Report for 2005OH26B: Use of Persulfate and Peroxymonosulfate Oxidants for the Destruction of Groundwater Contaminants

Publications

- Articles in Refereed Scientific Journals:
    - Rastogi Aditya and Dionysios D. Dionysiou*, Iron Mediated Activation of Peroxymonosulfate and Persulfate for Destruction of Chlorophenols. Paper in preparation.
- Conference Proceedings:
    - Rastogi Aditya*, Souhail R. Al-Abed, and Dionysios D. Dionysiou, Treatment of PAHs and PCBs using sulfate radical based oxidation processes, Accepted for Poster Presentation of the General Papers, Division of Environmental Chemistry, 232nd American Chemical Society (ACS) National Meeting, September 10-14, 2006, San Francisco, California
    - Rastogi Aditya , Souhail Al-Abed, and Dionysios D. Dionysiou*, Destruction of PAHs and PCBs in Water Using Sulfate Radical-Based Catalytic Advanced Oxidation Processes, Accepted for Poster Presentation, 1st European Conference on Environmental Applications of Advanced Oxidation Processes (EAAOP), September 7-9, 2006, Chania, Greece.
    - Rastogi Aditya, Souhail Al-Abed, and Dionysios D. Dionysiou*, Iron-Peroxymonosulfate: A Novel Sulfate Radical Based Advanced Oxidation Technology for Degradation of PCBs. Submitted for Oral Presentation at The 12th International Conference on Advanced Oxidation Technologies for Treatment of Water Air and Soil, Sept. 25-28, 2006, Pittsburgh, Pennsylvania.

Report Follows

Program: **Ohio Water Resource Center; Ohio State University**
Project ID: **2005OH26B**
Title: **Use of Persulfate and Peroxymonosulfate Oxidants for the Destruction of Ground Water Contaminants**
PI: **Dionysios D. Dionysiou, PhD., Associate Professor, Department of Civil and Environmental Engineering, University of Cincinnati**

Summary of Research Accomplishments-Scientific Dissemination of Results

Peer-Reviewed Journal Publications (* denotes corresponding author)

1) Aditya Rastogi and Dionysios D. Dionysiou*, Iron Mediated Activation of Peroxymonosulfate and Persulfate for Destruction of Chlorophenols. Paper in preparation.

Presentations in State, National, and International Conferences (* denotes presenting author)

1) Aditya Rastogi*, Souhail R. Al-Abed, and Dionysios D. Dionysiou, Treatment of PAHs and PCBs using sulfate radical based oxidation processes, Accepted for Poster Presentation of the General Papers, Division of Environmental Chemistry, 232nd American Chemical Society (ACS) National Meeting, September 10-14, 2006, San Francisco, California

2) Aditya Rastogi, Souhail Al-Abed, and Dionysios D. Dionysiou*, Destruction of PAHs and PCBs in Water Using Sulfate Radical-Based Catalytic Advanced Oxidation Processes, Accepted for Poster Presentation, *1st European Conference on Environmental Applications of Advanced Oxidation Processes (EAAOP)*, September 7-9, 2006, Chania, Greece.

3) Aditya Rastogi, Souhail Al-Abed, and Dionysios D. Dionysiou*, Iron-Peroxymonosulfate: A Novel Sulfate Radical Based Advanced Oxidation Technology for Degradation of PCBs. Submitted for Oral Presentation at *The 12th International Conference on Advanced Oxidation Technologies for Treatment of Water Air and Soil*, Sept. 25-28, 2006, Pittsburgh, Pennsylvania.

Summary

This study investigates the fundamentals and applications of novel advanced oxidation technologies (AOTs) for ground water treatment. This new class of AOTs involves iron (Fe (II), Fe (III)) or hydrogen peroxide (H_2O_2) based activation of peroxymonosulfate (PMS) or persulfate (PS) to generate sulfate and hydroxyl radicals. These radicals are extremely reactive and readily attack organic contaminants present in groundwater.

Among the three AOTs evaluated during the study, Fe (II)-PMS system was found to be most effective in the removal of a model contaminant (4-chlorophenol) in short term studies lasting 4 hrs. The Fe (II)-PMS process was optimized with respect to Fe (II) and PMS molar concentrations. The performance of the proposed catalytic systems was also tested for long term degradation of 4-chlorophenol and was compared to other established AOTs like Fenton reagent. The Fe (II) – PS based catalytic system showed maximum TOC removal with significant residual oxidant at the end of 8 days. The stable nature of oxidant will give new direction to the development of the modern AOTs that can act for much longer time even after the application of oxidants.

AOTs using soluble iron as catalyst have been widely reported to suffer from the problem of iron precipitation. In the work presented here, approaches adopted to prevent iron precipitation included use of citric acid as a chelating agent for iron, phosphate buffer to maintain low pH and thiosulfate-oxidant redox couple to maintain iron in the soluble Fe (II) state in the solution. The use of citric acid showed improved process efficiencies and the optimum concentration of citric acid was determined in Fe (II)-PMS, Fe (II)-PS based catalytic systems. Systems employing thiosulfate-oxidant redox couple showed complete absence of precipitation but reduced contaminant removal efficiencies. The use of phosphate buffer led to a precipitate different from that observed in unbuffered systems and lower process efficiencies.

 The catalytic systems were also tested for chlorophenols with increasing degree of chlorination and with other priority contaminants like PCBs and PAHs with widely different structures and properties.

Introduction

Organic contaminants in ground water pose serious threat to the ecosystem due to their toxic nature and harmful effect on human and animals. Examples of such chemicals include chlorinated aromatics, polycyclic aromatic hydrocarbons (PAHs), pesticides, herbicides, endocrine disrupting chemicals (EDCs), toxins, and warfare agents. Many of such organic pollutants are regulated by the USEPA, and their removal from the contaminated water is of high priority. Consequently, the need for efficient treatment of these contaminants is imperative. In particular, for groundwater treatment, such technologies must be efficient for the *in-situ* treatment of contaminants since pump-and-treat remedial strategies are usually very expensive. In addition, *in-situ* biological

processes are not always applicable for many groundwater contaminants because of their high toxicity *[1-4]*.

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. The final products formed are carbon dioxide, water and, depending upon the precursor chemical composition, other ionic inorganic residues such as chloride. 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 AOTs include ozonation, UV/H_2O_2, sonolysis, the Fenton Reagent (Fe^{2+}/H_2O_2), Fenton-like reactions (Fe^{3+}/H_2O_2 with and without UV-light irradiation), electron beams and γ-irradiation and TiO_2-photocatalysis *[4-6]*. However, for groundwater applications, only certain AOTs are applicable. These include the dark Fenton Reagent and other dark-based AOTs, such as the systems proposed in this study.

One of the most established homogeneous AOTs, even at a large scale, is Fenton Reagent. However, for groundwater remediation, this technology faces certain limitations. First, Fe (II) reacts very rapidly with H_2O_2 resulting in the generation of high concentrations of hydroxyl radicals that are not effectively utilized due to their short half-life. Second, the highly unstable nature of H_2O_2 leaves the system without any residual oxidants for post-treatment contamination events. These process limitations can be overcome by replacing H_2O_2 with a more stable oxidant such as persulfate or peroxymonosulfate.

Persulfate has recently been studied as an oxidant alternative for treating organic contaminants in contaminated soil and groundwater *[7]*. Persulfate anions ($S_2O_8^{2-}$) can be thermally or chemically activated by transition metal ions to produce sulfate free radicals ($SO4^{\bullet-}$) which are very powerful oxidants capable of degrading numerous organic contaminants. High aqueous solubility and stability in the subsurface, relatively low cost and benign end products makes persulfate-based oxidation a promising alternative among the advanced oxidation process (AOPs) for remediation of contaminated soil and ground water applications *[8]*.

Peroxymonosulfate (PMS) is used as a powerful oxidant for a wide variety of industrial and consumer applications *[9]*. Peroxymonosulfate often oxidizes faster than hydrogen peroxide and it is slightly more powerful as an oxidant ($E^0_{HSO5^-/HSO4^-}$ = +1.82V; $E^0_{H2O2/H2O}$ = +1.76V) *[10]*. Anipsitakis et al. recently studied the cobalt (Co) based activation of peroxymonosulfate for degradation of chlorophenols (CPs). Co-PMS system was found to be superior than Fenton reagent and showed no pH limitation for degradation of 2, 4-DCP and atrazine *[11]*. However, use of cobalt may adversely affect the quality of environmental systems.

In this study, we evaluated the performance of iron based activation of PMS and PS for the destruction of numerous ground water contaminants namely Fe^{2+}/PMS, Fe^{3+}/PMS, Fe^{2+}/PS and Fe^{3+}/PS. Hydrogen peroxide based activation of persulfate and peroxymonosulfate was also studied to develop an alternative advanced oxidation process for contaminant removal. These technologies are based on the generation of hydroxyl and sulfate radicals, which are among the most powerful oxidizing species found in nature. Degradation of series of chlorophenols (4-CP, 2,4-CP,2,4,6-CP, 2,3,4,5-CP), naphthalene (a PAH) and 2-chlorobiphenyl (a PCB) were evaluated using Fe/PMS and Fe/PS system. Further, the iron availability in the solution was manipulated with chelating agents and by utilizing thiosulfate-oxidant redox couples.

Project Objectives

The primary objective of this study was to develop a novel and versatile class of advanced oxidation processes based on iron mediated activation of peroxymonosulfate and persulfate for the degradation of a variety of ground water contaminants. The objectives include evaluation of:

1) Activation of PS and PMS individually by Fe (II), Fe (III) and H_2O_2.
2) Effect of molar concentration of oxidant and iron on contaminant and TOC removal efficiencies.
3) Feasibility of using chelating agent, phosphate buffer and thiosulfate-oxidant redox couple to avoid iron precipitation commonly observed in such catalytic systems.
4) Versatility of catalytic systems by
   a. Testing the degradation of variety of priority contaminants with widely different properties.
   b. Investigating long term application of catalytic process.

Merits of the project

A novel class of sulfate radical based AOTs (Fe(II)/PS and Fe(II)/PMS) was successfully tested for degradation of variety of ground water contaminates including a series of chlorophenols (4-CP, 2,4-CP, 2,4,6-CP, 2,3,4,5-CP), naphthalene and 2-chlorobiphenyl. In the proposed technologies, the kinetics of the reaction of iron with PMS or PS are slower compared to that of Fenton Reagent. The stable nature of oxidants allows efficient use of such chemicals for significantly longer duration giving new direction to the development of modern AOTs. Application of citric acid, an environmental friendly chelating agent, as reported in this study was found to reduce the precipitation of iron and can be used to improve the degradation efficiency significantly.

Methods, Procedure and facilities

Chemical Used:
The following chemicals were used as received:
2-chlorobiphenyl (99+%, AccuStandard), naphthalene (99+%, fisher Scientific), $Na_2S_2O_8$ (98%, Sigma Aldrich), Methanol (99%, Fisher Scientific), Acetonitrile (Fisher Scientific), $FeSO_4.7H_2O$ (98%, Fisher Scientific), $Fe_2(SO4)_3.4H_2O$ (99+%, Fisher Scientific) and Oxone (95%, Aldrich, manufactured by DuPont). 4-chlorophenol (99.5% , suplco), 2,4-chlorophenol (99.5% ,Supelco), 2,4,6- chlorophenols (99.5%, Supelco) , 2,3,4,5-chlorophenol (99%, Supelco), hydrogen peroxide (30% v/v, Fisher science), sodium phosphate, phosphoric acid, citric acid (99.8%, Sigma Aldrich), sodium thiosulfate (99.5%, Fisher Scientific), methanol (HPLC grade, Fisher), sodium nitrite (99.99% , Fisher), starch (Fisher Scientific), potassium iodide (99.5%, Fisher), acetonitrile (HPLC grade, Fisher).

All chlorophenols were analyzed with an Agilent 1100 series HPLC system with a Quart Pump and UV-diode array detector. The column used for the analysis of chlorophenols was Eclipse XDB-C8 column, obtained from Agilent. Different mobile phase composition and wavelength was used for individual chlorophenol analysis. Naphthalene was also analyzed by Agilent 1100 series HPLC system. A discovery RP amide C-16 column from Supelco was used to analyze naphthalene concentration.

In case of experiments with 2-chlorobiphenyl samples were extracted using hexane/acetone mixture (hexane: acetone = 70:30 v/v) and analyzed by GC/MS (Hewlett-Packard 6890) in accordance with EPA method for chlorinated biphenyl analysis.
Total organic carbon (TOC) in samples was analyzed using a Shimadzu TOC 5050A analyzer equipped with VCSH-ASI system.

The concentration of remaining oxidant (persulfate, peroxymonosulfate) was analyzed using iodometric procedure described by Kolthoff and Carr [12]. 10 ml sample was transferred in a 50 ml conical flask and top of flask was sealed with paraffin after addition of 2 gm of potassium iodide. After vigorous shaking to dissolve potassium iodide, flask was left aside for 15 minute. Finally approximate 1 ml of glacial (~6.5 M) acetic acid was added to the flask and the amount of evolved iodine was determined by titration with standardized thiosulfate solution. Starch indicator was used for a clear end point in titration.

Two different types of batch experimental procedure were used for degradation experiments. In first type of procedure, contaminant concentration was monitored with time (kinetic batch experiment) whereas in second type of experiment procedure (batch experiments) only initial and final samples were taken.

All kinetic batch experiments were conducted in 500-ml narrow neck flask at ambient room temperature. After addition of chemicals, the flask was sealed from the top using Teflon cap with a sampling port. Sampling was performed by withdrawing 5 ml solution from sampling port of the reactor by using gas-tight syringe. The sample was

placed in 10 ml borosilicate vials with Teflon caps. To stop the catalytic reaction in sample, excess amount of methanol or sodium nitrite was added as quenching agent. In most of the cases degradation was monitored for four hours.

40 ml clean EPA vials with Teflon cap were used for batch experiments. Prior to experiment, predetermined amount of SQ-water was transferred into the vial and then appropriate amount of contaminant, oxidant and iron stock was added to achieve the predefined molar ratios of contaminant, oxidant and iron. To achieve continuous mixing, vials were placed in the tumbler (30 rpm). Initial and final samples were taken to find the efficiency of the process. After four hours samples were quenched with excess amount of methanol, a well known quenching agent for sulfate and hydroxyl radicals, to stop the chemical oxidation reaction. In case of TOC analysis of samples, sodium nitrite was used as quenching agent, which shows similar quenching properties as of methanol.

In all the experiments, oxidant and iron was added at predetermined molar ratios with respect to the contaminant. It is represented as molar ratio of **contaminant: oxidant: iron**. As an example, if one of the degradation experiments has molar ratios 1:10:5, this means that molar ratio of contaminant and oxidant is 1:10 and molar ratio of contaminant and iron is 1:5.

In most of the degradation experiments, initial concentration of 4-chlorophenol was 50 mg/L (0.389 mM). In case of comparative degradation runs of chlorophenols, initial concentration of 0.194 mM was used for all the chlorophenols. The initial concentrations of other contaminants were 5 mg/L (26.5 μM) for 2-chlorobipehnyl and 20 mg/L (156 μM) for naphthalene.

Results:

Activation of oxidants

In our previous studies *[13]*, Fe (II) was found to be an effective catalyst for the activation of PS/PMS for sulfate radical generation. The capability of Fe (III) for activating H_2O_2 is well documented. Hence, the activation of oxidants using Fe (II) and Fe (III) was investigated in an attempt to gain further insights on these transition metal-based catalytic systems. It has also been reported that H_2O_2 can activate persulfate to produce sulfate radicals *[14]. H*ence, this investigation was designed to perform a comparative study of the potentials of three different catalysts Fe (II), Fe (III) and H_2O_2 which activate sulfate radical generating oxidants by mechanisms unique to each catalyst.

1. Fe (II) based activation

A set of experiments, as described in materials and method, were performed to evaluate the effect of oxidant and iron concentration on the degradation of 4-CP, one of the target contaminants chosen for this study. These experiments were performed maintaining a constant oxidant (PMS) and Fe (II) molar ratio (1:1) and changing their relative amount with respect to the contaminant. The oxidant and Fe (II) concentrations were varied from 0.389 mM to 19.44 mM which correspond to 1:1 to 1:50 molar ratio of contaminant and oxidant or Fe (II).
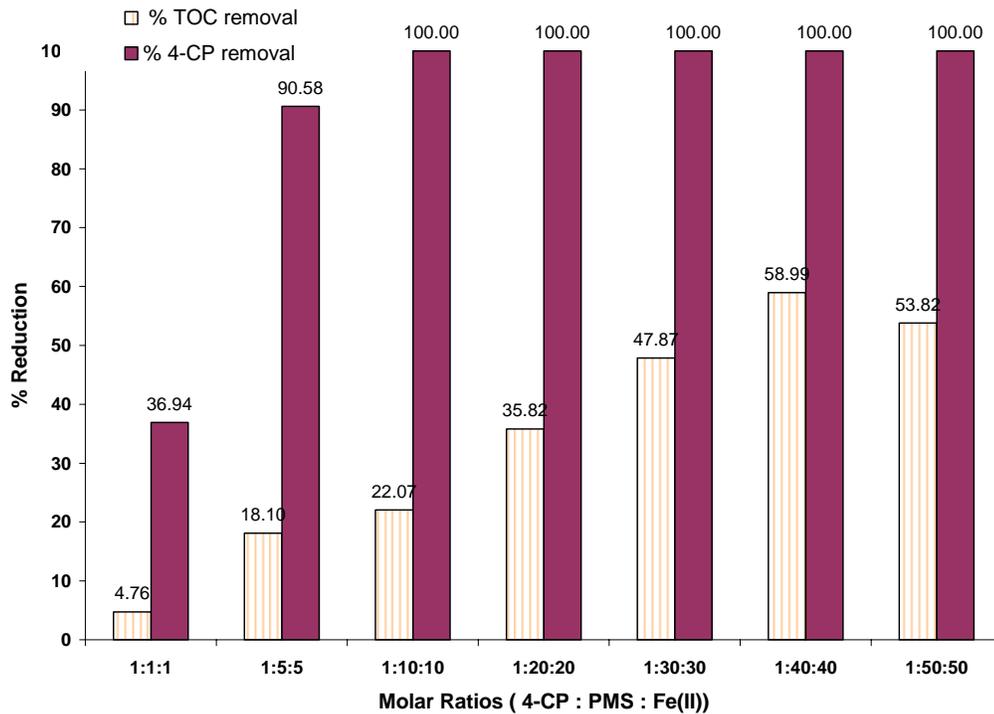
Figure 1: Effect of Fe (II) and PMS amount for 4-CP degradation and TOC removal using Fe(II)-PMS system. $[4\text{-}CP]_0 = 0.389$ mM, $[PMS]_0 = [Fe(II)]_0 = 0.389 - 19.44$ mM

From Figure-1 it can be seen that Fe (II) is very effective in degrading 4-CP by activation of PMS. It was also observed that with increase in concentration of oxidant and Fe (II), increasing compound degradation and TOC removal was observed. In 4 hours, 58% TOC removal was observed when 19.44 mM PMS and Fe (II) were used. It is interesting to note that the TOC removal was not directly proportional to the oxidant and Fe (II) concentrations. At higher concentrations of oxidant and Fe (II) (11.66 mM – 19.44 mM), the extent of TOC removal increases less than proportionally. This might be occurring due to the increased loss of sulfate radicals to undesirable side-reactions at high concentrations of oxidant (PMS) and Fe (II).

2. Fe (III) based activation

Activation by Fe (III) was tested by maintaining a constant oxidant (PS or PMS) and Fe (III) molar ratio (1:1) and changing their relative amounts with respect to the contaminant. In 4 hours, a maximum degradation of 33% was observed indicating that activation of PMS by Fe (III) is less effective than by Fe (II) where 100% removal was observed in all but one case. A similar trend in degradation was observed for activation of PS by Fe (III). PS performed slightly better than PMS for degrading 4-CP when activated by Fe (III) (Figure-2).
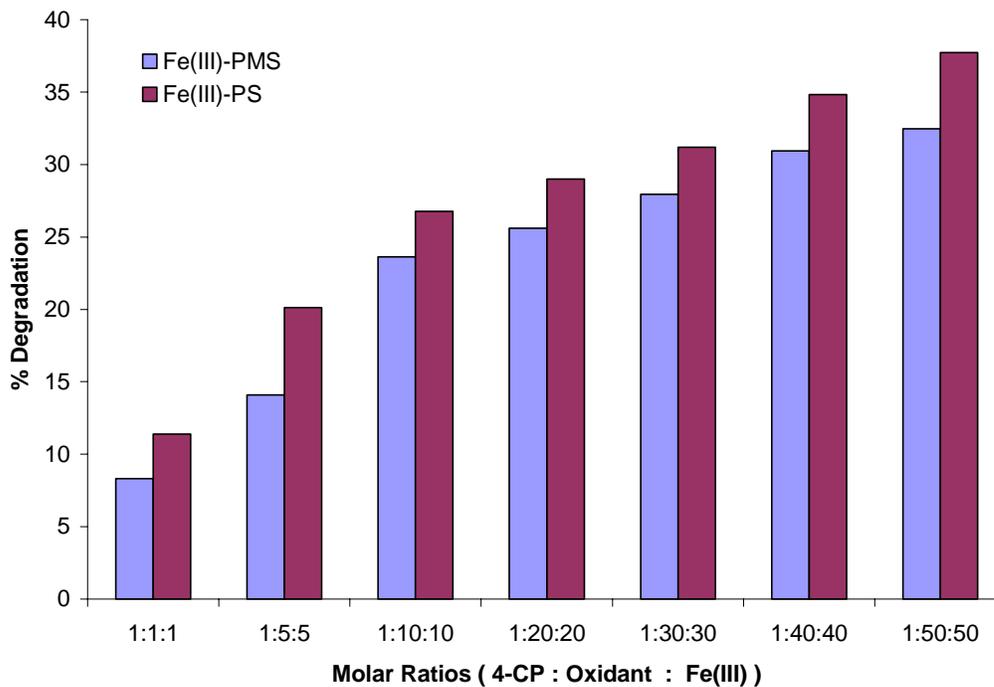
Figure 2: Degradation of 4-CP using Fe (III)-PMS and Fe (III)- PS based catalytic systems. $[4\text{-CP}]_0 = 0.389$ mM, $[Fe(III)]_0 = [PMS]_0 = [PS]_0 = 0.389 - 19.44$ mM. (All molar ratios are based on the initial concentration of the contaminant)

3. Hydrogen peroxide based activation

Based on a previously reported study *[14]*, a feasibility of using H_2O_2 for activating PS and PMS was performed. A control test using only H_2O_2 or persulfate showed no significant loss of contaminant in 4 hours of reaction time. As seen in Figure-3, in H_2O_2 / PMS systems, less than 15 % to 65% degradation of 4-chlorophenol was observed at low (0.39 mM – 3.9 mM) and higher H_2O_2 (19.44 mM) concentrations respectively (Figure-3). Systems with PS yielded 20% more degradation than those with PMS. A higher

amount of hydrogen peroxide and oxidant will be required to achieve degradation of contaminants comparable to levels as seen for Fe (II).
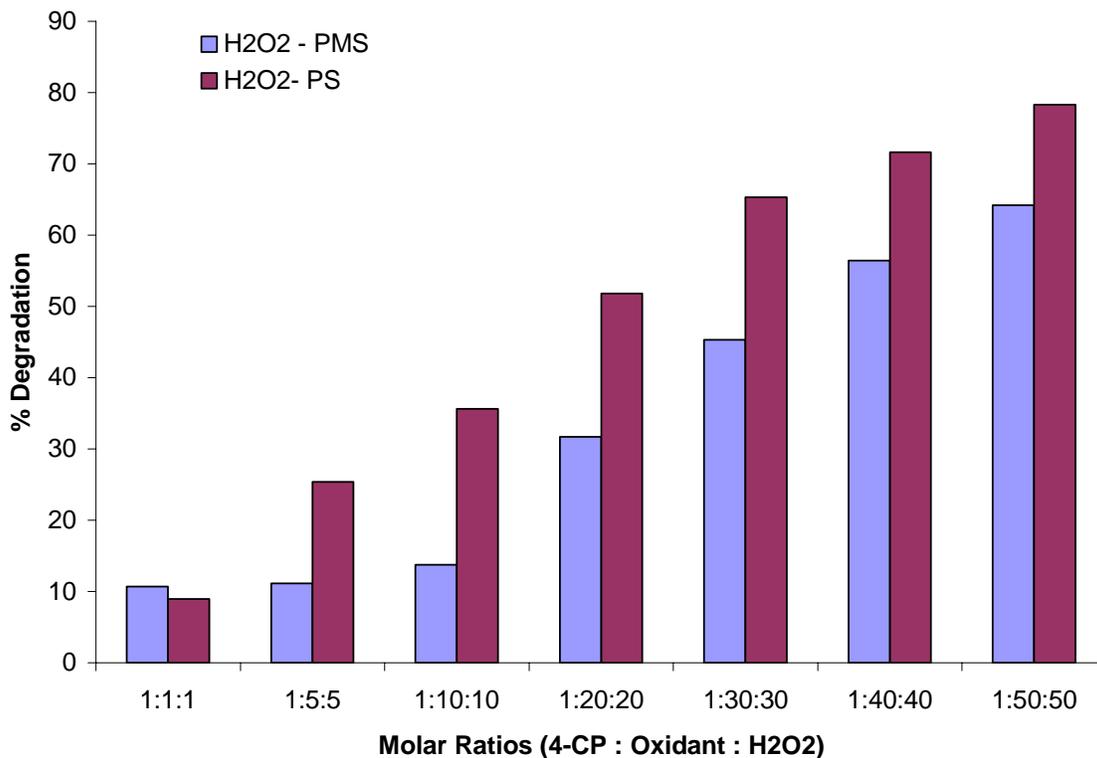
Figure 3: Degradation of 4-CP using H_2O_2 -PMS and H_2O_2- PS based catalytic systems. $[4\text{-}CP]_0 = 0.389$ mM, $[H_2O_2]_0 = [PMS]_0 = [PS]_0 = 0.389 – 19.44$ mM

Effect of molar concentration of Fe (II) and oxidant

It was determined from the previous sets of experiments that Fe (II) is most effective in activating the oxidants (both PS and PMS) for degradation of target contaminants. To further determine the variation in effectiveness of Fe (II) as an activator, the Fe (II): oxidant ratio was progressively changed in the following experiments to gain more insights into the role of each component.

Preliminary experiments were performed using constant oxidant concentration and different Fe (II) concentrations to evaluate the effect of the latter on degradation efficiency. 35% degradation of 4 –CP was observed in a system with PMS: Fe (II) with 5:1 *([Fe (II)]$_0$=0.389 mM)* molar ratio. Increasing the molar ratio of oxidant (PMS) and Fe (II) from 5:1 to 5:5 *([Fe (II)]$_0$=1.94 mM)* led to 95% removal of 4-chlorophenol (Figure – 4). This indicates that a comparable amount of Fe (II) with respect to oxidant is required for achieving higher degradation efficiency.
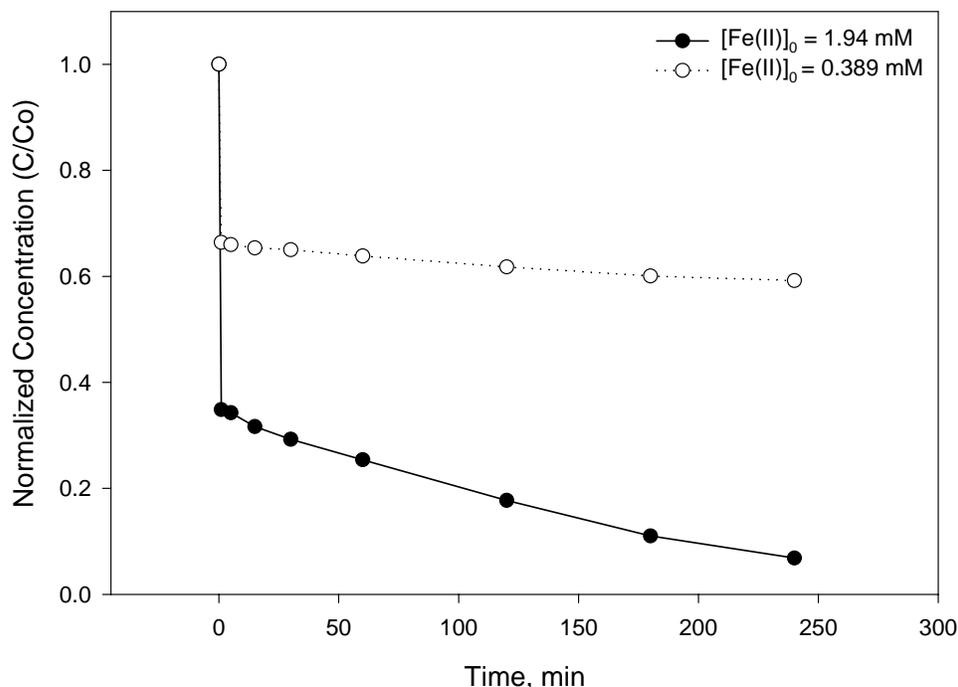
Figure 4: Effect of Fe (II) concentration in degradation of 4-CP using Fe (II)-PMS system. [4-CP]$_0$=0.389 mM, [PMS]$_0$ = 1.94 mM

Experiments were conducted to determine the effect of Fe(II) concentration on degradation efficiency by changing Fe (II) molar concentration from 0.39 mM to 19.44 mM (corresponding to 1:1 to 1:50 molar ratio of 4-CP : Fe(II)) while keeping the oxidant concentration constant (3.9 mM). Increased degradation efficiency and TOC removal was observed when Fe (II) concentration was increased from 0.39 mM to 3.9 mM. Further increase in Fe (II) concentration drastically reduces the degradation efficiency and TOC removal as seen in Figure-5. Radicals generated through the activation of PMS may be getting consumed in the oxidation of Fe (II) to Fe (III) at high Fe (II) concentrations leading to reduced availability of radicals for oxidation of contaminant and TOC removal from the system. These experiments strongly suggest that an optimum amount of Fe (II) is required to effectively activate the oxidant for contaminant removal.

Experiments were conducted to determine the effect of oxidant concentration on degradation efficiency by changing oxidant molar concentration from 0.39 mM to 19.44 mM (corresponding to 1:1 to 1:50 molar ratio of 4-CP: oxidant) while keeping the Fe (II) concentration constant (3.9 mM). Contaminant removal was found to increase with increasing concentration of oxidant in solution (Figure-6). TOC removal was seen on initially increasing the oxidant concentration (from 0.389 to 7.78 mM). However, on increasing oxidant concentration any higher (11.67 mM – 19.44 mM) resulted in a decreasing trend in TOC removal. Based on the results of these experiment, 2:1 molar ratio of PMS and Fe (II) was found to be optimum. The minimum oxidant concentration for complete removal of 4-chlorophenol was 3.9 mM which corresponds to 1:10 molar ratio of 4-CP and oxidant.
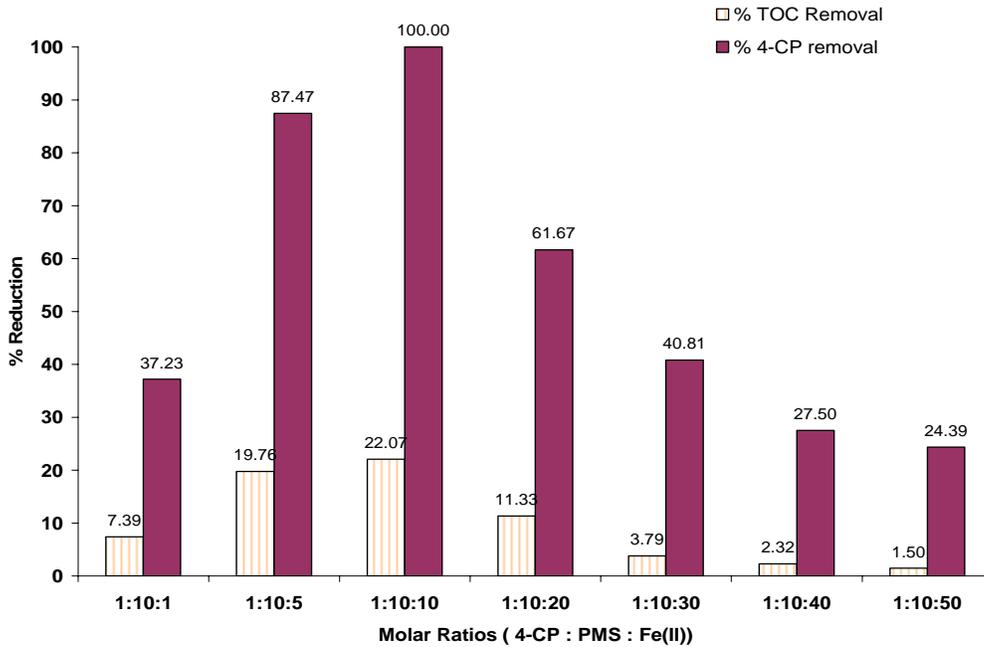
Figure 5: Effect of Fe (II) concentration for 4-CP degradation and TOC removal using Fe (II)-PMS system. $[4-CP]_0 = 0.389$ mM, $[PMS]_0=3.89$ mM, $[Fe (II)]_0= 0.389 – 19.44$ mM
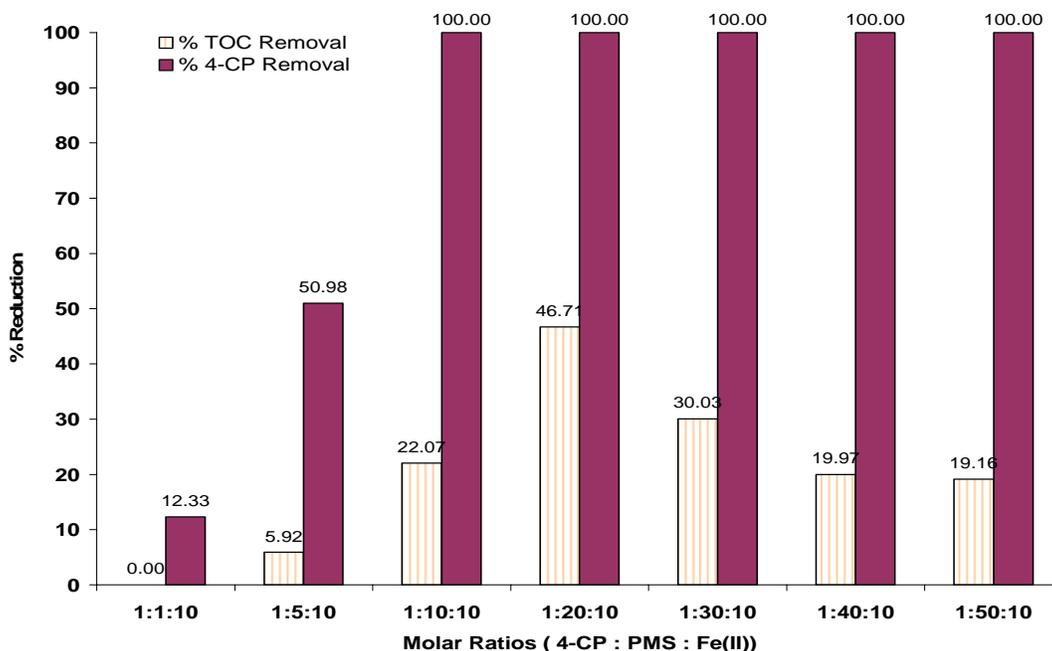
Figure 6: Effect of PMS concentration for 4-CP degradation and TOC removal using Fe (II)-PMS system. $[4\text{-}CP]_0 = 0.389$ mM, $[Fe\ (II)]_0 = 3.89$ mM, $[PMS]_0 = 0.389 - 19.44$ mM

In the process of activation, Fe (II) changes to Fe (III). However, even at moderate concentrations Fe (III) tends to precipitate out as oxides and hydroxides as these have very low solubilities at most of pH values. Iron in precipitated form is effectively removed from the system as it does not take part in any reactions rendering the crucial re-conversion of Fe (III) to Fe (II) impossible. Hence, to maintain the iron in the solution, different approaches were tested.

1. **Effect of phosphate buffer**

The effect of phosphate buffer on contaminant removal efficiencies was studied using 100 mM phosphate buffer in Fe (II)-PMS system. In the presence of phosphate buffer, heavy precipitation accompanied with decrease in degradation efficiency. Removal of catalyst leads to decrease in efficiency of contaminant removal as it can be seen in Figure-7. It can be assumed that practically all the catalyst was removed from the system in less than one hour as no further degradation was observed after that.
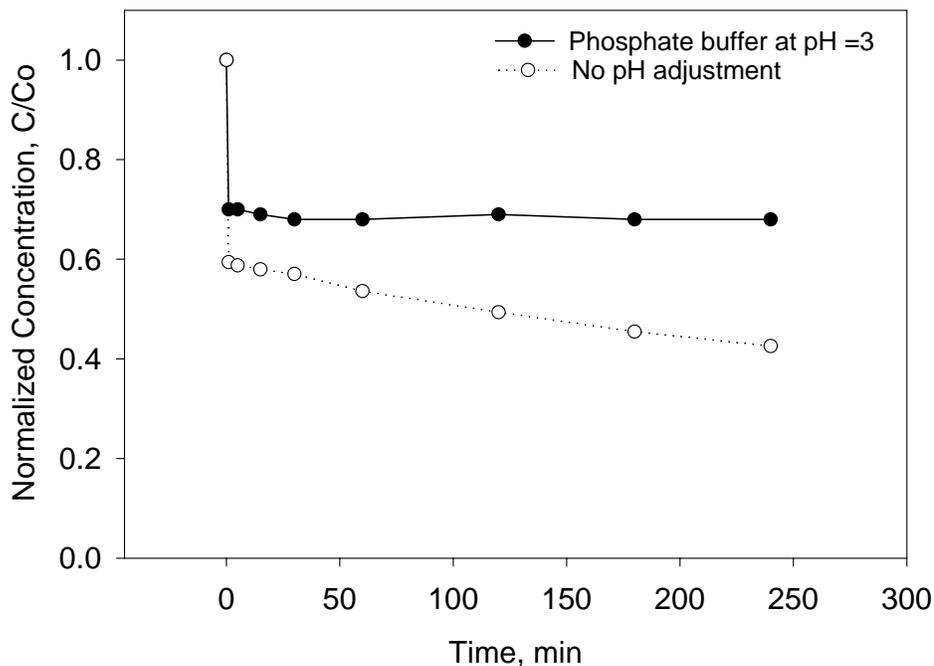
Figure 7: Effect of phosphate buffer on degradation of 4-CP using Fe (II)-PMS system. $[4\text{-CP}]_0 = 0.389$ mM, $[\text{Fe (II)}]_0 = 1.94$ mM, $[\text{PMS}]_0 = [\text{PS}]_0 = 1.94$ mM, buffer concentration = 100 mM

2. **Effect of thiosulfate**

The addition of a reducing agent such as sodium thiosulfate to a persulfate solution can form a persulfate- thiosulfate redox system, which has been reported to promote persulfate oxidation in polymerization processes *[15]*. The activation of persulfate-thiosulfate system by metal ions can be explained by redox cycle dependent upon the valence state of the metal. Liang et al. *[7]* postulated the mechanism of persulfate-thiosulfate activated by a complex anion containing ferrous ion to produce the sulfate free radical.

$$Fe^{3+} + S_2O_3^{2-} \longrightarrow Fe^{2+} + \tfrac{1}{2} S_4O_6^{2-}$$

$$x\, Fe^{2+} + y\, S_2O_3^{2-} \longrightarrow \text{Complex anion}$$

$$S_2O_8^{2-} + \text{Complex anion} \longrightarrow SO_4^{\bullet-} + SO_4^{2-} + Fe^{3+}$$
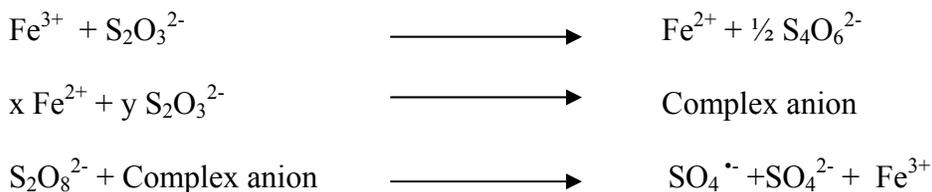
Since the formation of the complex ion which ultimately leads to the generation of sulfate radicals does not involve the oxidant, this activation, though proposed for PS, should theoretically be valid for PMS too. The effect of thiosulfate concentration for

activating both oxidants was studied by changing the molar concentration of thiosulfate from 0.2 mM to 3.9 mM and maintaining constant concentrations of the oxidants and Fe (II).

From Figure-8 it can be seen that increasing the thiosulfate concentration leads to decrease in degradation of 4-chlorophenol. Normally in Fe (II)-PMS system, the solution color changes to orange/brown due to formation of Fe (III). At high thiosulfate concentration, no color change in solution was observed. It seems that presence of thiosulfate prevents the oxidation of Fe (II) to Fe (III) hence indirectly reducing the activation of oxidant and decreasing the degradation efficiency. Similar trend of decrease in efficiency was observed in case of Fe (II)-PS system.
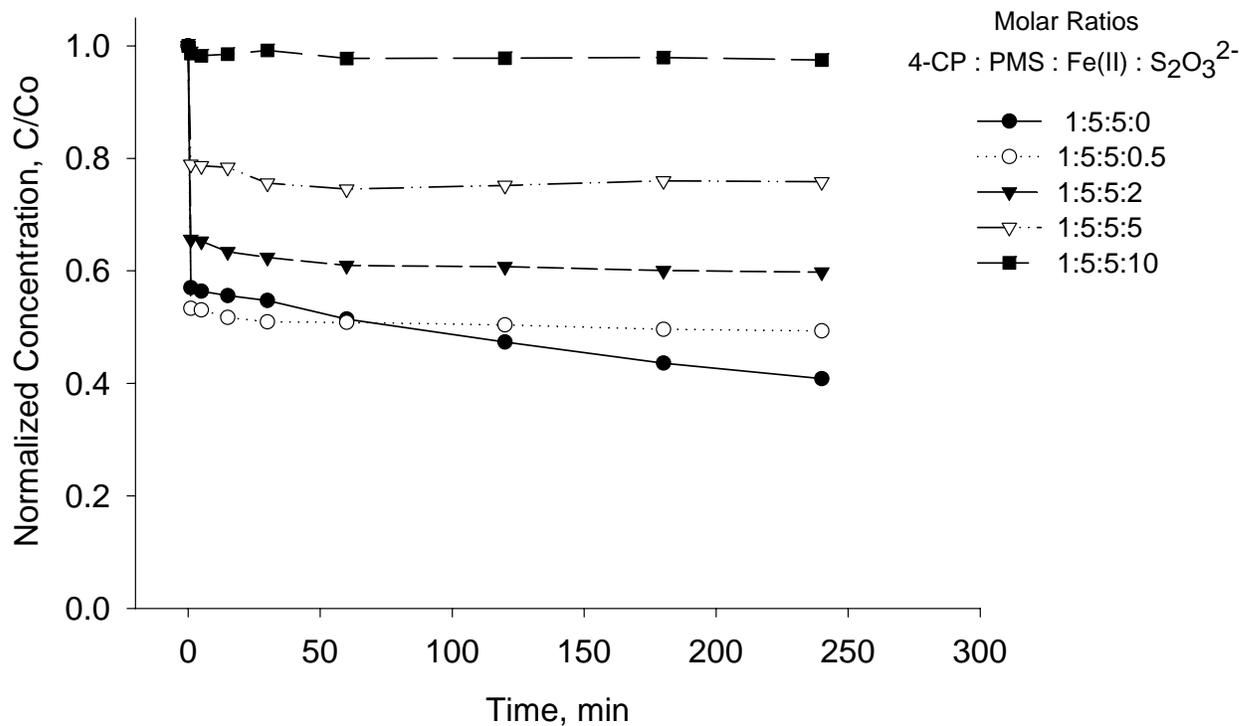
3. Effect of chelating agent

Iron chelating agents have been used in Fenton's reaction to control the rate of reactive hydroxyl radical formation [16]. A complexing agent functions by making coordinate bond(s) with metals and thus maintaining the metal ions in solution. The obstacle of keeping ferrous ion available in solution can be overcome by employing complexing agents in conjugation with Fe (II). Citric acid has been used by many researchers as complexing agent since it is a natural multidentate organic complexing agent which is environmentally friendly and readily biodegradable [17].

- **Fe (II) – Persulfate system**

Citric acid was used in this study to maintain the slow availability of Fe (II) in the solution for activation of oxidant. Five different molar concentrations of citric acid were used to test the effect of citric acid concentration on the degradation of 4-chlorophenol using Fe (II)-PS system. These concentrations were selected such that metal: ligand ratio was in range of 1:0.02 to 1:2.

From Figure-9 it can be seen that increase in degradation of 4-chlorophenol was observed in presence of citric acid. Increasing trend in degradation was observed up to metal: ligand ratio 1:0.2, after which the increase in citric acid concentration led to a decrease in % removal. This happens because when the chelating agent is present in relatively high concentrations, it binds the metal and reduces its availability in solution. A lower amount of chelating agent, even after binding to some of the Fe (II), leaves considerable amount of Fe (II) in solution for the activation reaction.
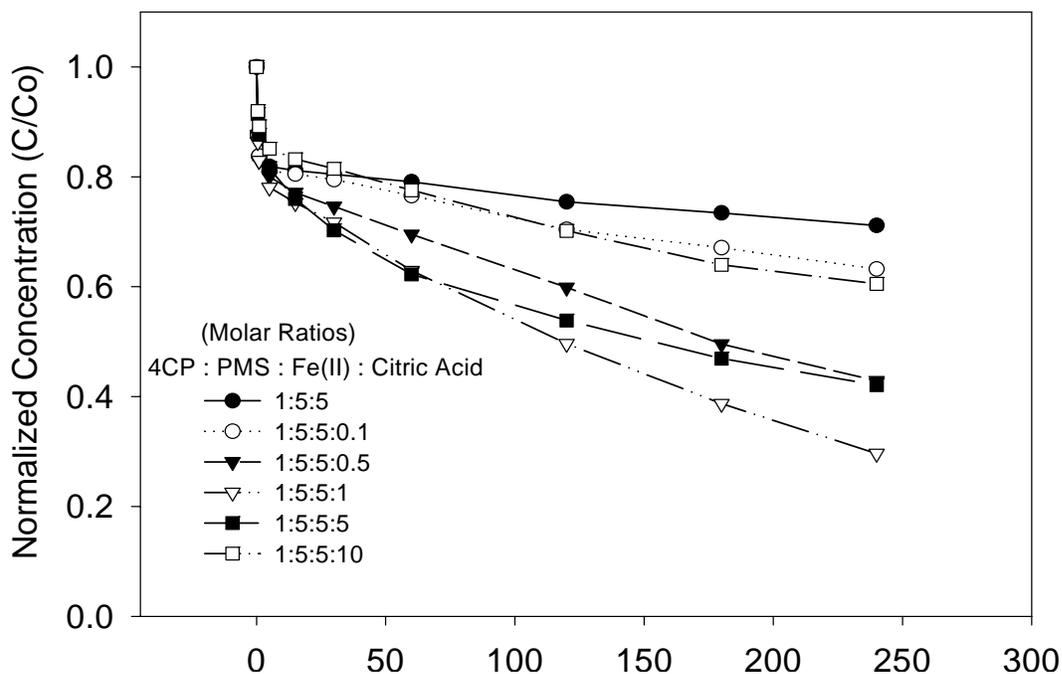
Figure 9: Effect of chelating agent concentration (citric acid) on degradation of 4-CP using Fe (II)-PS system. $[4\text{-CP}]_0 = 0.389$ mM, $[Fe (II)]_0 = 1.94$ mM, $[PS]_0 = 1.94$ mM, $[Citric Acid]_0 = 0.0389 - 3.89$ mM

- **Fe (II) – PMS system**

A different type of degradation pattern was observed when citric acid was used in Fe (II)-PMS system. A significant influence of the order of chemical addition was observed.

In Figure-10, when citric acid was not present, degradation of 4-CP continued after 4 hours. In presence of citric acid, degradation of 4-CP reduced drastically after only one hour. In the Figure-10 it can be seen that presence of citric acid only improved the initial degradation. After 1 minute, the degradation curve starts to flatten rapidly most likely due to binding of citric acid with the available catalyst preventing any further degradation of 4-chlorophenol.
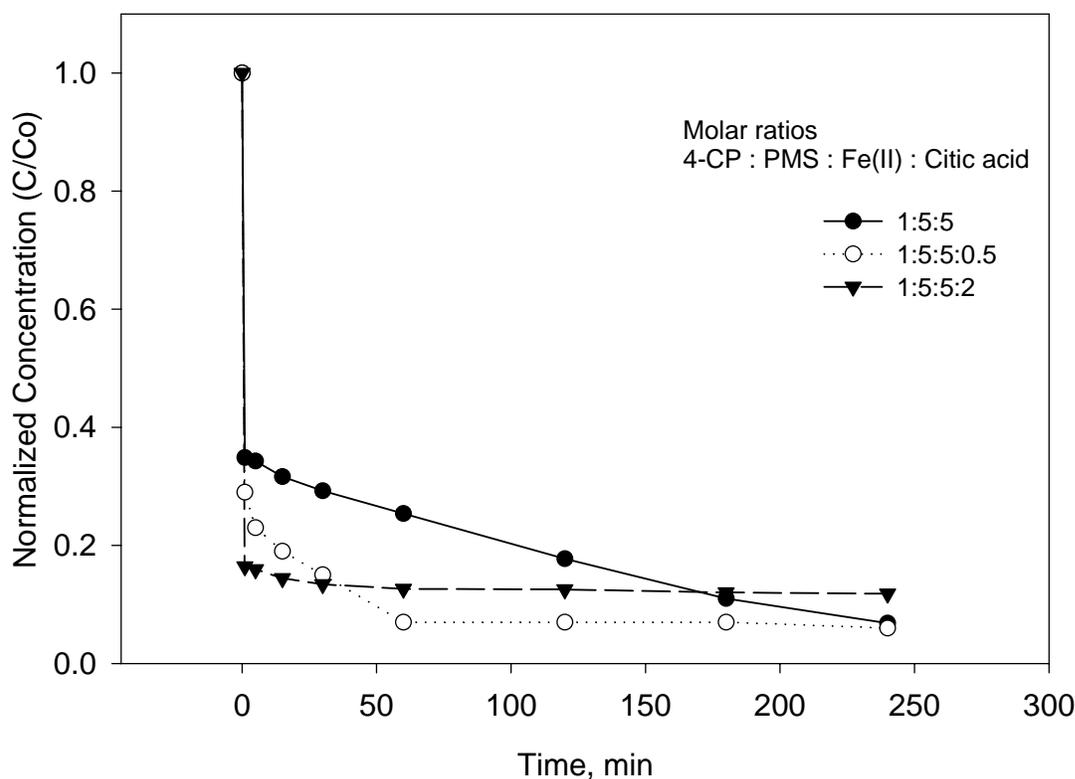
Figure 10: Effect of chelating agent concentration (citric acid) on degradation of 4-CP using Fe (II)-PMS system. $[4\text{-CP}]_0 = 0.389$ mM, $[\text{Fe (II)}]_0 = 1.94$ mM, $[\text{PMS}]_0 = 1.94$ mM, $[\text{Citric Acid}]_0 = 0.194 - 0.778$ mM

Versatility of catalytic systems

The catalytic systems were tested for chlorophenols with increasing degree of chlorination and with other priority contaminants like PCBs and PAHs with widely different structures and properties. This variety of contaminants was selected to test the versatility of the catalytic system under study. The performance of the system was also tested for long term degradation of model organic contaminants and was compared to other established AOTs like Fenton reagent.

a) Long term experiment using various catalytic systems

Owing to their stable nature, persulfate and peroxymonosulfate should be available in the system for long time. Experiments were run for 8 days comparing the three different catalytic oxidation systems under study: Fe (II)-PMS, Fe (II) –PS, and Fe (II)-H_2O_2.

With Fe (II) concentration constant at 1.94 mM in all three units, 50 % TOC removal was observed with Fenton reagent as opposed to 75 % and 93 % in Fe (II)-PMS and Fe (II)-PS systems. Higher Fe (II) concentration led to a decrease in TOC removal in the Fe (II)-PS and Fe (II) –PMS systems whereas no major change in TOC removal ($\sim$ 50%) was observed in the system with Fenton reagent. In both PMS and PS based system highest TOC removal was observed when oxidant and Fe (II) was used in 2:1 molar ratio.

In case of Fe (II)-PS, highest TOC removal per unit oxidant consumption was observed. Close to 60% of oxidant was remaining even after 8 days and 93% TOC removal. This shows the superiority of Fe (II)-PS system over other catalytic systems for long term application.
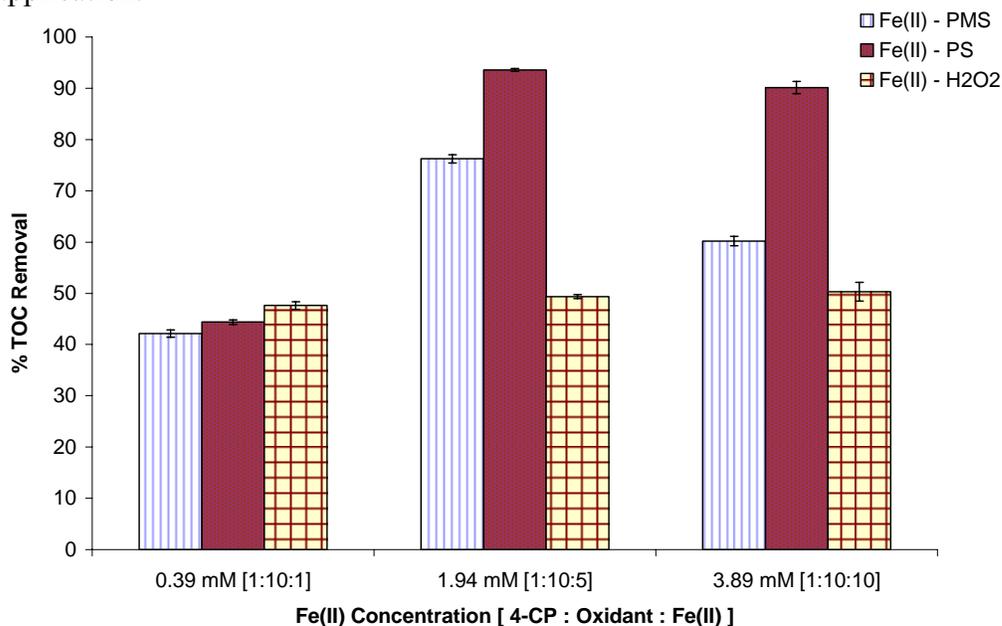
Figure 11: TOC removal efficiency for three different catalytic systems. Experiment duration = 8 days. [4-CP]$_0$ = 0.389 mM, [H_2O_2]$_0$= [PMS]$_0$= [PS]$_0$=0.389 mM, [Fe (II)]$_0$ = 0.389 – 3.89 mM
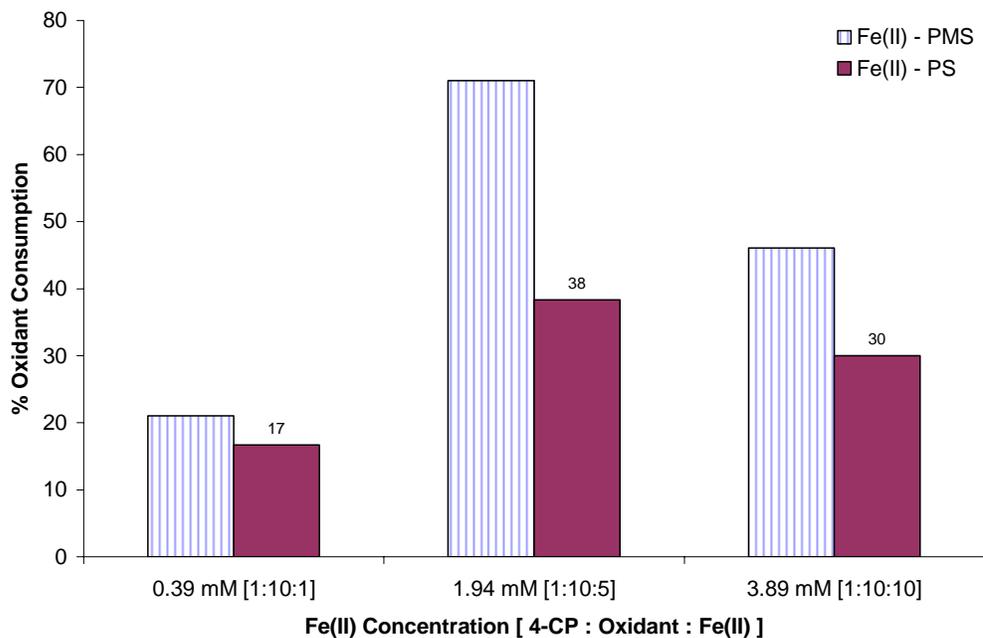
Figure 12: Oxidant consumption for three different catalytic systems. Experiment duration = 8 days. $[4\text{-}CP]_0 = 0.389$ mM, $[H_2O_2]_0 = [PMS]_0 = [PS]_0 = 0.389$ mM, $[Fe(II)]_0 = 0.389 - 3.89$ mM

b) Degradation of series of chlorophenols using Fe (II)/PS, Fe (II)/PMS systems
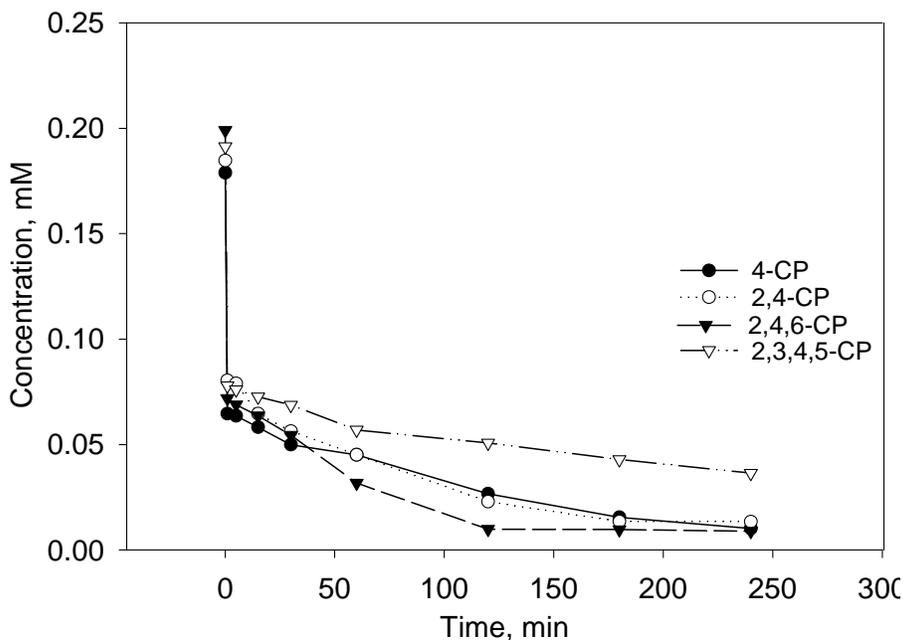
Figure 13: Degradation of series of chlorophenols using Fe (II)-PMS catalytic system. $[4\text{-}CP]_0 = [2,4\text{-}CP]_0 = [2,4,6\text{-}CP]_0 = [2,3,4,5\text{-}CP]_0 = 0.194$ mM, $[PMS]_0 = [Fe(II)]_0 = 0.97$ mM
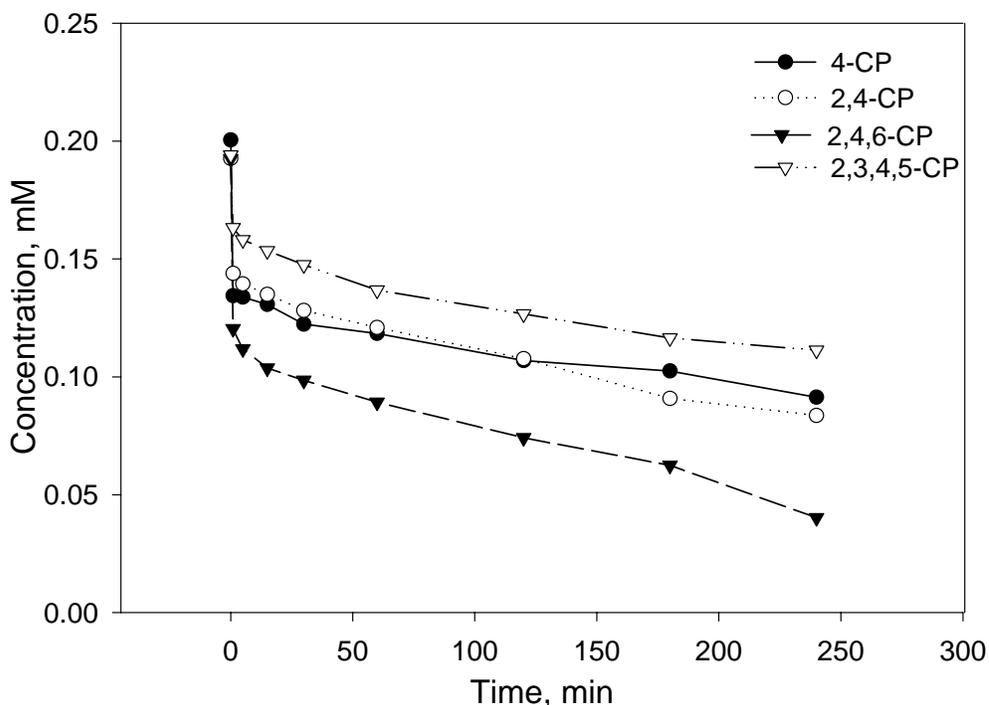
Figure 14: Degradation of series of chlorophenols using Fe(II)-PS catalytic system. [4-CP]$_0$ = [2,4-CP]$_0$ = [2,4,6-CP]$_0$ = [2,3,4,5-CP]$_0$ = 0.194 mM, [PS]$_0$ = [Fe(II)]$_0$ = 1.94 mM

To study to applicability of catalytic process for removal of chlorophenols with varying levels of chlorination, degradation of 4-CP, 2,4-CP, 2,4,6-CP and 2,3,4,5-CP was studied using Fe(II)-PMS and Fe(II)-PS system.

From Figure-13 it can be seen that Fe (II)-PMS catalytic system is capable of degrading variety of chlorophenols with comparable effectiveness. It is hypothesized that the degradation of chlorophenols takes place in two distinct steps, first the Fe II) activates the oxidant and generate radicals which destroy chlorophenols. This is a fast step and takes less then 1 min for completion. Then Fe (III) converts to Fe (II) by redox in a slow step, causing degradation which is markedly slower than that seen initially but continues until all the oxidant is consumed.

Degradation of 4-CP, 2,4-CP , 2,4,6-CP and 2,3,4,5-CP using Fe(II)-PS catalytic system, led to varying degradation profiles. Degradation of 4-CP and 2, 4-CP followed similar trends but 2,4,6-TCP degraded with a much faster rate possibly due the less steric hindrance offered by this compound, which facilitates the radical attack.

Overall, it was demonstrated that both the catalytic systems Fe (II)-PMS and Fe (II)-PS are capable of degrading a variety of chlorophenols and the oxidation system performs very comparably with increase in chlorination in phenol ring.

c) Degradation of PAHs and PCBs using Fe (II)/PS, Fe (II)/PMS systems

Preliminary experiments were performed to test the degradation of model polycyclic aromatic compound, naphthalene using Fe (II)-PMS and Fe (II)-PS system. The results are summarized in Table-1. In case of naphthalene, Fe (II)-PS catalytic system was more effective than Fe (II)-PMS system as seen in Table-1. Increasing trends in degradation efficiencies were observed with increase in oxidant concentration under fixed Fe (II) concentration. These preliminary experiments demonstrate the feasibility of these catalytic processes for degradation of naphthalene (a model PAHs). Further experiments will be performed to optimize the degradation of naphthalene using Fe (II)-PMS and Fe (II) - PS process.

Table 1: Summary of naphthalene removal efficiencies by Fe (II)-PMS and Fe (II)-PS systems

Molar Ratio	% Degradation	
Naphthalene : Oxidant : Fe(II)	PMS	PS
1:1:1	41.34	43.6
1:5:1	62.69	75.8
1:10:1	76.87	83.77
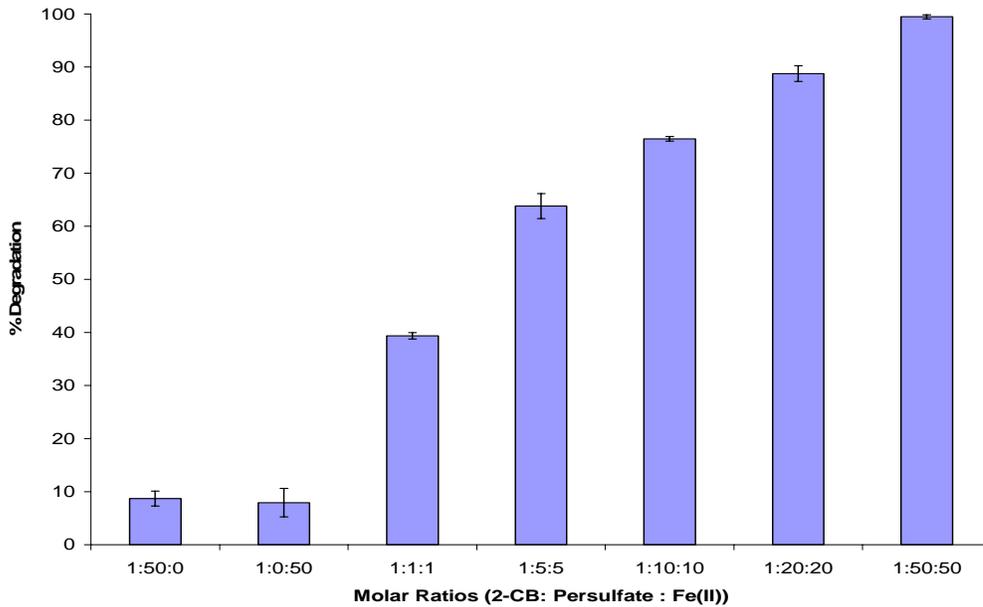
Figure 15: Degradation of 2-chlorobiphenyl using Fe (II)-PS catalytic system. $[2\text{-CB}]_0$ = 26.5 μM $[PS]_0$= $[Fe\,(II)]_0$ = 26.5 μM – 1.325 mM

Near complete degradation of 2-chlorobiphenyl was achieved in 4 hours, when 1.325 mM oxidant and Fe (II) was used (Figure-15). Similar results were obtained in case of Fe (II)-PMS system. More kinetic experiments will be performed in future to optimize the process with respect to catalyst and oxidant.

Conclusion

Three different kinds of catalytic systems were evaluated for degradation of a variety of contaminants. Fe (II)-PMS catalytic system was found to be superior to other systems in the short term experiments. In general, degradation efficiencies of Fe (II) based catalytic systems were better than Fe (III) based catalytic systems. In both catalytic systems with Fe (II), a 2:1 molar ratio of oxidant (PMS and PS): Fe (II) was found to be optimum for degradation of chlorophenols. Citric acid used as a chelating agent led to a significant increase in degradation for Fe (II)-PS systems, the optimum molar ratio of Fe (II): citric acid being 1:0.2. Contrary to previously reported literature *[7, 15]*, the presence of thiosulfate did not help in increasing the degradation. Highest TOC removal was observed in Fe (II)-PS system in case of long term degradation experiments. The stable nature of persulfate and its slow activation by iron makes the Fe (II)-PS system ideal for longer lasting ground water treatment. Fe (II) based catalytic systems was also found effective in degrading a variety of organic contaminants including chlorophenols, naphthalene and 2-chlorobiphenyl.

References

1) Rivas F. J., Beltran F. J., Frades J., Buxeda P., Oxidation of p-Hydroxybenzoic Acid by Fenton's Reagent, *Water Research*, **35**, 2, 387-396, **2001**.

2) Fernandez J., Bandara J., Lopez A., Albers P., Kiwi J., Efficient photo-assisted Fenton catalysis mediated by Fe ions on Nafion membranes active in the abatement of non-biodegradable azo-dye, *Chemical Communications*, 1493-1494, **1998**.

3) Chamarro E., Marco A., Esplugas S., Use of Fenton Reagent to Improve Organic Chemical Biodegradability, *Water Research*, **35**, 4, 1047-1051, **2001**.

4) Chiron S., Fernandez-Alba A., Rodriquez A., Garcia-Calvo E., Pesticide Chemical Oxidation: State of the Art, *Water Research*, **34**, 2, 366-377, **2000**.

5) Herrera-Melian J. A., Tello Rendon E., Dona Rodriguez J. M., Viera Suarez A., Valdes Do Campo C., Perez Pena J., Arana Mesa J., Incidence of Pretreatment by Potassium Permanganate on Hazardous Laboratory Wastes Photodegradability, *Water Research*, **34**, 16, 3967-3976, **2000**.

6) Xu Y., Comparative studies of the $Fe^{3+/2+}$-UV, H_2O_2-UV, TiO_2-UV/vis systems for the decolorization of a textile dye X-3B in water, *Chemosphere*, *43*, 1103-1107, **2001**.

7) Liang, C., Bruell, C. J., Marley, M. C. & Sperry, K. L., Persulfate oxidation for in situ remediation of TCE. I. activated by ferrous ion with and without a persulfate–thiosulfate redox couple. *Chemosphere* **55**(9), 1213-1223, **2004**

8) Huang, K., Zhao, Z., Hoag, G. E., Dahmani, A. & Block, P. A. Degradation of volatile organic compounds with thermally activated persulfate oxidation. *Chemosphere* **61**(4), 551-560, **2005**

9) Meunier, B. Potassium Monopersulfate - just another primary oxidant or a highly versatile oxygen atom donor in metalloporphyrin-mediated oxygenation and oxidation reactions. *New journal of chemistry*, *16* (1-2), 203-211, **1992**

10) Betterton, E. A.; Hoffmann, M. R. Kinetics and mechanism of the oxidation of aqueous hydrogen sulfide by peroxymonosulfate. *Environ. Sci. Technol.*, *24* (12), 1819-1824, **1990**

11) Anipsitakis, G. P.; Dionysiou, D. D. Degradation of Organic Contaminants in Water with Sulfate Radicals Generated by the Conjunction of Peroxymonosulfate with Cobalt. *Environ. Sci. Technol.*, *37* (20), 4790-4797, **2003**

12) Kolthoff, I. M.; Carr, E. M. Volumetric Determination of Persulfate in the Presence of Organic Substances. *Anal. Chem.*, *25* (2), 298-301, **1953**

13) Anipsitakis, G. P.; Dionysiou, D. D. Radical Generation by the Interaction of Transition Metals with Common Oxidants. *Environ. Sci. Technol.*, *38* (13), 3705-3712, **2004**

14) Lunenok-Burmakina, V. A.; Lezina, G. G.; Emel'yanov, V. B., Mechanism of hydrogen peroxide oxidation by peroxydisulphate ions. *Ukrainskii Khimicheskii Zhurnal (Russian Edition)* **54**(12), 1267-9, **1988**

15) Riggs, J.P., Rodrigues, F.,. Polymerization of acrylamide initiated by the persulfate–thiosulfate redox couple. J.Polym. Sci.: Part A-1 **5**, 3167–318, 1967

16) Pignatello, J.J., Day, M.,. Mineralization of methyl parathion insecticide in soil by hydrogen peroxide activated with iron(III)–NTA or –HEIDA complexes. *Hazard. Waste Hazard. Mater.* **13** (2), 237–244, **1996**

17) Francis, A.J., Dodge, C.J.,. Remediation of soils andwastes contaminated with uranium and toxic metals. *Environ. Sci. Technol.* **32** (24), 3993–3998, **1998**

D. D. Dionysiou   - 22 -   Groundwater Treatment
University of Cincinnati   with Iron/Peroxymonosulfate
and Iron/Persulfate Oxidants