants such as peroxymonosulfate or persulfate might affect the quality of the water and therefore the efficiency of the process proposed. However, our preliminary experiments (see Chapter 2) suggest that the concentration of the sulfates released following efficient treatment of contaminated water is generally very low. For the complete destruction for example of 50 mg/L of 2,4-DCP the sulfates released from the use of peroxymonosulfate were 177 mg/L. Similarly, for the destruction of 8 mg/L of atrazine the sulfates further released in solution were only 28 mg/L, when the secondary drinking water limit for sulfates has been set at 250 mg/L. Moreover, in many industrial effluents
where degradation of organic compounds or oxidation of toxic pollutants (i.e., as arsenite) is the major concern, the addition of an inorganic anion (such as persulfate or peroxymonosulfate ion) to enhance the degradation or oxidation rate of the pollutants may be justified. Anyway, in the case that the presence of sulfates in the water is still a significant issue, specific technologies are available for their removal or reuse. Sulfate ion removal can be easily achieved when the water flows through an ion exchange resin [i.e., strong base anion resin of polystyrene divinylbenzene matrix with -N'(CH₃)₃ functional groups], which prefers this divalent ion (40). Another alternative is to regenerate the oxidant in another form (persulfate). For instance, regeneration of persulfate from sulfates can be achieved with electrolysis (51).
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APPENDIX

Supporting Information

Table S1 – GC conditions employed for the analysis of phenol and daughter products

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Chromatograph</td>
<td>Hewlett Packard 6890</td>
</tr>
<tr>
<td>Detector</td>
<td>Mass Selection</td>
</tr>
<tr>
<td>Column</td>
<td>Glass capillary column SUPELCO Equity 5, Diameter 0.25 mm, Length 30 m</td>
</tr>
<tr>
<td>Carrier and flow rate</td>
<td>Helium at 1.5 mL/min</td>
</tr>
<tr>
<td>Inlet temperature</td>
<td>250°C</td>
</tr>
<tr>
<td>Detector temperature</td>
<td>250°C</td>
</tr>
<tr>
<td>Temperature program</td>
<td>50°C for 5 min to 220°C at 20°C/min</td>
</tr>
<tr>
<td></td>
<td>5 min final time</td>
</tr>
</tbody>
</table>

Figure S1. The GC chromatograph of a standard showing the peaks corresponding to 2-chlorophenol, phenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 4-chlorophenol.

Figure S2. The GC-MS spectrum of phenol corresponding to the 7.71 min peak on S1.

Figure S3. The GC chromatograph of a sample corresponding to the transformation of phenol with the CoCl₂/Oxone system at reaction time of 20 min showing the peaks corresponding to 2-
chlorophenol, phenol, 2,4-dichlorophenol and 4-chlorophenol. Compare with S1. Other conditions as in Figure 1 of the manuscript.

Figure S4. The GC-MS spectrum of phenol corresponding to the 7.74 min peak on S3. Compare with S2.

Figure S5. The GC chromatograph of a sample corresponding to the transformation of 2,4-dichlorophenol with the CoSO$_4$/Oxone system at reaction time of 240 min showing the peak corresponding to pentachloroacetone. Conditions: [2,4-DCP]$_0$= 500 mg/L, mol ratios KHSO$_5$:2,4-DCP= 30:1 and KHSO$_5$:Co= 100:1, sample quenched with MeOH.

Figure S6. The GC-MS spectrum of pentachloroacetone corresponding to the 8.76 min peak on S5.

Figure S7. The GC chromatograph of a sample corresponding to the transformation of 2,4-dichlorophenol with the CoCl$_2$/Oxone system at reaction time of 5 min showing the peaks corresponding to 2,4-dichlorophenol and 2,4,6-trichlorophenol. Conditions: [2,4-DCP]$_0$= 500 mg/L, mol ratios KHSO$_5$:2,4-DCP= 60:1 and KHSO$_5$:Co= 100:1, sample quenched with MeOH.

Figure S8. The GC-MS spectrum of 2,4,6-trichlorophenol corresponding to the 11.08 min peak on S7.
Figure S9. The GC chromatograph of a sample corresponding to the transformation of 2,4-dichlorophenol with the CoCl$_2$/Oxone system at reaction time of 10 min showing the peaks corresponding to 2,4-dichlorophenol, 2,4,6-trichlorophenol and 2-nitro-4,6-dichlorophenol. Conditions: [2,4-DCP]$_0$= 1000 mg/L, mol ratios KHSO$_5$:2,4-DCP= 30:1 and KHSO$_5$:Co= 100:1, sample quenched with NaNO$_2$.

Figure S10. The GC-MS spectrum of 2-nitro-4,6-dichlorophenol corresponding to the 11.68 min peak on S9.

Figure S11. The GC chromatograph of a sample corresponding to the transformation of 2,4-dichlorophenol with the CoCl$_2$/Oxone system at reaction time of 6 days showing the peaks corresponding to 1,1,3,3-teatrachloroacetone, pentachloroacetone, 2,4-dichlorophenol and 2,4,6-trichlorophenol. Conditions: [2,4-DCP]$_0$= 1000 mg/L, mol ratios KHSO$_5$:2,4-DCP= 5:1 and KHSO$_5$:Co= 100:1, pH$_0$= 7.0 with 0.01M NaHCO$_3$ and KHSO$_4$.

Figure S12. The GC-MS spectrum of 1,1,3,3-teatrachloroacetone corresponding to the 8.49 min peak on S12.
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