Activation of Persulfate and Its Environmental Application

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Abstract: Persulfate is one of the strongest oxidants, and offers some advantages over other oxidants because it is a solid at ambient temperature with the ease of storage and transport, high stability, high aqueous solubility and relatively low cost. These features let it to be a promising choice for wastewater treatment and in situ chemical oxidation of organic pollutants in environmental remediation. Reactions of persulfate with organic pollutants, however, are generally slow at ambient temperature, and activation of persulfate is necessary to accelerate the process. Upon activation, persulfate can produce the highly oxidative species, sulfate free radicals, which can react with a variety of organic pollutants. Persulfate can be activated to generate sulfate free radicals by thermal, chemical and photochemical techniques. Many studies have been conducted to investigate efficiencies of activated persulfate for the chemical degradation of environmental pollutants. This paper gives a review on the activation of persulfate and its environmental application, including the following activation methods: heat, UV light, transitional metal, activated carbon, microwave and integrated techniques.

Keywords: persulfate; activation; pollutant; oxidation; degradation; remediation.

1. Introduction

The advanced oxidation processes (AOPs) have been widely studied for the treatment of drinking water and industrial effluents. Generally, most AOPs are based on the generation of the highly reactive oxidizing species, hydroxyl radicals (Buxton et al., 1988), which could degrade a variety of organic pollutants. The activated persulfate oxidation, in recent years, is an emerging approach for the removal of organic compounds in water and soil (Xu et al., 2010). This technology is based on the production of sulfate radicals (SO₄•⁻), and has attracted great scientific and technological interest in the
area of water treatment and in situ chemical oxidation in the remediation of soil and groundwater (Anipsitakis and Dionysiou, 2004; Anipsitakis et al., 2006; Fang and Lo, 2011).

Persulfate ($S_2O_8^{2-}$) is one of the strongest oxidants and has the higher potential ($E^0 = 2.01$ V) than $H_2O_2$ ($E^0 = 1.76$ V). It offers some advantages over other oxidants as a solid chemical at ambient temperature with the ease of storage and transport, high stability, high aqueous solubility and relatively low cost. These features let it to be a promising choice for cleanup applications. Reactions of persulfate with organic pollutants, however, are generally slow at ambient temperature, and activation of persulfate is necessary to accelerate the process. Some activation methods, such as heat, ultraviolet light, and transition metal activation have been suggested to activate persulfate to generate sulfate free radicals ($SO_4^{•−}$). Comparison with $OH^•$ (1.8–2.7 V), $SO_4^{•−}$ demonstrated higher standard reduction potential (2.5–3.1 V) at neutral pH. At acidic pH, they both demonstrated similar reduction potential. In general, $SO_4^{•−}$ was more selective for oxidizing organic pollutants than hydroxyl radicals (Neta et al., 1988; Buxton et al., 1999; Anipsitakis and Dionysiou, 2004).

Since persulfate oxidation at ambient temperature is usually not effective, it is commonly used with UV light or under high temperature to initiate its radical oxidation mechanisms. Sulfate free radicals, generated from photolytic or heat decomposition of persulfate (Eq. 1), may initiate a series of radical chain reactions (Eqs. 1-11) (Berlin, 1986), where organic compounds (i.e., $M$ in Eq. 2) are usually degraded.

$$\text{heat/}h\gamma$$
$$S_2O_8^{2−} \rightarrow 2SO_4^{•−} \quad (1)$$
$$S_2O_8^{2−} + M \rightarrow 2SO_4^{•−} + M^• \quad (2)$$
$$SO_4^{•−} + H_2O \rightarrow HO^• + HSO_4^{−} \quad (3)$$
$$SO_4^{•−} + M \rightarrow M^• + \text{products} \quad (4)$$
$$HO^• + M \rightarrow M^• + \text{products} \quad (5)$$
$$M^• + S_2O_8^{2−} \rightarrow 2SO_4^{•−} + \text{products} \quad (6)$$
$$SO_4^{•−} + HO^• \rightarrow \text{chain termination} \quad (7)$$
$$SO_4^{•−} + M^• \rightarrow \text{chain termination} \quad (8)$$
$$2SO_4^{•−} \rightarrow \text{chain termination} \quad (9)$$
$$HO^• + M^• \rightarrow \text{chain termination} \quad (10)$$
$$2HO^• \rightarrow \text{chain termination} \quad (11)$$
$$2M^• \rightarrow \text{chain termination} \quad (12)$$

Since other used oxidants, such as hydrogen peroxide and ozone, have relatively short lifetimes in the subsurface as compared with persulfate, persulfate are being studied as a potential alternative oxidant for the remediation of groundwater and soil contaminated with toxic organic contaminants. In addition, persulfate has been widely studied for the treatment of water and wastewater. In this paper, we reviewed the activation methods of persulfate and its environmental application, including heat, UV light, transition metal, activated carbon, microwave, and integrated activation techniques.

2. Activation of Persulfate

2.1. Thermal Activation
Huang et al. (2002) studied the kinetics of heat-assisted persulfate oxidation of methyl tert-butyl ether (MTBE) in aqueous solutions at various pH, temperature, oxidant concentration and ionic strength levels. The MTBE degradation was found to follow a pseudo-first-order decay model. The rate constants of MTBE degradation by persulfate (3 1.5 mM) at pH 7.0 and ionic strength 0.11 M were 0.13 \times 10^{-4}, 0.48 \times 10^{-4}, 2.4 \times 10^{-4} and 5.8 \times 10^{-4} s^{-1} at 20, 30, 40 and 50 °C, respectively. The reaction had the activation energy of 24.5 \pm 1.6 kcal mol^{-1} and was influenced by temperature, oxidant concentration, pH and ionic strength. Increases in the reaction temperature and persulfate concentration might significantly accelerate the MTBE degradation. However, increasing both pH and ionic strength would decrease the reaction rate. Several reaction intermediates were identified, including tert-butyl formate, tert-butyl alcohol, acetone and methyl acetate. These intermediate compounds were also degraded by persulfate. Additionally, MTBE degradation by persulfate in a groundwater was much slower than in phosphate-buffer solutions, most likely due to the presence of bicarbonate ions (free radical scavengers) in the groundwater. Subsequently, Huang et al. (2005) investigated the extent and treatability of the degradation of 59 volatile organic compounds (VOCs) with thermally activated persulfate process. The results indicated that persulfate oxidation was effective in degrading many VOCs including chlorinated ethenes (CEs), BTEXs and trichloroethanes. Most of the targeted VOCs were rapidly degraded under the experimental conditions while some showed persistence to the persulfate oxidation. Compounds with "C=C" bonds or with benzene rings bonded to reactive functional groups were readily degraded. Saturated hydrocarbons and halogenated alkanes were much more stable and difficult to degrade. For those highly persulfate-degradable VOCs, degradation was well fitted to a pseudo first-order decay model. The degradation rates increased with increasing reaction temperature and oxidant concentration.

Liang et al. (2003) found that trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA) were readily oxidized at 40, 50 and 60 °C as a result of thermally activated persulfate oxidation while only limited TCE degradation and no TCA degradation was observed at 20 °C. In aqueous systems, activation energies for the TCE and TCA oxidation at an oxidant/contaminant molar ratio of 10/1 were 97.74 \pm 3.04 KJ mol^{-1} and 163.86 \pm 1.38 KJ mol^{-1} at pH 6 and an ionic strength of 0.1, respectively. Aqueous system experiments revealed that the oxidation reactions proceeded more rapidly at increased persulfate/contaminant molar ratios. In soil slurries, the organic carbon \( f_{oc} \) exhibited significant competition for sulfate free radicals produced. It was anticipated that higher temperatures, longer treatment times, and higher dosages of persulfate were required for the effective treatment of target contaminants in soil systems than in aqueous systems. Furthermore, the kinetics of dissolved TCE oxidation by thermally activated persulfate was investigated in a phosphate-buffered solution (Liang and Bruell, 2008). The results indicated that the degradation rate of TCE by persulfate could be described by the kinetic rate equation \(-d[TCE]/dt = 5.59 \times 10^{-4} \times [TCE]^{0.8} \times [S_{2}O_{8}^{2-}]^{0.2} \times M^{-1} \times min^{-1}\) within the limits of the experimental conditions (i.e., 40 °C, ionic strength 0.1, pH 7, TCE 0.14~0.52 mM, and \( S_{2}O_{8}^{2-} \) 13.5~43.7 mM). This equation indicated that the thermally activated persulfate oxidation of TCE was pseudo zero order with respect to TCE (and therefore independent of the initial TCE concentration) and fractional order with respect to persulfate. This result might serve as a starting point for modeling of the TCE/persulfate system. In another study, the kinetics and products of chlorinated ethene oxidation with heat-activated persulfate were determined (Waldemer et al., 2007). The kinetics
of chlorinated ethene disappearance were pseudo-first-order, and the apparent activation energies for tetrachloroethene (PCE), TCE, cis-1,2-dichloroethene (cis-DCE) and trans-1,2-dichloroethene (trans-DCE) were 101 ± 4, 108 ± 3, 144 ± 5 and 141 ± 2, respectively. Some chlorinated byproducts were observed, but most of the parent material was completely dechlorinated. In addition, the thermally activated persulfate degradation of a recalcitrant pollutant dichlorobenzene was studied in an aqueous medium and in soil slurry (10% total solids) (Bougie and Dube, 2007). In an aqueous medium, a complete degradation of dichlorobenzene was observed at 50 and 60 °C for a reaction time of 6 h. In soil slurry, a degradation of 90% and 100% was observed after 6 h at 50 and 60 °C, respectively. At 40 °C, the degradation was 64% in an aqueous medium and 26% in soil slurry. In both media, the activation energy of reaction was 115 and 153 kJ mol⁻¹, respectively. Thus, it was more efficient to increase the activation temperature in soil slurry than in an aqueous medium.

The effectiveness of persulfate oxidation for the destruction of tetrachlorobiphenyl in subsurface soils was evaluated (Yukselen-Aksoy et al., 2010). Kaolin and glacial till soils were selected as representative low permeability soils. High temperature and high pH were used in order to maximize PCB destruction. In addition, the effects of oxidant dose and reaction time were investigated. The optimal dose for persulfate was 30% for the maximum oxidation. The persulfate activation with temperature of 45 °C was superior to persulfate activation with high pH (pH 12), where higher PCB degradations were observed for kaolin and glacial till soils. PCB destruction increased with reaction time, where the maximum degradation was achieved after 7 days. The highest PCB destruction was achieved with thermal activation at 45 °C using a dosage of 30% persulfate at pH 12 for kaolin and glacial till soils after 7 days. In another study, batch reactor experiments were performed to determine the effects of solids on the oxidation of PCE by sodium persulfate in aqueous solution (Costanza et al., 2010). Repeated doses of sodium persulfate, undertaken to overcome the inherent solids oxidant demand, improved the rate and extent of PCE oxidation in reactors containing reference solids; however, no improvement was observed in reactors containing field soils. Additionally, no improvements in PCE oxidation were observed after pretreating Great Lakes and Appling soils with 15 g kg⁻¹ of sodium persulfate or 30% hydrogen peroxide to remove oxidizable fractions, or acetic acid to remove the carbonate fraction. Based on these results, in situ treatment of Great Lakes and Appling soils with heat-activated persulfate was not anticipated to result in substantial PCE oxidation, while in situ treatment of Fort Lewis soils was anticipated to result in PCE oxidation. This work demonstrated the need to perform soil-specific contaminant treatability tests rather than soil oxidant demand tests when determining oxidant dosage requirements. In addition, the kinetics of heat-facilitated persulfate oxidation of p-chloroaniline (PCA) in aqueous solutions was measured at five different temperature conditions and at four different oxidant concentrations (Zhang et al., 2011). The PCA degradation followed a pseudo-first-order decay model when the persulfate was excessive. The pseudo-first-order rate constants of PCA degradation by persulfate (50 mmol L⁻¹) at pH 7.0 are 0.12 x 10⁻⁴, 0.28 x 10⁻⁴, 0.43 x 10⁻⁴, 0.83 x 10⁻⁴, 1.32 x 10⁻⁴ s⁻¹ at 10, 20, 30, 40 and 50 °C, respectively. Under the above reaction conditions, the activation energy of reaction was 49.97 kJ mol⁻¹. The observed rate was a function of temperature and oxidant concentration. The raising temperature and increasing persulfate concentration could significantly accelerate the PCA degradation.
Recently, thermally activated persulfate (PS) to stimulate the oxidation of 1,1,1-trichloroethane (TCA) in groundwater remediation was investigated (Gu et al., 2011). The effects of various factors including temperature, initial TCA concentration, PS/TCA molar ratio, solution pH, and common constituents in groundwater such as Cl\(^-\), HCO\(_3\)^-, SO\(_4\)^{2-}, and NO\(_3\)^- anions and humic acid (HA) were evaluated. The experimental results showed that TCA could be completely oxidized in 2 h at 50 °C with a PS/TCA molar ratio of 100/1, indicating the effectiveness of thermally activated PS oxidation for TCA removal. The TCA oxidation was fitted to a pseudo-first-order kinetic model, and the rate was found to increase with the increased temperature and PS/TCA molar ratio, but to decrease with increased initial TCA concentration. In addition, acidic conditions were favorable to TCA removal and enhancement of the initial solution pH value (from pH 3 to 11) would decrease the TCA degradation rate. Anions Cl\(^-\) and HCO\(_3\)^- had negative effects on TCA removal, whereas the effects of both SO\(_4\)^{2-} and NO\(_3\)^- were negligible. With 5~10 mg L\(^{-1}\) of HA in solution, an inhibitive effect was observed, indicating that dissolved organic matter consumed some of the oxidant. However, the anticipated effectiveness in groundwater from a real contaminated site was not achieved because of the complex solution matrix. On the other hand, the TCA degradation mechanism derived from GC/MS analytical results confirmed formic acid, dichloromethane, and trichloromethane as the primary intermediates, and therefore, two TCA decomposition pathways were proposed. The results indicated that thermally activated PS oxidation was a highly promising technique for TCA-contaminated groundwater remediation, but more complex constituents in groundwater should be carefully considered for its practical application.

2.2. Photochemical Activation

Huang and Huang (2009) utilized the two processes in conjunction for the complete degradation of bisphenol A (BPA). A two-stage oxidation process (UV-\(\text{Na}_2\text{S}_2\text{O}_8/\text{H}_2\text{O}_2/\text{Fe}^{(II,III)}\)) was applied to mineralize BPA at neutral pH. This technique took advantage of the high oxidation potential of sulfate free radicals and use persulfate as the 1st-stage oxidant to oxidize BPA to less complex compounds (stoichiometric ratio: \([\text{S}_2\text{O}_8^{2-}]_0/[\text{BPA}]_0 = 1\)). Afterwards, the traditional photo-Fenton process was used to mineralize those compounds to CO\(_2\). During the 2nd-stage reaction, other oxidants (\(\text{H}_2\text{O}_2\) and iron alone) were also employed to observe the extent of enhancement of photo-Fenton. Further, qualitative identification of both hydroxyl and sulfate radicals was performed to evaluate their dominance under different conditions. The BPA degradation in this UV/persulfate process formulated a pseudo-first order kinetic model well, with a rate constant of approximately 0.038 min\(^{-1}\) (25 °C), 0.057 min\(^{-1}\) (35 °C), and 0.087 min\(^{-1}\) (50 °C), respectively. The much lower activation energy (\(E = 26\) kJ mol\(^{-1}\)) was further calculated to clarify that the thermal-effect of an illuminated system differed from single heat-assisted systems. The final total organic carbon (TOC) removals of BPA by the use of such two-stage oxidation processes were 25~34%, 25%, and 87~91% for additional Fe(II,III) activation, \(\text{H}_2\text{O}_2\) promotion, and Fe(II,III)/\(\text{H}_2\text{O}_2\) promotions, respectively. In addition, Salari et al. (2009) investigated the photooxidative decolorization of C.I. Basic Yellow 2 (BY2) using UV radiation in the presence of persulfate in a rectangular photoreactor. \(\text{S}_2\text{O}_8^{2-}\) and UV-light showed negligible effect when they were used independently. The removal efficiency of BY2 was sensitive to
the operational parameters such as initial concentrations of S$_2$O$_8^{2−}$ and BY2, light intensity, flow rate and pH. The conversion ratios of BY2 at the volumetric flow rates of 330, 500 and 650 mL min$^{-1}$ were 84%, 79% and 51% in 30 min, respectively. The results showed that light intensity was a beneficial parameter for dye removal. In the presence of S$_2$O$_8^{2−}$, the photooxidation quantum yield obtained was higher than direct photolysis quantum yield, suggesting that photodecay of BY2 was dominated by photooxidation. The results also showed that applying a desired persulfate concentration could reduce the electrical energy.

Three distinctive phases of butylated hydroxyanisole (BHA) reactivity toward UV/S$_2$O$_8^{2−}$ at acidic, neutral, and basic pH range were examined (Lau et al., 2007), where 80-100% mineralization has been observed within an hour of irradiation under 254 nm. A reduction in solution pH during the reaction was observed mainly due to the complete conversion of S$_2$O$_8^{2−}$ to sulfate ion together with proton generation. Seven measurable intermediates were found via an oxidation and dimerization process at all tested pH levels. The BHA decay mechanisms were quite different in acidic condition and at other pH levels. There were three unique intermediates that were only detectable at pH 3 via two additional pathways. This was due to the generation of weaker oxidants or radicals which resulted in a slower degradation of the BHA, and therefore, the accumulation of these intermediates to detectable levels. The rate of BHA decay generally increased from low to high pH levels; however, the corresponding mineralization at higher pH was retarded due to the futile process of recombining radicals and involvement of intermediates. Therefore, neutral pH was suggested to be the optimum condition in terms of mineralization and moderate efficiency in removal of BHA. In addition, Criquet et al. (2009) studied the photolysis of S$_2$O$_8^{2−}$ for the removal of acetic acid in aqueous solution and compared with the H$_2$O$_2$/UV system. The SO$_4^{−}$ radicals generated from the UV irradiation of S$_2$O$_8^{2−}$ yielded a greater mineralization of acetic acid than the 'OH radicals. Acetic acid was oxidized by SO$_4^{−}$ radicals without significant formation of intermediate by-products. Increasing system pH resulted in the formation of 'OH radicals from SO$_4^{−}$ radicals. The maximum acetic acid degradation occurred at pH 5. The results suggested that above this pH, competitive reactions with the carbon mineralized inhibited the reaction of the solute with SO$_4^{−}$ and also 'OH radicals. Scavenging effects of two naturally occurring ions were tested; in contrast to HCO$_3^{−}$ ions, the presence of Cl$^{−}$ ions enhanced the efficiency of the S$_2$O$_8^{2−}$/UV process towards the removal of acetate. It was attributed to the formation of the Cl$^{−}$/radical and its great reactivity towards acetate.

Recently, Lin et al. (2011) investigated both the feasibility of using a UV/SPS (sodium persulfate) process to treat phenol in aqueous phase and the effect of pH on degradation efficiency and TOC removal. The results revealed that a high initial persulfate concentration (i.e., 84 mM) and a lower initial phenol concentration (i.e., 0.5 mM) resulted in rapid and complete phenol degradation within 20 min. For all three pHs evaluated (i.e., 3, 7 and 11), complete phenol degradation was also achieved after 30 min of treatment by UV/SPS oxidation processes (i.e. under an SPS/phenol molar ratio of 84/0.5) with pseudo-first-order rate constants $k_{obs,phenol}$ of 0.14-0.16 min$^{-1}$ (average half-life $t_{1/2}$ = 4.5 min). The UV-Vis spectrum scanning of the aqueous solution during treatment identified the development of brown color in the wavelength range of 400-460 nm. The colored intermediate compounds formed were suspiciously similar to those observed during Fenton treatment. However, a more aggressive oxidation at pH 11 showed a rapid and more complete removal of TOC in aqueous
phase. Therefore, it was recommended that UV photolytic persulfate activation under basic pH was a preferred condition for the treatment of phenol.

2.3. Transition Metal Activation

2.3.1. Ferrous Ion or Chelated Ferrous Ion Activation

Liang et al. (2004a) used ferrous ion Fe\(^{2+}\) to activate persulfate to produce SO\(_4^{2-}\) for the degradation of TCE. The experiments under various molar ratios of S\(_2\)O\(_8^{2-}\)/Fe\(^{2+}\)/TCE in an aqueous system indicated that partial TCE degradation occurred almost instantaneously and then the reaction stalled. Either destruction of SO\(_4^{2-}\) in the presence of excess Fe\(^{2+}\) or the rapid conversion of all Fe\(^{2+}\) to Fe\(^{3+}\) limited the ultimate oxidizing capability of the system. Sequential addition of Fe\(^{2+}\) in small increments resulted in an increased removal efficiency of TCE. Therefore, Fe\(^{2+}\) played an important role in generating SO\(_4^{2-}\). An observation of oxidation-reduction potential (ORP) variations revealed that the addition of sodium thiosulfate (Na\(_2\)S\(_2\)O\(_3\)) to the ferrous ion activated persulfate system could significantly decrease the strong oxidizing conditions. It was hypothesized that the thiosulfate induced reducing conditions might convert Fe\(^{3+}\) to a lower valence state Fe\(^{2+}\), making the Fe\(^{2+}\) available to activate persulfate decomposition. The sequential addition of thiosulfate after the initial stalling of ferrous ion activated persulfate oxidation of TCE, resulted in an improvement in TCE removal. The ferrous ion activated persulfate-thiosulfate redox couple resulted in fairly complete TCE degradation in aqueous systems in a short time frame. In soil slurry systems, TCE degradation was slower in comparison to aqueous systems. Subsequently, they used a chelating agent (i.e., citric acid) in attempt to manipulate the quantity of ferrous ion in solution to investigate oxidation of dissolved trichloroethylene (TCE) in aqueous and soil slurry systems by activated persulfate (Liang et al., 2004b). In an aqueous system, a chelate/Fe\(^{2+}\) molar ratio of 1/5 (e.g., S\(_2\)O\(_8^{2-}\)/chelate/Fe\(^{2+}\)/TCE ratio of 20/2/10/1) was the lowest acceptable ratio to maintain sufficient quantities of Fe\(^{2+}\) activator in solution resulting in nearly complete TCE destruction after only 20 min. The availability of Fe\(^{2+}\) was controlled by adjusting the molar ratio of chelate/Fe\(^{2+}\). In general, high levels of chelated ferrous ion concentrations resulted in faster TCE degradation and more persulfate decomposition. However, if initial ferrous ion contents were relatively low, sufficient quantities of chelate must be provided to ensure the chelation of a greater percentage of the limited ferrous ion present. Citric acid chelated ferrous ion was effective for TCE degradation within soil slurries but required longer reaction times. Additionally, the use of citric acid without the addition of supplemental Fe\(^{2+}\) in soil slurries, where the citric acid apparently extracted native metals from the soil, appeared to be somewhat effective at enhancing persulfate oxidation of TCE over extended reaction times. A comparison of different chelating agents revealed that citric acid was the most effective. Liang et al. (2007) also found when persulfate was activated by the continuous addition of Fe\(^{2+}\) in a system where TCE and PCE were present as dense nonaqueous phase liquids (DNAPLs), the presence of hydroxypropyl-β-cyclodextrins (HP-β-CD) increased the dissolved contaminant concentrations and the contaminants were attacked preferentially, most likely because of a controlled and slower rate of generation of the SO\(_4^{2-}\). Liang et al. (2008) furthermore presented a simulated persulfate oxidation of TCE in porous media (glass beads and a sandy soil). In the absence of TCE in the column, the persulfate flushing exhibited a longer
residence time and revealed a moderate persulfate interaction with soils. In TCE treatment experiments, the results indicated that the water or persulfate solution would push dissolved TCE from the column. Therefore, the effluent TCE concentration gradually increased to a maximum when about one pore volume was replaced with the flushing solution in the column. The presence of Fe$^{2+}$ within the column caused a quick drop in effluent TCE concentration and more TCE degradation was observed. When a TCE solution was flushing through the soil column, breakthrough of TCE concentration in the effluent was relatively slow. In contrast, when the soil column was flushed with a mixed solution of persulfate and TCE, persulfate appeared to preferentially oxidize soil oxidizable matter rather than TCE during transport. Hence, persulfate oxidation of soil organics might reduce the interaction between TCE and soil (e.g., adsorption) and facilitate the transport of TCE through soil columns resulting in faster breakthrough. Additionally, Liang et al. (2009) investigated the applicability of ethylenediaminetetra-acetic acid (EDTA) chelated Fe$^{3+}$ in activating persulfate for the destruction of TCE in aqueous phase under pH 3, 7 & 10. Fe$^{3+}$ and EDTA alone did not appreciably degrade persulfate. The presence of TCE in the EDTA/Fe$^{3+}$ activated persulfate system could induce faster persulfate and EDTA degradation due to iron recycling to activate persulfate under a higher pH condition. Increasing the pH led to the increase in pseudo first order rate constants for TCE, S$_2$O$_8^{2-}$ and EDTA degradations, and Cl$^-$ generation. Accordingly, the experiments at pH 10 with different EDTA/Fe$^{3+}$ molar ratios indicated that a 1/1 ratio resulted in a remarkably higher degradation rate at the early stage of reaction as compared with the results by other ratios. Higher persulfate dosage under the EDTA/Fe$^{3+}$ molar ratio of 1/1 resulted in greater TCE degradation rates. In addition, the increase in persulfate concentration might also lead to an increase in the rate of persulfate consumption.

Killian et al. (2007) investigated the feasibility of activated persulfate for the destruction of BTEX and PAHs in soil contaminated by manufactured gas plants. The sulfate free radicals were generated by either the sequential addition of iron (II) solutions or by a single addition of a citric acid chelated iron (II) solution. The sequentially added iron destroyed 86% of the total BTEX concentration and 56% of the total PAHs concentration in the soil. The citric acid chelated iron destroyed 95% of the total BTEX concentration and 85% of the total PAHs concentration. A second dose of persulfate and citric acid chelated iron (II) resulted in the destruction of 99% of the total BTEX concentration and 92% of the total PAHs concentration. In both the sequential and chelated iron studies, the lower molecular weight BTEX compounds were oxidized to a greater extent than the higher molecular weight BTEX compounds, whereas the oxidation of PAH compounds showed no preference to molecular weight. In another study, Cao et al. (2008) found the rate of lindane oxidation was proportional to the concentration of persulfate, and when the ferrous iron to persulfate concentration ratio was less than 1, the reaction rate was also proportional to the ferrous iron concentration. The reaction rates were substantially higher when the solution pH was less than 1.5 or greater than 11. The final products were chloride and carbon dioxide, suggesting complete lindane oxidation. The reaction half-life of oxidation of 0.0172 mM lindane with 4.2 mM persulfate and 0.108 mM ferrous iron was approximately 27.18 h. Compared with the classical Fenton's reaction, persulfate has relatively longer lifetime in water. In addition, Liang et al. (2008b) focused on the evaluation of activated persulfate (PS) for the degradation of benzene, toluene, ethylbenzene and xylene. The results indicated that BTEX were effectively oxidized by PS in aqueous and soil slurry systems at 20 °C. The degradation
rates of BTEX increased with the increased persulfate concentration. For two PS/BTEX molar ratios of 20/1 and 100/1, the observed aqueous phase BTEX degradation half-lives ranged from 3.0 to 23.1 days and 1.5 to 20.3 days in aqueous and soil slurry systems, respectively. In the interest of accelerating contaminant degradation, Fe and chelated Fe\(^{2+}\) activated persulfate oxidations were investigated. For all iron activation experiments, BTEX and persulfate degradations occurred instantaneously and resulted in partial BTEX removals. It was speculated that the incomplete degradation reaction might be due to the cannibalization of SO\(_4^{−}\) in the presence of excess Fe\(^{2+}\). Furthermore, the effects of various chelating agents, including hydroxylpropyl-β-cyclodextrin (HPCD), ethylenediaminetetraacetic acid (EDTA), and citric acid (CA), on maintaining available Fe\(^{2+}\) and activating PS for the degradation of benzene were studied. The results indicated that HPCD and EDTA might be less susceptible to chelated Fe\(^{2+}\). In contrast, CA was a more suitable chelating agent in the iron activated persulfate system and with a PS/CA/Fe\(^{2+}\)/B molar ratio of 20/5/5/1, benzene could be completely degraded within a 70 min period.

Chen et al. (2009) evaluated the feasibility of using ferrous ion-activated persulfate oxidation to remediate groundwater contaminated with methyl tert-butyl ether (MTBE). In this study, batch experiments were conducted to evaluate the effects of various factors on the efficiency of MTBE degradation, including persulfate concentration, ferrous ion concentration, and persulfate coupled with hydrogen peroxide. The results showed that ferrous ion-activated persulfate oxidation was capable of degrading MTBE efficiently. Persulfate and ferrous ion concentrations correlated with MTBE degradation rate. However, excess addition of ferrous ion resulted in the decreased MTBE degradation rate most likely because of competition for sulfate free radicals between ferrous ion and MTBE. Two main byproducts of MTBE degradation, tert-butyl formate and tert-butyl alcohol, were detected in the experiments; both were, however, subsequently degraded. The results of sulfate analysis showed that proper addition of ferrous ion could prevent unnecessary persulfate decomposition. In another study, Li et al. (2009) investigated degradation of diphenylamine (DPA) in aqueous solution by persulfate. Effects of pH, persulfate concentration, ionic strength, temperature and catalytic ions Fe\(^{3+}\) and Ag\(^{+}\) on the degradation efficiency of DPA by persulfate were examined in batch experiments. The degradation of DPA by persulfate followed the pseudo-first-order kinetic model. Increasing the reaction temperature or persulfate concentration might significantly accelerate the DPA degradation. Fe\(^{2+}\) and Ag\(^{+}\) ions could enhance the degradation of DPA, and Ag\(^{+}\) ion was more efficient than Fe\(^{3+}\) ion. However, the increase of either the pH value or ionic strength would decrease the rate of DPA degradation. N-Phenyl-4-quinoneimine, N-carboxyl-4-quinoneimine, 4-quinoneimine and oxalic acid were identified as the major intermediates of DPA degradation, and a primary pathway for the degradation of DPA was proposed. The degradation of DPA in surface water, groundwater and seawater was also tested by persulfate, and more than 90% of DPA could be degraded at room temperature in 45 min at an initial concentration of 20 mg L\(^{-1}\). In addition, Xu et al. (2010) investigated the oxidative degradation of an azo dye orange G (OG) in aqueous solutions by the persulfate/Fe\(^{2+}\) reagent. Effects of pH, dosages of persulfate and Fe\(^{2+}\), temperature, and the presence of inorganic ions Cl\(^{−}\), NO\(_3^{−}\), HCO\(_3^{−}\) and H\(_2\)PO\(_4^{−}\) on OG degradation were examined in batch experiments. The OG degradation by the persulfate/Fe\(^{2+}\) reagent followed the first-order kinetic model. Under an optimum condition ([persulfate] = 4 mM, [Fe\(^{2+}\)] = 4 mM and pH 3.5), the OG degradation in aqueous
solutions with an initial concentration of 0.1 mM was achieved by 99% within 30 min. The OG degradation increased with an increased dosage of both persulfate and Fe$^{2+}$. The experimental results showed that increasing the reaction temperature from 293 to 313 K was beneficial to the OG degradation, but not as efficient as chemical activation with Fe$^{2+}$ at ambient temperature. In the meantime, the apparent activation energy for the OG degradation was determined to be 92.2 KJ mol$^{-1}$. Furthermore, the results demonstrated that the OG degradation could be significantly inhibited due to the existence of inorganic ions in a sequence of NO$_3^-$ < Cl$^-$ < H$_2$PO$_4^-$ < HCO$_3^-$$. The experiments also demonstrated that the persulfate/Fe$^{2+}$ reagent could degrade OG in aqueous solutions to a higher degree than the Fenton's reagent, which was beneficial to the mineralization of azo dyes.

Ferrous-catalyzed persulfate oxidation of dissolved aniline was investigated in aqueous systems under a variety of ferrous ion concentrations and temperature (Anotai et al., 2011a). The result showed that the addition of ferrous ions accelerated the degradation of aniline by persulfate. For the thermally activated persulfate oxidation experiment, the optimum persulfate/aniline concentration ratio at 30 $^\circ$C was 20/1. This ratio gave the highest aniline removal of 45%. For the ferrous ion catalyzed persulfate oxidation experiment, there was marginal difference in the result for the various ferrous ion/oxidant molar ratios. Thus, another series of experiment was conducted to determine the optimum ratio, and a ferrous ion/persulfate molar ratio of 1.25/1 showed the highest removal efficiency. In another study, the elimination of pesticides by persulphate activated with Fe$^{2+}$ showed high oxidation rates due to the oxidation effectiveness of sulfate free radicals SO$^{4-}$ (Vicente et al., 2011). Effects of iron addition policy, reaction temperature and persulfate concentration were studied employing diuron as target pollutant. Different amounts of Fe$^{2+}$ (from 5 to 86 mg L$^{-1}$) were used, either adding this iron source at the beginning of the reaction or continuously feeding Fe$^{2+}$ for 30, 60 and 120 min. The effect of persulfate concentration was studied at 500 and 735 mg L$^{-1}$. The reactions were carried out at 20 and 50 $^\circ$C with an initial diuron concentration of 20 mg L$^{-1}$. The effectiveness of the process was evaluated based on the degradation of diuron and total organic carbon removal. Not only the total amount of Fe$^{2+}$ used but also the mode of addition of this activator seemed to have big influence on diuron oxidation and mineralization. An increase of the temperature improved the oxidation and mineralization rate. Using stoichiometric amounts of persulfate and iron, complete diuron removal and 64% of TOC conversion were achieved at 50 $^\circ$C by continuously adding the iron solution. A kinetic model capable of describing diuron oxidation and mineralization was proposed and successfully validated. Finally, diuron degradation by persulphate was lower if free radical scavengers, such as carbonate ions (500 mg L$^{-1}$ NaHCO$_3$), presented in the media. In addition, Kusic et al. (2011) applied iron (Fe$^{2+}$ and Fe$^0$) activated persulfate oxidation for degradation of a reactive azo dye C.I. Reactive Red 45 (RR45) in water matrix. The Fe$^{2+}$/S$_2$O$_8^{2-}$ and Fe$^0$/S$_2$O$_8^{2-}$ processes were maintained in a dark as well as with UV light assistance. This study was to develop the flexible mathematical/mechanistic model (MM), which would predict not only the conversion of parent pollutant, i.e. decolorization of model dye solution, but also the mineralization of model pollutant, and could keep the predictive power regardless the process operating conditions. The pH dependent mechanism describing both organic and inorganic ferric complexes formation as one of the major limitations of iron activated processes, as well as iron activated persulfate oxidation, was built in the model. The developed MM showed a high accuracy in predicting the degradation of RR45 considering both decolorization and mineralization, as well as the
profiles of iron species, persulfate decomposition, the subsequent formation of sulfate and pH changes during the treatment. The good agreement of the data predicted and the empirically obtained was confirmed by calculated root mean square deviation values.

2.3.2. Zero-Valent Iron Activation

The oxidation of 2,4-dinitrotoluene (DNT) by persulfate activated with zero-valent iron Fe\(^0\) was studied through a series of batch experiments (Oh et al. 2010). The mechanism for Fe\(^0\) activation was investigated by comparing with Fe\(^{2+}\), and the effects of persulfate-to-iron ratio and pre-reduction on DNT oxidation were examined. DNT was stable in the presence of persulfate and transformed only when Fe\(^0\) was added. Most DNT was degraded oxidatively by Fe\(^0\)-activated persulfate, whereas direct reduction of DNT by Fe\(^0\) was unimportant. The rate of DNT degradation increased with higher Fe\(^0\) dose, presumably due to increasing activation of persulfate by Fe\(^0\) and Fe\(^{2+}\). In contrast to the Fe\(^0\)-persulfate system, where complete oxidation DNT was achieved, only \(\leq 20\%\) of DNT was degraded and the reaction was terminated rapidly when Fe\(^0\) was replaced with equimolar Fe\(^{2+}\). This indicated that Fe\(^0\) was more effective than Fe\(^{2+}\) as activating agent and potentially more suitable for environmental application. The reduction products of DNT were more rapidly oxidized by persulfate than DNT, suggesting that converting the nitro groups of NACs to amino groups prior to oxidation could greatly enhance their oxidation. This suggested that a sequential Fe\(^0\) reduction-persulfate oxidation process might be an effective strategy to promote NAC degradation. In another study, Liang and Lai (2008) described the use of zero valent iron Fe\(^0\) for activated persulfate oxidation of trichloroethylene (TCE). The results indicated that in the absence of TCE, there was a lag time for persulfate decomposition when the reaction was activated by Fe\(^0\). An initial pH drop in the Fe\(^0\)/PS system to acidic conditions was accompanied by the persulfate decomposition and a decrease in oxidation-reduction potential values. Furthermore, in the TCE/Fe\(^0\)/PS system, the rapid TCE degradation was accompanied by the rapid persulfate decomposition and chloride ion formation as the result of TCE mineralization. The SEM image of Fe\(^0\) exhibited significant corrosions of Fe\(^0\) after persulfate oxidation. Acicular aggregate formation in the absence of TCE and coarse aggregate formation in the presence of TCE were observed. Moreover, the XRD spectrum revealed the formation of magnetite over the surface of Fe\(^0\) after contact with persulfate. Therefore, Fe\(^0\) activated persulfate oxidation offered a fast and effective way for the remediation of TCE contamination. In addition, the usage of zerovalent iron (ZVI) activated persulfate to induce sulfate free radical oxidation of both aqueous and solid phase naphthalene (Nap) was investigated by Liang and Guo (2010). The results showed that the removal of Nap particles occurred through an indirect route. Specifically, Nap released through dissolution from the pure Nap particles was subsequently oxidized in the aqueous phase by SO\(_4^{2-}\). Rapid destruction of dissolved Nap created a greater concentration gradient between the solid and aqueous phases. This caused more Nap particles to be dissolved which were then available for the subsequent oxidative destruction of dissolved Nap. The rate constant \(k_{\text{obs,Nap}}\) of ZVI activated persulfate degradation of dissolved Nap was 3.74 min\(^{-1}\). The overall dissolution mass transfer coefficients for the Nap particles were \(3.0 \times 10^{-2}\) min\(^{-1}\) with initial 10 mg Nap in 40 mL water, and found to be proportional to the quantities of the Nap particles present. The net result of the dissolution
of Nap particles and the destruction of dissolved Nap by oxidation was the removal of Nap particles. Sequential additions of ZVI at a lower concentration to slow down the formation of SO$_4^{\cdot-}$ could prevent the scavenging of SO$_4^{\cdot-}$ by ZVI and enhance the removal of Nap particles.

In the literature, another efficient advanced oxidation process, which is based on the zero-valent iron-mediated composition of peroxydisulfate (PDS) that results in the generation of very strong oxidizing species (sulfate free radicals) in aqueous solution, was also reported (Zhao et al. 2009). The results showed that ZVI significantly improved the degradation efficiencies of 4-chlorophenol in the presence of PDS at ambient temperature. The optimum loading of ZVI was 0.20 g L$^{-1}$, and 88% removal of 4-chlorophenol was observed in 1 h. The addition of methanol and tert-butyl alcohol as hydroxyl free radical and sulfate free radical scavengers proved the presence of sulfate free radicals in the ZVI-PDS reaction system. The degradation of 4-chlorophenol was accompanied by the formation of hydroquinone, 1,4-benzoquinone, and small molecule compounds such as oxalic acid and succinic acid, and the hydroquinone pathway was regarded as the main step in the oxidation of 4-chlorophenol. Chloride ion release and formation of oxidation intermediates were evidence of 4-chlorophenol degradation involving sulfate free radicals.

2.3.3. Mineral Activation

Liang et al. (2010) investigated the feasibility of activated persulfate oxidation of methyl tert-butyl ether (MTBE), using pyrite (FeS$_2$) as the source of ferrous ion activator. Under the FeS$_2$-activated S$_2$O$_8^{2-}$ condition, the sulfate free radical SO$_4^{\cdot-}$ is the predominant reactive species generated. The oxidation reactions were able to completely degrade MTBE when given sufficient doses of FeS$_2$ and S$_2$O$_8^{2-}$ and sufficient reaction time (e.g., 3 g L$^{-1}$ FeS$_2$ and 5 g L$^{-1}$ Na$_2$S$_2$O$_8$ within 4 h). The generation and subsequent degradation of the primary MTBE degradation intermediate products, including tert-butyl formate, tert-butyl alcohol, methyl acetate and acetone, were observed. The detailed reaction mechanism proposed for a SO$_4^{\cdot-}$ driven oxidation process indicated that the destruction of MTBE most likely happened through $\alpha$-hydrogen abstraction via attack of the SO$_4^{\cdot-}$ at the intermediate methoxy group. In another study, Ahmad et al. (2010) investigated persulfate dynamics in the presence of subsurface minerals as a basis for understanding persulfate activation for in situ chemical oxidation (ISCO). The mineral-mediated decomposition of persulfate was investigated with four iron and manganese oxides and two clay minerals at both low pH (<7) and high pH (>12). The manganese oxide birnessite was the most effective initiator of persulfate for degradation of nitrobenzene, and the iron oxide goethite was the most effective mineral for degradation of hexachloroethane. A natural soil and two soil fractions were used to confirm persulfate activation by synthetic minerals. The results demonstrated that synthetic iron and manganese oxides could activate persulfate, but iron and manganese oxides in the natural soil did not show the same reactivity, most likely due to the lower masses of the metal oxides in the soil relative to the masses in isolated mineral systems. In addition, Oh et al. (2011) evaluated activation of persulfate using pyrite FeS$_2$ or iron sulfide FeS with 2,4-dinitrotoluene as a model contaminant. Pyrite was able to activate persulfate to degrade DNT, but the degradation of DNT was rapidly halted presumably due to the low water solubility of pyrite and the presence of trace dissolved oxygen. In contrast, FeS was effective in
activating persulfate to continuously and completely degrade DNT. The separate experiments with Fe\(^{2+}\) and HS\(^{-}\) suggested that Fe\(^{2+}\), rather than HS\(^{-}\), released from FeS was involved in persulfate activation and was necessary for rapid degradation of DNT. Furthermore, the reduction products of DNT were oxidized much faster than DNT by FeS-activated persulfate. Recently, it was reported that iron oxide magnetic nanoparticles (Fe\(_3\)O\(_4\), MNPs) could effectively activate persulfate to produce sulfate free radicals (Yan et al., 2011). The kinetics of sulfamonomethoxine (SMM) degradation was studied in the system of MNPs and S\(_2\)O\(_8\)\(^{2-}\). A complete removal of the added SMM (0.06 mmol L\(^{-1}\)) was achieved within 15 min with the addition of 1.20 mmol L\(^{-1}\) S\(_2\)O\(_8\)\(^{2-}\) and 2.40 mmol L\(^{-1}\) MNPs. There was an optimum concentration of MNPs because it might also act as a SO\(_4^{2-}\) scavenger at higher concentration. It was further observed that the addition of MNPs in several batches for a given total amount of the activator was favorable to enhancing the degradation of SMM. A degradation mechanism was proposed on the basis of identification of the degradation intermediates of SMM with liquid chromatography combined with mass spectroscopy.

3.3. Activated Carbon or Basic Oxygen Furnace Slag Activation

For remediation of TCE contaminated groundwater, activated carbon (AC) has been used to adsorb and reduce the TCE concentration and to manage contaminant migration. Additionally, AC might also act as an activator of persulfate to generate sulfate free radical for contaminant destruction. The combined use of AC and persulfate to treat TCE was examined (Liang et al., 2009). The degradation of persulfate in the presence of AC followed a first-order kinetic behavior, and the faster persulfate degradation was observed when elevated AC dosage was used. Higher initial persulfate concentration resulted in a decrease of the persulfate degradation rate. Upon persulfate oxidation, the AC surface properties were altered. The adsorption behavior for the original AC fitted the pseudo-second-order kinetic model while the pseudo-first-order kinetic model was suitable for predicting oxidized AC performance. During the persulfate oxidation of TCE with AC as an activator, the results showed that TCE removal could be a net result of adsorption and oxidation, in which a partial mineralization of TCE to release chloride occurred. In addition, persulfate (PS) oxidative degradation of an azo dye acid orange 7 (AO7) in an aqueous solution was studied in the presence of suspended granular activated carbon (GAC) at ambient temperature (Yang et al., 2011). It was observed that there existed a remarkable synergistic effect in the GAC/PS combined system. Higher PS concentration and GAC dosage resulted in higher AO7 degrading rate. Near-neutral was the optimal initial pH. Adsorption had an adverse effect on AO7 degradation. AO7 had not only a good decolorization, but a good mineralization. The decomposition of PS followed a first-order kinetics behavior both in the presence and in the absence of AO7. The radical mechanism was studied and three radical scavengers (methanol, tert-butanol and phenol) were used to determine the kind of major active species taking part in the degradation of AO7 and the location of degradation reaction. It was assumed that the degradation of AO7 did not occur in the liquid phase, but in the porous bulk and boundary layer on the external surface of GAC. The SO\(_4^{2-}\) or HO\(^{•}\), generated on or near the surface of GAC, played a major role in the AO7 degradation. The recovery performance of GAC was also studied through the GAC reuse experiment.
Tsui et al. (2009) evaluated the feasibility of remediating tetrachloroethylene (PCE) contaminated groundwater (with initial PCE concentration of approximately 20 mg L$^{-1}$) via persulfate oxidation activated by basic oxygen furnace slag ($\text{S}_2\text{O}_8^{2-}$/BOF slag) with the addition of biodegradable surfactant (Tween 80). The results indicated that only 15% of PCE could be removed in experiment with the addition of $\text{S}_2\text{O}_8^{2-}$ only ($\text{S}_2\text{O}_8^{2-}$/PCE = 30/1). The PCE removal could be increased to 31% while both $\text{S}_2\text{O}_8^{2-}$ and BOF slag (10 g L$^{-1}$) were added. This indicated that BOF slag was able to activate persulfate, and caused the decrease in PCE concentration via oxidation process. The results also revealed that the PCE degradation rate increased to 92% with the presence of Tween 80 ($\text{S}_2\text{O}_8^{2-}$/Tween 80/PCE = 30/2/1). In the presence of 10 g L$^{-1}$ BOF slag, the reaction rate constant ($k_{\text{obs}}$) values were $3.1 \times 10^{-3}$, $8.7 \times 10^{-3}$, $1.6 \times 10^{-2}$, and $5.8 \times 10^{-2}$ h$^{-1}$, as the $\text{S}_2\text{O}_8^{2-}$/Tween 80/PCE molar ratios were 30/0/1, 30/0.5/1, 30/1/1 and 30/2/1, respectively. The reaction rate constant increased as the Tween 80 concentration increased. The significantly increased $k_{\text{obs}}$ could be caused by the enhanced solubilization of PCE by Tween 80. The increase in initial surfactant concentration would cause the increase in the solubilization of PCE, and thus enhanced the oxidation rate. This was confirmed by the total amount of chloride ions produced after the reaction. The results indicated that BOF slag activated persulfate oxidation enhanced by surfactant addition was a potential method to efficiently and effectively remediate chlorinated solvent contaminated groundwater.

3.4. Microwave-Assisted Activation

Microwave (MW)-activated persulfate oxidation with or without active carbon (AC) has been reported for the degradation of an azo dye acid orange 7 (Yang et al., 2008). It was found that AO7 (up to 1000 mg L$^{-1}$) was completely decolorized within 5–7 min under an 800 W MW furnace. The presence of chloride ion will delay the decolorization rate while activated carbon will enhance the decolorization rate. Subsequently, Lee et al. (2009) used microwave-induced persulfate to decompose persistent and bioaccumulative perfluorooctanoic acid (PFOA) in water at 60, 90, and 130 °C, respectively. Microwave–hydrothermal treatment was carried out in a microwave digestion system, which provided 800 W of microwave energy with a frequency of 2450 MHz at full power. Persulfate was an efficient oxidant for degradation of PFOA even at the room temperature of 27 °C. Higher temperature accelerated the PFOA decomposition rate, but an extremely high temperature (130 °C) would lead to the formation of significant amounts of radical oxidants thus causing lower mineralization efficiency. The solution pH value was another important factor to influence the degradation rate, and the decomposition rate in acidic condition was 1.1–7.4 times faster than in alkaline condition.

3.5. Integrated Activation

Anipsitakis and Dionysiou (2004) explored 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. The comparison of the results with
respect to the transformation of 2,4-dichlorophenol and the extent of organic carbon removal led to the construction of the following order of efficiencies: UV/K$_2$S$_2$O$_8$ > UV/KHSO$_5$ > UV/H$_2$O$_2$ for the UV/Ox processes and UV/Fe(III)/H$_2$O$_2$ > UV/Fe(II)/H$_2$O$_2$ > UV/Co(II)/KHSO$_5$ > UV/Ag(I)/K$_2$S$_2$O$_8$ for the UV/M/Ox processes. In another study, the oxidation of polyvinyl alcohol (PVA) by persulfate activated with heat, Fe$^{2+}$, and zero-valent iron (Fe$^{0}$) was investigated via batch experiment. Increasing the temperature from 20 to 60 °C or 80 °C accelerated the oxidation rate of PVA, which achieved complete oxidation in 30 and 10 min, respectively. At 20 °C, the addition of Fe$^{2+}$ or Fe$^{0}$ to the persulfate-water system significantly enhanced the oxidation of PVA. The optimal persulfate to Fe$^{2+}$ or Fe$^{0}$ molar ratio was 1:1. The complete oxidation of PVA was obtained by Fe$^{0}$ activated persulfate in 2 h. The synergistic activation of persulfate by heat and Fe$^{2+}$ or Fe$^{0}$ also enhanced the oxidation of PVA in the persulfate-water system. By using CC-MS analysis, an oxidation product of PVA was identified as vinylacetic acid C$_4$H$_6$O$_2$, which was readily biodegradable. The results suggested that the oxidative treatment of PVA by activated persulfate was a viable option for the pretreatment of PVA-laden wastewater to enhance its biodegradability. In addition, feasibility of degradation of Triton X-100 as a widely used and resistive surfactant in aqueous media was studied via some homogeneous and heterogeneous AOPs of UV/TiO$_2$, UV/H$_2$O$_2$ and UV/S$_2$O$_8^{2-}$ (Saien et al., 2011). For treatment of solutions containing 20 mg L$^{-1}$ of Triton X-100, the optimum conditions were 5.0 mg L$^{-1}$ of nano TiO$_2$, 270.3 mg L$^{-1}$ of KPS, and 34.0 mg L$^{-1}$ of H$_2$O$_2$, initial natural pH of 5.4 and temperature of 45 °C. Under these conditions, the degradation efficiencies for the UV/TiO$_2$, UV/H$_2$O$_2$ and UV/S$_2$O$_8^{2-}$ processes were 71.9% (in 60 min), 80.9% (in 60 min) and 98.5% (in only 30 min), respectively. It was found that simultaneous application of these heterogeneous and homogeneous AOPs (UV/TiO$_2$/H$_2$O$_2$ or S$_2$O$_8^{2-}$ was not desirable due to some physicochemical retarding effects. The influence of temperature on the reaction was examined in the range of 15-45 °C, and a kinetic power law model jointed with the Arrhenius equation was introduced. A pseudo first order reaction was appropriate for UV/S$_2$O$_8^{2-}$ and UV/TiO$_2$ processes under the optimum condition, while this order for UV/H$_2$O$_2$ process was 2.27. Meanwhile, the initial rate of degradation in UV/TiO$_2$ process could be described well by the Langmuir-Hinshelwood kinetic model. The analysis of energy consumptions (thermal and electrical) revealed that increasing in temperature was an effective factor for lowering the energy cost of the preferred process of UV/S$_2$O$_8^{2-}$. The degradation of an azo dye acid orange 7 by three common peroxides persulfate, peroxymonosulfate (PMS) or hydrogen peroxide under various activation conditions, i.e., heat (25-80 °C), UV light (254 nm), or anions (SO$_4^{2-}$, NO$_3^-$, CO$_3^{2-}$, HCO$_3^-$, HPO$_4^{2-}$ and Cl$^-$), was investigated (Yang et al., 2010). The order of AO7 degradation efficiencies by heat activation was PS » PMS > H$_2$O$_2$. PS oxidation activated by heat (> 50 °C) was an effective degradation technology, while PMS and H$_2$O$_2$ were hardly activated. When assisted by UV, peroxides could all be activated and degrade AO7 quickly. In addition, PMS could be activated by some anions, but PS and H$_2$O$_2$ could not. The activation efficiencies of PMS by SO$_4^{2-}$ and NO$_3^-$ were negligible, whereas remarkable by HCO$_3^-$, HPO$_4^{2-}$, Cl$^-$ and CO$_3^{2-}$. For HCO$_3^-$, HPO$_4^{2-}$, Cl$^-$, the activation efficiencies became higher with the increase of anion concentration. For CO$_3^{2-}$, however, the activation efficiency was higher at lower concentration.
4. Environmental Application

In recent years, in situ chemical oxidation has become a promising remediation technology for soil and groundwater. ISCO is usually performed by injecting chemical oxidant, such as hydrogen peroxide, permanganate, ozone, or persulfate, into the soil or water (Seol et al., 2003). Among the various oxidants available for this process, persulfate is the newest and least studied, but has received increasing attention. In addition to its high oxidative potential, persulfate is moderately stable at the subsurface environments and has the potential to be transported from the point of injection to target pollutants in field site. Furthermore, persulfate has been widely studied for the treatment of water and wastewater. The environmental application of activated persulfate is summarized in Table 1.

5. Conclusion and Prospects

This paper gives a review on the activation of persulfate and its environmental application, including heat, UV light, transitional metal, activated carbon, microwave and integrated activation techniques. In the future, more activation methods for persulfate should be studied, and persulfate will be widely used for the treatment of water and wastewater as well as in situ chemical oxidation of organic pollutants in remediation of soil and groundwater. In addition, antibacterial activity of activated persulfate and its environmental application is an impending task.

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Acknowledgments

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References


