

Chapter 2

Magnetic Nanoparticles and Their Heterogeneous Persulfate Oxidation Organic Compound Applications

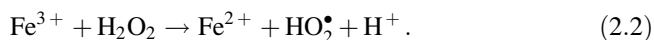
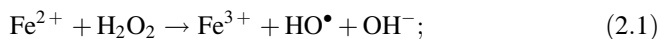
Cheng-Di Dong, Chiu-Wen Chen and Chang-Mao Hung

Abstract Nano-zero-valent iron (nZVI), Fe^0 , has been successfully used to transform and degrade contaminants in soils and water. Additionally, it has been used as a catalyst to heterogeneously activate persulfate ($\text{Na}_2\text{S}_2\text{O}_8$, PS) for the treatment of various contaminants. The nZVI-PS oxidation system has received increasing attention because of its successful use in the treatment of sediments contaminated with recalcitrant organic compounds; treated sediments have improved considerably to meet remediation goals, such as the remediation goal for polycyclic aromatic hydrocarbons (PAHs). The presence of PAHs in sediments is a major concern because of the risks posed to aquatic ecosystems through bioaccumulation in food chains. To minimize ecological risks posed by contaminated sediments, it is imperative to develop processes that can degrade the sorbed PAHs. Efforts have been focused on identifying the most effective PS oxidant for obtaining the maximum acceptable PAH compound concentration. Moreover, the oxidation of PAHs in sediments by PS along with the simultaneous activation of the PS by nZVI, which is a source of catalytic ferrous iron, has been investigated. The determination and quantification of PAHs in sediment samples were performed using gas chromatography coupled to mass spectrometry (GC-MS). An adequate amount of PS must be present because it is the source of sulfate radicals, which are responsible for the degradation of PAHs. Results have indicated that the addition of a larger amount of nZVI to a PS-slurry system can enhance the PS oxidation process, suggesting that nZVI assists PS in the ex-situ treatment of PAH-contaminated sediments. Thus, nZVI-assisted PS is a promising choice for organic compound treatment for environmental remediation. This paper presents a study on magnetic nanoparticles and the heterogeneous PS oxidation of the nanoparticles and organic compounds (PAH-contaminated sediment), conducted in our laboratory.

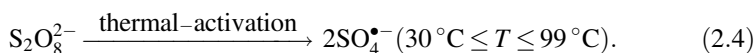
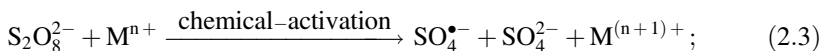
C.-D. Dong · C.-W. Chen · C.-M. Hung (✉)
Department of Marine Environmental Engineering,
National Kaohsiung Marine University, Kaohsiung City, Taiwan
e-mail: hungcm1031@gmail.com

2.1 Overview of Persulfate Oxidation Processes Used for Organic Compound Treatment

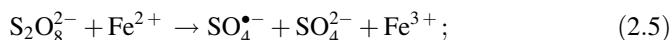
Advanced oxidation processes (AOPs) are chemical treatments used for removing organic (and sometimes inorganic) materials; they involve the use of highly reactive radicals generated from various combinations of reactants, such as O_3/UV , TiO_2/UV , H_2O_2/O_3 , and transition metal/ H_2O_2 [1, 2]. Among AOPs, those that involve the Fenton reagent and activated persulfate ($Na_2S_2O_8$, PS) are the most powerful, and they have been used for treating polluted wastewater in the last decade. In a regular Fenton process, ferrous ions (Fe^{2+}) are used to catalyze hydrogen peroxide (H_2O_2), generating a highly reactive oxidizing species—hydroxyl radicals (HO^\bullet) that are strong nonspecific oxidants. These radicals are highly reactive and capable of decomposing organic compounds at high diffusion-controlled rates (10^7 – $10^{10} M^{-1} s^{-1}$). Furthermore, HO^\bullet can effectively oxidize almost all organic compounds. The primary Fenton reactions include the following reactions [3]:



Typically, H_2O_2 reduces the ferric species, $Fe(III)$, in catalytic reactions. The rates of ferrous consumption and ferrous regeneration differ appreciably. The rapidly exhausted ferrous ions terminate the Fenton reaction and shorten the period of efficient degradation of the target compounds. Recently, attention paid to the use of PS has been increasing because PS has been recognized as an emerging oxidizing agent that can be used for degrading a broad range of organic contaminants. PS has drawn considerable attention because of its unique characteristics [4, 5]. In general, subjecting PS to highly reactive sulfate radical ($SO_4^{\bullet-}$)-based AOPs can produce powerful oxidizing species, such as $SO_4^{\bullet-}$, which can be potentially used for treating dye effluents [6, 7]. PS ($S_2O_8^{2-}$) is used more frequently than H_2O_2 as an oxidant for in situ chemical oxidation remediation of environments contaminated with organic pollutants; the chemical oxidation is performed at room temperature, but the direct reaction of PS with most reductants is slow [8]. When appropriately activated, PS converts to $SO_4^{\bullet-}$ [9], which has an oxidation potential of 2.6 V. This value is greater than that of hydroxyl radicals (approximately 2.8 V), which are one-electron oxidants that can potentially remove contaminants. Numerous studies have been conducted to investigate the efficiency of activated PS for the chemical oxidation of pollutants. Generally, PS can be chemically activated by transition metal ions (M^{n+}) or thermally activated to generate $SO_4^{\bullet-}$ [10].



Thermal activation of PS has been considered as a prominent method, particularly after intensive study and application in the detoxification of numerous organic pollutants at contaminated sites. The temperature required for the thermal activation has been experimentally shown to be in the range of 35–130 °C [11]. Zhao et al. found that thermal activation was one of the most effective methods of activating PS for the removal of PAHs in soil when the temperature was increased from 40 to 60 °C [12]. Cuypers et al. showed that the extent of PAH oxidation by persulfate increased with an increase in the temperature in the range of 20–70 °C (for oxidation durations up to 24 h) [4]. Furthermore, the thermally activated-PS-based oxidation of target compounds in soil slurries was strongly inhibited by the high organic carbon content in the soil [13]. Generally, oxidation involving thermally activated PS is energy-consuming. However, this crucial heterogeneous catalytic process has attracted considerable attention in materials chemistry, and the effectiveness of the chemical activation process has been improved using high-performance Fe(II), which generates $\text{SO}_4^{\bullet-}$ and HO^\bullet in a manner similar to that in the Fenton reaction in accordance with (2.5) and (2.6). If a sufficient quantity of Fe(II) ions, which act as electron donors, is present, PS anions can also be catalytically decomposed to form $\text{SO}_4^{\bullet-}$.

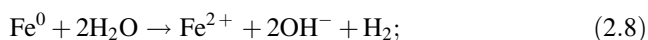
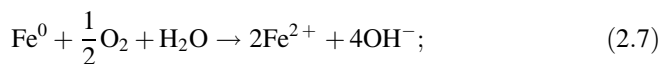


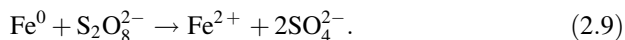
Generally, various types of catalysts have been widely used for the treatment of dye-contaminated wastewater. For example, Wang et al. prepared zero-valent iron (ZVI) catalysts for the degradation conversion of acid orange 7 (AO7); the degradation conversion involved PS activation through ultrasonic irradiation [14]. Nguyen et al. assessed the feasibility of using activated carbon as a supporting material for Fe_2MnO_4 catalysts in the oxidation of methyl orange at pH 3.0; they reported that treating activated carbon with HNO_3 can functionalize the carbon surface through the formation of carboxyl groups [15]. Additionally, a recent study described an efficient technique for the catalytic oxidation of the azo dye Orange G (OG) in an aqueous stream. The technique involved using a Fe^{2+} /PS reagent in the temperature range of 20–40 °C at pH 3.5. It was observed that the degradation of OG increased with both Fe^{2+} and PS doses [16]. Yang et al. discovered that PS oxidation can be used for degrading AO7 in the presence of suspended granular activated carbon (GAC); they observed a synergistic effect in a GAC/PS combined system [17]. The results of these studies showed the potential of PS to degrade organic contaminants.

Metal oxides, particularly iron oxides, are promising heterogeneous catalysts because of their natural abundance, low cost, and environmentally friendly properties, and they can be used as PS activators [18]. Iron oxides exist in the environment in different forms. The synthesis and use of iron oxide nanomaterials with novel properties and functions have been widely studied; their nanoscale size and superparamagnetism are responsible for their novel properties. Recently, there has

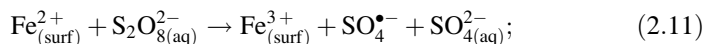
been considerable interest in the environmental applications of magnetite (Fe_3O_4) and ZVI, such as the oxidation of organic compounds in dye-contaminated wastewater [14, 19]. This compound improves the PS oxidation properties by accelerating the degradation rate through the formation of $\text{SO}_4^{\bullet-}$. Lin et al. investigated the substantial conversion of the azo dye AO7 to sodium sulfanilamide and 1-amino-2-naphthol by using a Fe_3O_4 catalyst activated by peroxydisulfate in an electro/ Fe_3O_4 /peroxydisulfate process, and they found that the Fe_3O_4 particles were stable and reusable [20]. Zhu et al. reported that core-shell Fe- Fe_2O_3 nanostructure (FN) materials can be used as catalysts in the catalytic oxidation of methyl orange in aqueous solution. They also found that the conversion of methyl orange reached 90 % in an FN/ $\text{Na}_2\text{S}_2\text{O}_8$ process after 10 min [21]. Yan et al. observed that complete treatment eliminated sulfamonomethoxine highly efficiently within 15 min when 2.4 mmol/L Fe_3O_4 magnetic nanoparticles were used as the heterogeneous activator of 1.2 mmol/L PS [22].

The nanoparticles (<100 nm) discussed in this chapter are ZVI particles, and they exhibit a typical core-shell structure. The core consists primarily of zero-valent or metallic iron, and the mixed-valent [i.e., Fe(II) and Fe(III)] oxide shell forms as a result of the oxidation of the metallic iron. Iron typically exists in the environment as Fe(II)- and Fe(III)-oxide, and therefore, ZVI is a manufactured material. Thus far, applications of ZVI have been based primarily on the electron-donating properties of ZVI. Under ambient conditions, ZVI is reactive in water and can serve as an excellent electron donor; these qualities make it a versatile remediation material. Moreover, ZVI is a highly reactive material and is used for remediating various pollutants. Because ZVI has a considerably low standard reduction potential ($\text{Fe}^{2+} + 2\text{e}^- = \text{Fe}^0$, $E_0 = -0.447$ V; $\text{Fe}^{3+} + 3\text{e}^- = \text{Fe}^0$, $E_0 = -0.037$), elemental iron is thermo-dynamically stable in oxide forms under normal conditions. The pathways for reducing contaminants involve (i) adsorption of contaminants on the surface of ZVI, (ii) direct reduction of the adsorbed contaminants, and (iii) catalytic reduction by Fe(II) at the interface of ZVI and target products. The nanoscale ZVI particles show high surface-to-volume ratios and high surface activity [23]. However, the use of nano-zero-valent iron (nZVI) has a drawback: the formation of aggregates with the passage of time reduces the activity of nZVI [24]. In the past few years, researchers have focused on stabilizing nZVI and reducing the cost, thereby increasing the use of nZVI in environmental technologies. As an Fe^{2+} source, ZVI has been widely used for activating PS to produce $\text{SO}_4^{\bullet-}$ under aerobic conditions, anaerobic conditions, or through the direct reaction between nZVI and PS in accordance with the following equations [25]:





In addition, heterogeneous activation of PS involving direct transfer of electrons or surface bound Fe^{2+} from ZVI to PS may be an alternative mechanism (2.10 and 2.11, respectively) [26]. An advantage of using ZVI is that the generation of ferrous iron and recycling of ferric iron at the ZVI surface can prevent the accumulation of excess ferrous iron and reduce the precipitation of iron hydroxides during the reaction (2.12) [27].



So far, numerous preliminary studies have reported the synergistic effect of ZVI on persulfate and the remediation of pollutants in aqueous solutions. The findings have suggested that the presence of ZVI in a PS-water system can considerably enhance the oxidation of pollutants [28]. In particular, nZVI shows a surface area reactivity that is approximately 100 times greater than that of micro-zero-valent iron powder. Moreover, nZVI has been found to exhibit the greatest capability to activate PS in the process of degradation of pollutants [29]. However, to the best of our knowledge, no study has been conducted on the simultaneous and synergistic nZVI activation of PS for the removal of PAHs in sediments. The nZVI obtained in the current study was characterized by using environmental scanning electron microscopy coupled with energy dispersive spectroscopy (ESEM-EDS), X-ray diffraction (XRD), and a vibration magnetometer. This chapter reports a study on nZVI activation of PS for the removal of PAHs from sediments, performed at the National Kaohsiung Marine University, with the removal performance and associated factors as major considerations.

2.2 Removal of PAHs from Sediments by Using Magnetic Nanoparticles

Polycyclic aromatic hydrocarbons (PAHs) are a ubiquitous group of several hundred chemically-related environmentally persistent organic compounds with various structures and varied toxicity. They tend to persist in the environment and are widely found in natural media, such as soils, sediments, water, and air. In particular, because of their hydrophobic nature and low water solubility, they can rapidly associate with sediments [30–32]. The effect of PAHs is usually widespread and permanent in environmental media, and thus, PAHs can be eventually deposited and persist in bed sediment (as a sink) in the aquatic system. Their presence in

environmental matrices is of grave concern because of their high toxicity, carcinogenic effects, and environmental persistence. Such contamination may pose a risk of indirect exposure to humans exposed to PAHs through the consumption of foods [33, 34]. Among the various remediation techniques for PAH removal, chemical oxidation is considered promising and can overcome many limitations of other methods for the remediation of aquatic matrices contaminated by recalcitrant PAHs. In other words, the strong sorption of PAHs to a solid phase reduces their availability for microbial attacks, and high-molecular-weight PAHs (with 5 or 6 aromatic rings) are more recalcitrant to biological degradation [35, 36]. Therefore, attention focused on the development of technologies for the control of PAHs in the environment has been increasing.

The use of chemical techniques for PAH remediation has generated considerable interest, because these methods can offer a rapid and aggressive alternative that is less sensitive to the type and concentration of contaminant compared with biological processes. Therefore, the activation of PS by ferrous ions is known to be effective for PAH removal. The use of $\text{SO}_4^{\bullet-}$ prevents the treatment from producing large amounts of slurry (which are produced in the Fenton process). Activated PS used for PAH oxidation can be effective for up to 24 h [3, 37]. Iron is a typical candidate transition metal for environmental applications, and ferric ions are easily precipitated as iron hydroxides at neutral pH [38]. Owing to the buffer capacity of geological materials such as clay and sediment, their ability to maintain a low pH in a solution of ferrous ions is limited in practice. Therefore, numerous chelating agents are employed to maximize the catalytic activity of ferrous ions by preventing the loss of Fe(II); the chelating agents bind the ferrous ions to the hydrophilic sites of natural organic matter [39, 40]. Moreover, the use of nZVI overcomes the disadvantages of losing Fe(II).

Contaminated sediments were collected from the industrial port of southern Kaohsiung, Taiwan. This area receives from a steel refinery effluent that is polluted by organic and inorganic compounds. Several sediment samples were taken from the first 15–20 cm layer at the bottom with following collection (using an Ekman Dredge Grab Sampler (6" × 6" × 6"), from Jae Sung International Co., Taiwan), samples were immediately scooped into glass bottles that had been pre-rinsed with *n*-hexane, and stored in a refrigerator until they were used. The samples were free-dried for 72 h and sieved through a 0.5 mm mesh to ensure uniformity and kept at −20 °C in amber glass bottles that had been pre-rinsed with *n*-hexane and covered with aluminum foil until further processing and analysis. Table 2.1 presents the initial concentrations of the PAHs in the sediment. According to the number of aromatic rings, the 16 PAHs were divided into three groups: (i) 2- and 3-ring, (ii) 4-ring, and (iii) 5- and 6-ring PAHs. The PAHs pollutant level classification was suggested by Baumardi et al. [41]: (i) low, 0–100 ng/g; (ii) moderate, 100–1000 ng/g; (iii) high, 1000–5000 ng/g; and (iv) very high, >5000 ng/g. Sediments from river mouth region can be characterized as moderate to high PAHs pollution. The results can be used for regular monitoring, and future pollution prevention and management should target the various industries in this region for reducing pollution. Moreover, the results of

Table 2.1 Initial concentration of PAHs in sediment

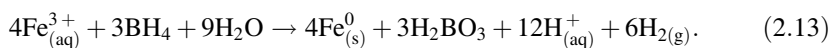
PAHs	Chemical formula	Concentration (ng/g)
<i>2-ring</i>		
1. Naphthalene (NA)	C ₁₀ H ₈	273
<i>3-ring</i>		
2. Acenaphthalene (ACY)	C ₁₂ H ₈	160
3. Acenaphthene (ACE)	C ₁₂ H ₁₀	265
4. Fluorene (FL)	C ₁₃ H ₁₀	238
5. Phenanthrene (PH)	C ₁₄ H ₁₀	392
6. Anthracene (AN)	C ₁₄ H ₁₀	230
<i>4-ring</i>		
7. Fluoranthene (FLU)	C ₁₆ H ₁₀	503
8. Pyrene (PY)	C ₁₆ H ₁₀	525
9. Benzo[a]anthracene (BaA)	C ₁₈ H ₁₂	235
10. Chrysene (CH)	C ₁₈ H ₁₂	245
<i>5-ring</i>		
11. Benzo[b]fluoranthene (BbF)	C ₂₀ H ₁₂	224
12. Benzo[k]fluoranthene (BkF)	C ₂₀ H ₁₂	197
13. Benzo[a]pyrene (BaP)	C ₂₀ H ₁₂	273
14. Dibenzo[a,h]anthracene (DA)	C ₂₂ H ₁₄	95
<i>6-ring</i>		
15. Indeno [1,2,3-cd]pyrene (IP)	C ₂₂ H ₁₂	193
16. Benzo[g,h,i]perylene (BP)	C ₂₂ H ₁₂	176
ΣLPAHs: Total Light PAHs (1–7)	–	1559
ΣHPAHs: Total Heavy PAHs (8–16)	–	2667
ΣPAHs: Total PAHs	–	4226

previous studies carried out by the authors on the distribution of PAHs contained in the surface layers of harbor sediment show that sediment surface layers near river mouths have relatively higher PAHs concentrations [42]. This indicates that PAHs are borne by river flow and municipal runoffs to accumulate in the harbor sediment.

The concentration of PAHs (i.e., naphthalene (NA), acenaphthylene (ACE), acenaphthene (AC), fluorene (FL), phenanthrene (PH), anthracene (AN), fluoranthene (FLU), pyrene (PY), benzo[a]anthracene (BaA), chrysene (CH), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno [1,2,3-cd]pyrene (IP), dibenzo[a,h]anthracene (DBA), and benzo[g,h,i]perylene (BP)) in the extracts were analyzed using a GC (HP Agilent Technologies 6890 Gas Chromatography, USA), equipped with an Agilent 5975 mass selective detector (MSD). The GC was equipped with an Agilent 7683B split/splitless injector (splitless time: 1 min; flow: 60 mL/min); injector temperature was maintained at 300 °C. The transfer line and ion source temperature were 280 and 230 °C. Column being used to separate the PAH compounds was HP-5MS capillary column

(Hewlett-Packard, Palo Alto, CA, USA) with $30\text{ m} \times 0.25\text{ mm i.d} \times 0.25\text{ }\mu\text{m}$ film thickness. The carrier gas was helium at a constant flow rate of 1 mL/min . The column temperature was initially kept at $40\text{ }^\circ\text{C}$ for 1 min , gradually raised to $120\text{ }^\circ\text{C}$ at the rate of $25\text{ }^\circ\text{C/min}$, then increased to $160\text{ }^\circ\text{C}$ at the rate of $10\text{ }^\circ\text{C/min}$ and finally elevated to $300\text{ }^\circ\text{C}$ (final temperature was held for 15 min) at the rate of $5\text{ }^\circ\text{C/min}$. Mass spectrometer was operated in Selected Ion Monitoring (SIM) mode in the electron impact mode at 70 eV . The concentration of individual PAH in the solvent was quantified using the internal standard calibration method with 5-point standard curves ($r^2 = 0.99$). Figure 2.1 shows the total ion chromatogram for this analysis. The identities of 16 PAHs were confirmed by the retention time and abundance of quantification/confirmation ions in the authentic PAHs standards. A time sequence of PAH chromatographs showed that all of these peaks were found with respect to retention time of existing molecules.

nZVI particles were prepared by mixing equal volumes of 0.94 M NaBH_4 and 0.18 M FeCl_3 , following the reaction [43]:



The surface chemistry of magnetic nanoparticles is complex and plays a crucial role in various interactions. In this study, ESEM–EDS observations of the nanoparticles indicated that the nZVI formed small spherical particles, indicating a high degree of nanoparticle dispersion (Fig. 2.2). XRD spectra were used to characterize the phase structure of the nZVI nanostructures (Fig. 2.3). The broad peak reveals the existence of an amorphous phase of iron. The characteristic peak at $2\theta = 44.9^\circ$ confirmed the presence of fresh nZVI [44]. Figure 2.4 shows the magnetic hysteresis loops of fresh nZVI with a magnetic field cycle between -10

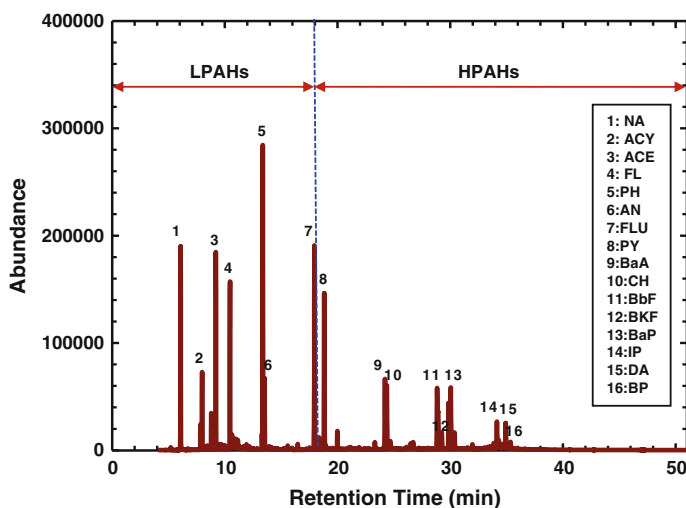


Fig. 2.1 Chromatograms of individual PAHs in slurry system are based on the measurements by GC–MS

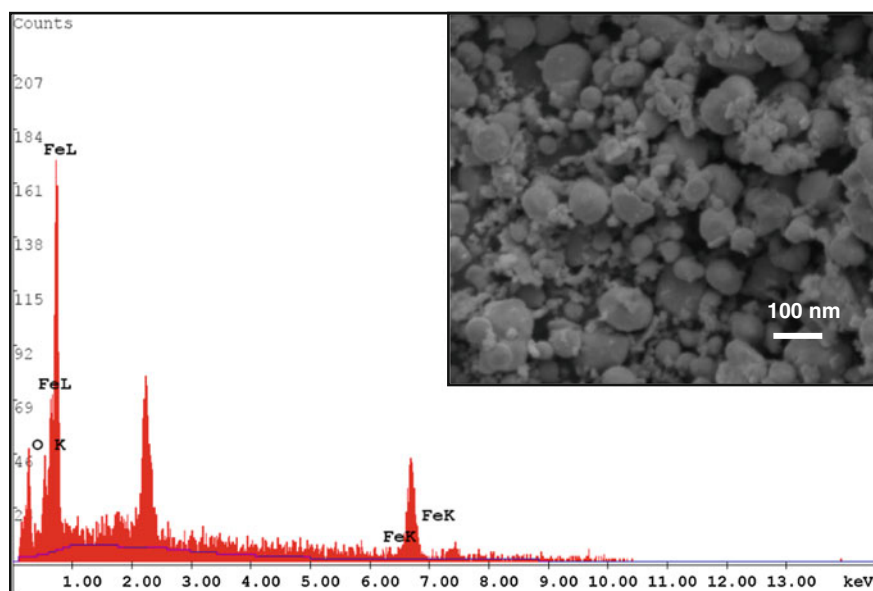
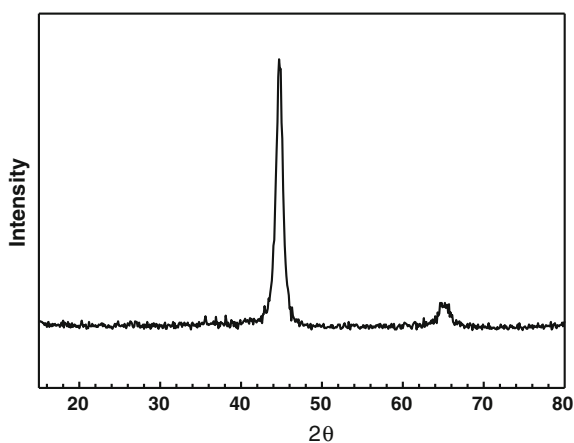


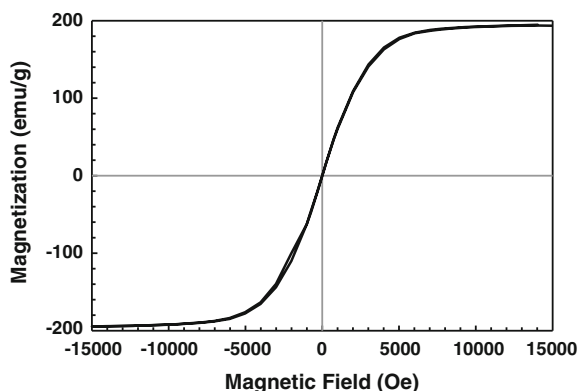
Fig. 2.2 ESEM-EDS photographs of nZVI particle at 10,000 \times in the PAH degradation reaction

Fig. 2.3 XRD pattern of nZVI particles used in the PAH degradation reaction



and +10 kOe at 300 K. The fresh nZVI showed strong magnetic properties at room temperature, and the M - H hysteresis curves passed the original spot, revealing the super-paramagnetic nature of magnetite nZVI materials. The saturation magnetization of the fresh and used samples was 194 emu/g, suggesting that nZVI can be easily separated from an aqueous phase by applying an external magnetic field.

Fig. 2.4 Magnetic hysteresis loops (at 300 K) of the nZVI particles used in the PAH degradation reaction



The effectiveness of PS oxidation for the degradation of PAHs in sediments was evaluated through a series of batch experiments [45, 46]. The results revealed that a high degree of PAH oxidation occurred at high PS concentrations [45]. At the highest PS dose of 170 g/L, the PAHs removal efficiency was only 39.1 %. Similarities were observed between persulfate and permanganate in terms of the degradation of individual PAH compounds, namely the degradation rates of 3-ring and 4-ring PAH compounds were higher for a higher oxidant dose. It was found that the highest PS dose of 170 g/L can remove 3-ring (4-ring) PAH compounds with a maximum efficiency of 30.8 % (50.2 %).

These results and the results presented in the literature [45, 46] show that ZVI plays two roles in the oxidation of PAHs by PS in the PS/nZVI system. One role is as a Fe^{2+} source; it reacts with $\text{S}_2\text{O}_8^{2-}$ and other compounds and reduces Fe^{3+} to produce Fe^{2+} . To evaluate the effect of the initial nZVI concentration on the PAH removal efficiency, experiments were conducted by changing nZVI loading at a fixed initial PS concentration of 170 g/L. The range of the nZVI dose used was 0.01–1 g/L. The degradation efficiency was 70.2, 78.3, 86.3, and 78.0 % for nZVI doses of 0.01, 0.1, 0.5, and 1 g/L, respectively. These results demonstrated that a larger amount of nZVI resulted in the production of a larger amount of ferrous ions, resulted in higher PAH degradation. In addition, the consumption of PS was proportional to the amount of available Fe^{2+} , which was immediately consumed by PS to generate $\text{SO}_4^{\bullet-}$ for the degradation of PAHs. Similar to the thermal activation of PS, the decomposition of PS was characterized by an initial fast stage in the first 18 h, after which the PS decomposition leveled off. However, increasing the nZVI dose up to 1 g/L reduced the PAH degradation efficiency. The reason was likely that excessive Fe^{2+} could also act as a scavenger of $\text{SO}_4^{\bullet-}$ [14]. Similar to other studies, an optimal value of the ratio of persulfate to nZVI may exist for the slurry treatment system. For the conditions employed in our study (1 g of soil and 25 mL of solution), the optimal conditions to achieve the highest PAH degradation were found to be 0.5 g/L of nZVI and 170 g/L of PS, which correspond to a sediment/PS/nZVI weight ratio of 1/4.25/0.0125.

Moreover, the activation of PS to generate $\text{SO}_4^{\bullet-}$ is more effective when Fe^{2+} is supplied continuously compared with a one-time supply [45, 46]. In particular, the oxidation of sorbed organic compounds such as PAHs can be inhibited by high organic matter content in sediments. Thus, the remediation of hydrophobic compounds in sediments with high organic content requires high amounts of a strong oxidant, powerful oxidation conditions, and a long reaction time. Our results showed that nZVI is a long-lasting activating agent that can meet the requirements of sustained oxidation of PS. In addition, the final pH fluctuated in the range of 5.6–6.8 because of the formation of OH^- by iron corrosion after the pH rapidly decreased to the range of 3–4 at an early stage because of the formation of SO_4^{2-} . In general, $\text{SO}_4^{\bullet-}$ was more selective than HO^\bullet in oxidizing organic compounds. During the decomposition of organic compounds in the ZVI system, the corrosion of ZVI was strongly influenced by the H^+ concentration [14]. Therefore, the pH of the treated sediments was among the crucial variables, since treated sediments should exhibit optimal functions in a marine ecological system.

2.3 Conclusions

This study used magnetic nanoparticles and heterogeneous persulfate oxidation for degrading organic compounds. The oxidation of organic compounds such as PAHs sorbed on the surface of the nanoparticles could be inhibited by high organic matter content in the sediment. Thus, the remediation of hydrophobic compounds in sediments with high organic content requires a large amount of a stable oxidant. The use of PS eliminated PAH compounds, and PS was consumed by non-target compounds in sediments. In general, the degradation was limited, which can be explained by considering several parameters: PAH availability, PAH reactivity, and sediment characteristics. Moreover, the reaction of PS with PAHs is generally slow at ambient temperature, and activation of PS is necessary to accelerate the oxidation process. Therefore, nZVI was used to activate PS for the oxidation of representative PAHs in sediments. An adequate PS dose must be provided because it is the source of sulfate radicals, which are responsible for the degradation of PAHs. An increase in the nZVI dose resulted in an increase in the PAH degradation efficiency because of increased activation of PS. As a PS-activating agent, nZVI is more effective and longer-lasting than Fe^{2+} and potentially more suitable for ex situ treatment of hydrophobic compounds such as PAHs that are strongly absorbed on the sediment. Furthermore, according to the present experimental data, magnetic nZVI showed superior performance in environmental treatment applications for organic compounds, and it may therefore facilitate the improvement of industrial processes for meeting increasingly stringent regulations pertaining to sediment discharges containing other organic compounds and help achieve environmental sustainability. In the future, additional methods for activating PS should be studied, and nZVI-activated PS is expected to be widely used for the treatment of organic compounds for the remediation of sediments.

References

1. A.S. Bokare, W. Choi, *J. Hazard. Mater.* **275**, 121 (2014)
2. M. Sievers, *Treatise Water Sci.* **4**, 377 (2011)
3. S.G. Venny, H.K. Ng, *Chem. Eng. J.* **180**, 1 (2012)
4. C. Cuypers, T. Grotenhuis, J. Joziassse, W. Rulkens, *Environ. Sci. Technol.* **34**, 2057 (2000)
5. H. Long, Y. Zhang, Y. Lei, *Sep. Purif. Technol.* **118**, 612 (2013)
6. A. Tsitonaki, B. Petri, M. Crimi, H. Mosbaek, R.L. Siegrist, P.L. Bjerg, *Critic. Rev. Environ. Sci. Tech.* **40**, 55 (2010)
7. X.R. Xu, S. Li, Q. Hao, J.L. Liu, Y.Y. Yu, H.B. Li, *Inter. J. Environ. Bioenergy* **1**, 60 (2012)
8. C.H. Yen, K.F. Chen, C.M. Kao, S.H. Liang, T.Y. Chen, *J. Hazard. Mater.* **186**, 2097 (2011)
9. S.H. Do, Y.J. Kwon, S.H. Kong, *J. Hazard. Mater.* **182**, 933 (2010)
10. A. Ghauch, A.M. Tuqan, N. Kibbi, S. Geryes, *Chem. Eng. J.* **213**, 259 (2012)
11. K.C. Huang, Z. Zhao, G.E. Hoag, A. Dahmani, P.A. Block, *Chemosphere* **61**, 551 (2005)
12. D. Zhao, X. Liao, X. Yan, S.G. Huling, T. Chai, H. Tao, *J. Hazard. Mater.* **254–255**, 228 (2013)
13. C.J. Liang, C.J. Bruell, M.C. Marley, K.L. Sperry, *Soil Sedim. Contam.* **12**, 207 (2003)
14. X. Wang, L. Wang, J. Li, J. Qiu, C. Cai, H. Zhang, *Sep. Purif. Technol.* **122**, 41 (2014)
15. T.D. Nguyen, N.H. Phan, M.H. Do, K.T. Ngo, *J. Hazard. Mater.* **185**, 653 (2011)
16. X.R. Xu, X.Z. Li, *Sep. Purif. Technol.* **72**, 105 (2010)
17. S.Y. Yang, X. Yang, X.T. Shao, R. Niu, L.L. Wang, *J. Hazard. Mater.* **186**, 659 (2011)
18. C. Tan, N. Gao, W. Chu, C. Li, *Sep. Purif. Technol.* **95**, 44 (2012)
19. S.C.N. Tang, I.M.C. Lo, *Water Res.* **47**, 2613 (2013)
20. H. Lin, H. Zhang, L. Hou, *J. Hazard. Mater.* **276**, 182 (2014)
21. L. Zhu, Z. Ai, W. Ho, L. Zhang, *Sep. Purif. Technol.* **108**, 159 (2013)
22. J. Yan, M. Lei, L. Zhu, M.N. Anjum, J. Zou, H. Tang, *J. Hazard. Mater.* **186**, 1398 (2011)
23. J. Cao, P. Clasen, W.X. Zhang, *J. Mater. Res.* **20**, 3238 (2005)
24. C. Noubactep, S. Caré, R. Crane, *Water Air Soil Pollut.* **223**, 1363 (2012)
25. Y. Furukawa, J.W. Kim, J. Watkins, R.T. Wilkin, *Environ. Sci. Technol.* **36**, 5469 (2002)
26. S.Y. Oh, D.S. Shin, *Soil Sedim. Contam.* **23**, 180 (2014)
27. D.H. Bremner, A.E. Burgess, D. Houlemare, K.C. Namkung, *Appl. Catal. B: Environ.* **63**, 15 (2006)
28. I. Hussain, Y. Zhang, S. Huang, *Appl. Catal. B: Environ.* **4**, 3502 (2014)
29. H. Li, J. Wan, Y. Ma, Y. Wang, M. Huang, *Chem. Eng. J.* **237**, 487 (2014)
30. C.C. Lin, S.J. Chen, K. Lin, M. Huang, *Environ. Sci. Technol.* **42**, 4229 (2008)
31. J.H. Tsai, S.J. Chen, K.L. Huang, Y.C. Lin, W.J. Lee, C.C. Lin, W.Y. Lin, *J. Mater. Res.* **179**, 237 (2010)
32. J.H. Tsai, S.J. Chen, K.L. Huang, W.Y. Lin, W.J. Lee, C.C. Lin, L.T. Hsieh, J.Y. Chiu, W.C. Kuo, *Sci. Total Environ.* **446–447**, 195 (2014)
33. M.M. O'Mahony, A.D.W. Dobson, J.D. Barnes, I. Singleton, *Chemosphere* **63**, 307 (2006)
34. B. Antizar-Ladislao, J. Lopez-Real, A.J. Beck, *Waste Manage.* **25**, 281 (2005)
35. P. Henner, M. Schiavon, J.L. Morel, E. Lichtfouse, *Analysis* **56**, 281 (1997)
36. P. Haapea, T. Tuhkanen, *J. Hazard. Mater.* **B136**, 244 (2006)
37. L.L. Johnson, T.K. Collier, J.E. Stein, *Aquat. Conserv. Mar. Freshw. Ecosyst.* **12**, 517 (2006)
38. P.K. Kakarla, T. Andrews, R.S. Greenberg, D. Zervas, *Remediat. J.* **12**, 23 (2002)
39. S. Tao, Y.H. Cui, J. Cao, F.L. Xu, R. Dawson, B.G. Li, *J. Environ. Sci. Health B* **37**, 141 (2002)
40. F. Vicente, J.M. Rosa, A. Santos, A. Romero, *Chem. Eng. J.* **172**, 689 (2011)
41. P. Baumar, H. Budzinski, P. Garrigues, *Environ. Toxicol. Chem.* **17**, 765 (1998)
42. C.D. Dong, C.F. Chen, C.W. Chen, *Mar. Pollut. Bull.* **85**, 665 (2014)

43. Y.P. Sung, X.Q. Li, W.X. Zhang, H.P. Wang, *Colloid. Surf. A: Physicochem. Eng. Aspects* **308**, 60 (2007)
44. Y.P. Sung, X.Q. Li, J. Cao, W.X. Zhang, H.P. Wang, *Adv. Colloid Interf. Sci.* **120**, 46 (2006)
45. C.F. Chen, N.T. Binh, C.W. Chen, C.D. Dong, J. *Air Waste Manage. Assoc.* **65**, 375 (2015)
46. C.W. Chen, N.T. Binh, C.M. Hung, C.F. Chen, C.D. Dong, J. *Adv. Oxid. Technol.* **18**, 15 (2015)

Advanced Materials

Manufacturing, Physics, Mechanics and Applications

Parinov, I.A.; Shun-Hsyung, C.; Topolov, V.Y. (Eds.)

2016, XXV, 707 p. 365 illus., 208 illus. in color.,

Hardcover

ISBN: 978-3-319-26322-9