

Remediation of Fuel Oil Contaminated Soils by Activated Persulfate in the Presence of MnO_2

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Abstract

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In this study, batch system experiments were carried out for evaluating the capability of persulfate (PS) to remediate fuel oil contaminated soils. Remediation was performed by spiking soil samples with fuel oil and then treating the mixture with sodium PS. Different controlling factors including pH (3, 6, and 9), PS concentrations (50–500 mmol/l), metal activators (ferrous sulfate, magnetite, and MnO_2), and temperature (25, 40, and 60°C) were considered. Results proved that PS oxidation is effective in fuel oil degradation. The best PS : Fe^{2+} molar ratios were reported 400 : 2 and 250 : 1 for silty clay and loamy sand soil samples, respectively. Lower pH was more of interest in removal of fuel oil by PS oxidation. MnO_2 improved fuel oil degradation when used together with metal activators. The results showed that when MnO_2 was used together with ferrous sulfate and magnetite at acidic condition (pH = 3), the removal efficiencies were the best. Increasing temperature from 25 to 60°C improved the fuel oil degradation in the PS oxidation batch system. The results showed that activating PS by using ferrous sulfate along with MnO_2 at acidic condition in 60°C could increase fuel oil degradation near to 58% in silty clay soil samples, while the degradation rate for loamy sand soil samples in similar conditions was 62%.

Keywords: fuel oil degradation; metal activators; persulfate oxidation; soil samples

Petroleum products may act as widespread environmental contaminants (IAKOVOU 2001) when accidentally released from pipelines, storage tanks, and many of facilities and processes (CHANG & LIN 2006). The releases may contain some toxic pollutants including common hazardous compounds such as polycyclic aromatic hydrocarbons (PAHs) and many aromatic volatile hydrocarbons like benzene, toluene, ethylbenzene, and xylenes (BTEX) that affect human health, water resources, ecosystems, and other receptors (SAMANTA *et al.* 2002; PINEDO *et al.* 2013). Biological and chemical degradation of fuel oil is more difficult in comparison with lower-

range petroleum hydrocarbons such as diesel and gasoline, which is due to their lower volatility, lower biodegradability, higher viscosity, and lower mobility (TSAI & KAO 2009). Many different advanced oxidation processes including peroxide oxidation, photochemical and sonochemical process, are efficient in degradation of organic pollutants from aqueous and soil media (MAHVI *et al.* 2009; MALEKI *et al.* 2010; GHOLAMI-BORUJENI *et al.* 2011).

Persulfate (PS) has been proved as a strong oxidant ($E^0 = 2.0$ V). Furthermore, PS can be converted to sulfate radicals (SO_4^-), which are more powerful oxidants ($E^0 = 2.6$ V). Different methods of activat-

ing PS to produce sulfate radical include the use of UV radiation (GAO *et al.* 2012), heat (TAN *et al.* 2012), and transition metals (LIU *et al.* 2012). Recently, chemical oxidation using PS has been a topic of interest (ZHAO *et al.* 2013; GUO *et al.* 2014). More particularly, using peroxymonosulfate (PMS) together with transition metals such as Fe^{2+} , Cu^{2+} , and Co^{2+} could form sulfate radicals as the dominant oxidizing agents (DO *et al.* 2009). Eq. (1) describes the reaction of diffusible sulfate radicals generation by transition metals. Eq. (2) expresses the theoretical decomposition of PS on oxidized metals (DO *et al.* 2009; LIANG *et al.* 2008).



In the activation process of PS, hydroxyl radicals ($E^0 = 2.6 \text{ V}$) may also be produced depending on pH (DO *et al.* 2013). Degradation of organic contaminants can possibly be influenced by both sulfate and hydroxyl radicals. The type of the prevailing radical depends on pH. LIANG *et al.* (2008) suggested that basic conditions are favourable for hydroxyl radical predominance while under acidic conditions sulfate radical is more prominent.

The objective of this study was to evaluate the effects of PS, which is activated by transition metals (Fe), on the treatment of fuel oil. For this reason different conditions including PS concentrations, activator types, pH, and temperature were considered. In this study, magnetite (Fe_3O_4) and ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were used as PS activators in a batch slurry system. The first step was determining the best PS/ M^{2+} molar ratios. In addition, the effects of MnO_2 together with ferrous sulfate and magnetite on progression of fuel oil degradation were investigated.

MATERIAL AND METHODS

Material. To prepare a standard curve, oil fuel was purchased from Tehran petrochemical refinery. Two kinds of soil samples were taken from a site with abundant oil occurrence, the characteristics of which are given in Table 1. Fuel oil adsorbed on soil was extracted with *n*-pentane (TNRCC 2001) (CORTES *et al.* 2012). Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) was used as the source of PS. PS was activated by ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and magnetite (Fe_3O_4).

The initial pH values (3, 6, and 9) of the batch reactor were adjusted with sodium hydroxide (NaOH) and nitric acid (HNO_3). All presented chemical materials and also solvents used for extraction and synthetic contamination of soil samples including acetone ($\text{C}_3\text{H}_6\text{O}$), *n*-hexane ($\text{CH}_3(\text{CH}_2)_4\text{CH}_3$), and *n*-pentane ($\text{CH}_3(\text{CH}_2)_3\text{CH}_3$) were purchased from Merck Company, Darmstadt, Germany.

Preparation of fuel oil-contaminated soils.

First, soil samples were contaminated by fuel oil in a batch system. For this reason, debris (gravel and pieces of wood or leaves) was separated from soil samples and passed through a 2-mm mesh screen. To prepare soil samples containing ca. 5000 mg/l fuel oil, two samples, A and B, were contaminated by injecting 2.1–2.2 ml of fuel oil (average density = 0.968) into a 1 l amber bottle containing 400 g of dried solids, and the homogeneity of the fuel oil distribution was assured by magnet mixing. The obtained initial concentration of total petroleum hydrocarbons (TPHs) of contaminated soil samples was equal to 5010–5270 mg/kg (DO *et al.* 2009,

Table 1. Properties of the soil samples before synthetic contamination

Analytical items	Sample A	Sample B
pH	7.8	8.3
Organic matter content (%)	0.116	2.43
Conductivity ($\mu\text{S}/\text{cm}$)	1910	216
Texture classification	silty-clay	loamy-sand
Clay (%)	38.4	12.2
Silt (%)	51.6	8.8
Sand (%)	9	79
Total element analysis (%)		
SiO_2	43.56	38.52
Al_2O_3	9.98	5.24
Fe_2O_3	5.86	2.6
CaO	13.82	24.91
Na_2O	0.26	0.34
K_2O	1.87	0.89
MgO	5.24	3.86
TiO_2	0.563	0.259
MnO	0.124	0.087
P_2O_5	0.112	0.071
S	0.096	0.008
LOI (loss on ignition)	18.26	13.49

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2010). The prepared soil samples were kept in a refrigerator until use. For their chemical analyses, X-ray fluorescence (PW1480 model; Philips, Amsterdam, The Netherlands) was used. The soil samples properties are reported in Table 1. Soil samples were characterized by a hydrometer analysis. According to the particle-size analysis, samples A and B were categorized as silty clay and loamy sand, respectively (ASTM 2007). The organic matter content of sample A (2.43%) was higher than that of sample B (0.116%), while pH of sample A (7.8) was lower than pH of sample B (8.3).

Experimental conditions and procedures. PS concentrations ranging from 50 to 500 mmol/l and Fe^{2+} concentrations ranging from 0.5 to 4 mmol/l were prepared using deionized water. In oxidation process, 7.5 ml of each prepared solution (PS and Fe^{2+}) was added into a 100-ml glass vial filled with 2.5 g of soil samples as a batch reactor. Along with each particular experiment, a sample containing pure water was used to determine the effect of PS and activator in different reactor conditions. To determine the effect of magnetite on the activation of PS, 0.125 g of magnetite was added to each sample. In addition, to investigate the effect of MnO_2 on Fe^{2+} capabilities to degrade fuel oil, 0.1 g of MnO_2 was mixed with prepared solutions. The initial pH was adjusted at 3, 6, and 9 by 1 molar NaOH or concentrated HNO_3 (14.13 molar). To evaluate the effect of temperature on fuel oil degradation, the process was conducted at 25, 40, and 60°C. After these preparations, vials were mounted on a shaking incubator (New Brunswick Innova 4048; Eppendorf, New York, USA) at 170 rpm for 2 h. The amounts of remaining fuel oil were extracted in the reaction system.

Analytical methods. For the extraction and analysis of fuel oil in soil samples, the Texas Natural Resource Conservation Commission Method 1005 was applied (TNRCC 2001). It is a standard method for the determination of hydrocarbons in soil samples using a chromatographic procedure (CORTES *et al.* 2012). To determine the effect of the oxidation process on degradation of different fuel oil hydrocarbon ranges, we used *n*-alkane markers including *n*-hexane (nC_6), *n*-dodecane (nC_{12}), *n*-octacosane (nC_{28}), and *n*-pentatriacontane (n-C_{35}) in calibration curve (Figure 1). Fuel oil concentrations (TPHs) were analyzed using gas chromatography with a flame ionization detector (FID) (CP-3800; Varian, Inc., Middelburg, The Netherlands). The temperature profile for column was: the initial temperature of 35°C (held for 8 min), heating to 100°C in 9°C/min steps (holding time of 8 min). The injector and detector temperature were maintained at 280 and 300°C, respectively. The pH, organic matter, and total element analysis (Table 1) were determined according to standard methods (ASTM 2007).

Statistical methods. To determine the effect of pH and temperature changes on TPHs degradation, all experiments were performed in triplicate. To find out any significant differences between three independent pH values (3, 6, and 9) and temperature measures (25, 40, and 60°C) on TPHs degradation, one-way analysis of variance (ANOVA) was applied. For this reason, the collected data were analyzed using the SPSS Ver. 22 software package.

RESULTS AND DISCUSSION

First, the chemical oxidation experiments were done in two soil samples. All reaction samples were

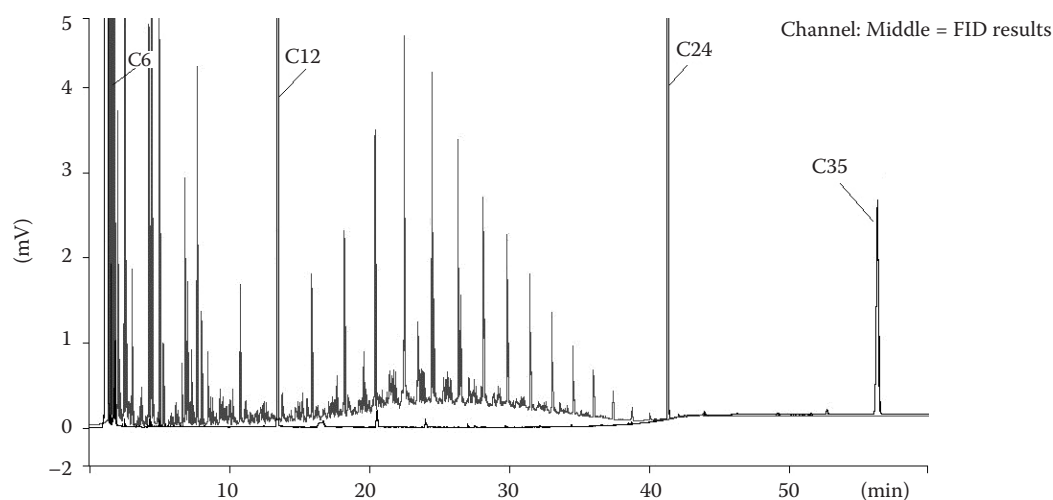
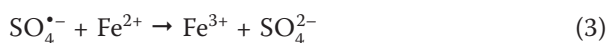


Figure 1. Calibration curve with *n*-alkane markers (C_6 – C_{35})

prepared in triplicate. The aim of choosing spiked soil samples was to evaluate oxidative ability of PS oxidants in the presence of reactive metals. Activator characteristics, oxidation environment, and soil properties were found as the main limitations of decontamination. The oxidation treatment of different PS concentrations (50–500 mmol/l) in a fixed concentration of ferrous ions (2 mmol/l) was examined for the degradation of fuel oil fractions after 2 h of reaction time and the best Fe^{2+} molar concentration (0.5–4 mmol/l) was obtained after fixing optimum PS was achieved from the previous step (Figure 2) (USMAN *et al.* 2014).

In the present study, the best molar ratios of PS/ Fe^{2+} for samples A and B were 400:2 and 250:1, respectively. It should be mentioned that although ferrous ions can activate PS, excess ferrous ions are also a scavenger of sulfate free radicals (Do *et al.* 2010). Other studies suggested that the optimum PS/ Fe^{2+} molar ratio for diesel degradation in both special soil and sand samples would be 100:1, with the highest reported efficacy of 38%. Although in aqueous solution for a specific target contaminant (e.g. trichloroethylene, benzene, toluene, ethylbenzene, xylene, or polyvinyl alcohol) it would be 1:1 (Do *et al.* 2010). Thus, the concentration of PS/ Fe^{2+} molar ratio should be controlled to decrease the adverse effects of ferrous ions on sulfate radical production (Figure 2). Equation (3) shows the scavenging effects between sulfate radical and ferrous ion (YEN *et al.* 2011).



Effects of activator types. The X-ray fluorescence (XRF) characteristics of MnO_2 and magnetite are presented in Table 2. The results of the XRF analysis revealed that Fe_2O_3 (94.26%) and MnO (76.25%)

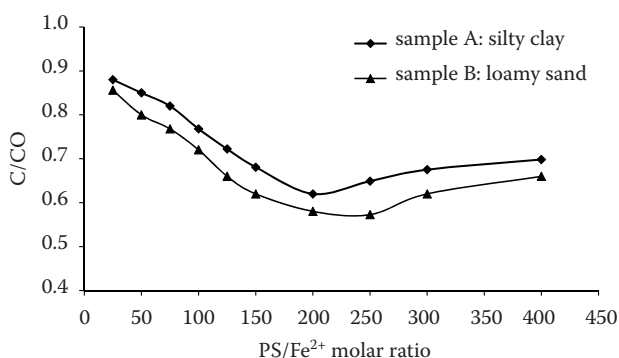


Figure 2. Fuel oil degradation depends on persulfate/ Fe^{2+} molar ratio at pH 3

Table 2. X-ray fluorescence properties of magnetite and MnO_2

Total element analysis (%)	Magnetite	MnO_2
SiO_2	3.21	3.11
Al_2O_3	0.42	1.24
Fe_2O_3	94.26	1.86
CaO	0.44	1.91
Na_2O	0.02	0.03
K_2O	0.04	0.29
MgO	0.25	0.58
TiO_2	0.619	0.52
MnO	0.42	76.25
P_2O_5	0.005	0.063
S	0.439	0.008
LOI (loss on ignition)	0.02	13.49

were the predominating elements in magnetite and MnO_2 , respectively.

The results showed that the degradation of TPH components was negligible when PS was applied solely as oxidant (8.5 and 10.5% for sample A and B, respectively). The reactivity of PS was also affected by adding manganese oxide (see Figure 3). Other studies indicated that when manganese dioxide was used along with Fe^{2+} , the possible crystal lines like jacobite (MnFe_2O_4), magnetite (Fe_3O_4), wüstite (Fe_{1-y}O), and maghemite ($\gamma\text{-Fe}_2\text{O}_3$) might be produced (MA *et al.* 2003; CAO *et al.* 2008; Jo *et al.* 2014). When MnO_2 was used along with magnetite, the efficiency of oxidation process improved, such that the fuel oil removal in sample A was increased from 35%

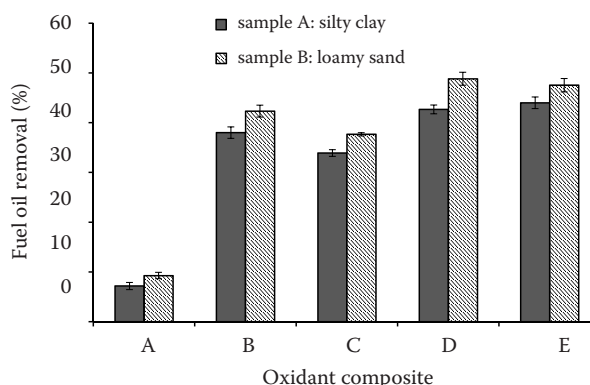


Figure 3. Fuel oil degradation at pH 3 by different oxidant composites ; A – solely persulfate (PS), B – PS + ferrous sulfate, C – PS + magnetite, D – PS + ferrous sulfate + MnO_2 , E – PS + magnetite + MnO_2

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(PS + magnetite) to 46% (PS + magnetite + MnO_2) (Figure 3). Our observations are in agreement with Do *et al.* (2013) who reported that the PS/ Fe_2O_3 - MnO composite was more effective in removing carbon tetrachloride than PS or PS/ Fe_2O_3 solely. MnO_2 also increased the efficiency of PS oxidation capability when sulfate heptahydrate solutions were used as activator, so that increased the fuel oil degradation from 40% (PS + ferrous sulfate solutions) to 44% (PS + ferrous sulfate solutions + MnO_2) in silty clay soil samples. The results of other studies showed that MnO_2 has a high potential in redox reactions and has a powerful electrochemical capacity. The modification of manganese oxide by adding Fe^{2+} has been investigated in electrochemistry studies (Do *et al.* 2010). It is possible that the electrochemical characteristics of manganese oxide with Fe^{2+} accelerate the reactivity of PS. This phenomena would happen through an electron transfer reaction leading to sulfate radicals generation (MINISCI *et al.* 1983).

Effect of pH. The degradation of fuel oil in both A and B soil samples was evaluated at various pH levels. Performance of all PS/ Fe^{2+} systems was examined at three levels of pH value (3, 6, and 9). For both activators (ferrous sulfate and magnetite), the fuel oil degradation went better in acidic condition (pH = 3) (Figure 4). The fuel oil degradation results at acidic condition (pH = 3) are presented in Figures 3 and 4. Previous studies showed that sulfate radicals, which are very strong radicals, predominate under acidic condition (XIE *et al.* 2012). The highest performance was achieved when ferrous sulfate was used together with MnO_2 for PS activation which was 50% for sample B. It might be explained by the fact that availability of Fe^{2+} is greater at lower pH values which can help accelerating the fuel oil degradation (Do *et al.* 2010). Although Do *et al.* (2009) claimed that optimum performance of diesel degradation in PMS/ Co^{2+} system would be at pH = 4–9, research indicates that acidic condition is more favourable for degradation of 2-chlorobiphenyl in the PS/ Fe^{2+} system (Do *et al.* 2009). Low efficiency of fuel oil removal at pH 9 in the present study might be explained by either the change of metals speciation (alteration Fe^{2+} to Fe^{3+}) or self-dissociation of oxidants (i.e. HSO_5^-) at high pH (Do *et al.* 2009).

The results of this investigation showed that the combination of ferrous ions and MnO_2 to activate PS was more effective in degradation of fuel oil. When magnetite was used together with MnO_2 as PS activator, the maximum rates of fuel oil degrada-

tion for sample A at pH 9, 6, and 3 were 37, 40, and 45%, respectively, while the degradation rates for sample B were 37, 42, and 49%, respectively. The combination of ferrous sulfate solutions and MnO_2 to activate PS in degrading fuel oil yielded similar results, where the maximum rates of fuel oil removals for sample A at pH 9, 6, and 3 were 36, 41, and 44%, respectively, and for sample B the rates were 36, 43, and 50%, respectively.

At lower pH, more Fe^{2+} might be released (USMAN *et al.* 2012) which leads to better efficiency of magnetite in fuel oil degradation at acidic condition. The XPS spectra of iron oxide-immobilized MnO_2 composite in the other studies exhibited the $\text{Fe}^{2+}:\text{Fe}^{3+}$ ratio of 0.68:0.32 (Jo *et al.* 2014). Fe^{2+} -bearing minerals like magnetite (Fe_3O_4) were found to be competitive to only Fe^{3+} oxides for oxidation of organic pollutants under heterogeneous condition (USMAN *et al.* 2012). Magnetite also has a tight structure and excellent stability for being used for many oxidation cycles (Do *et al.* 2009; USMAN *et al.* 2012). These results revealed that magnetite was effective to activate PS for oxidation of fuel oil in spiked soil samples at acidic condition.

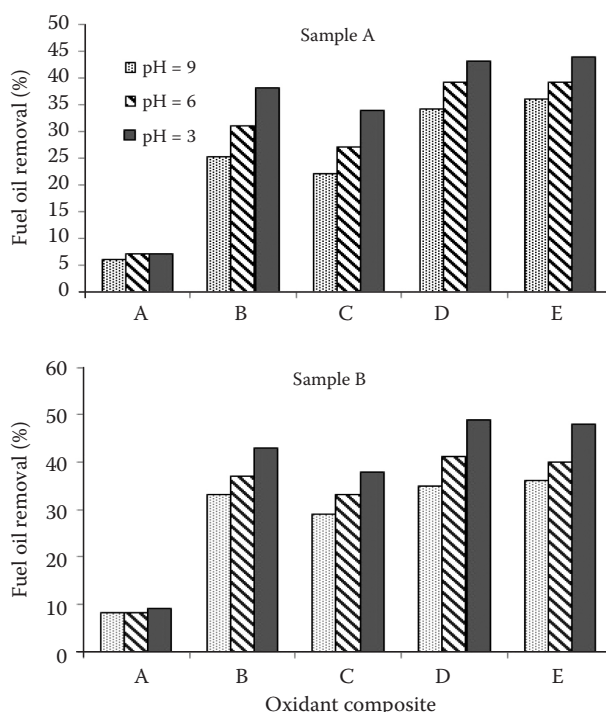


Figure 4. Fuel oil degradation at different pH values and oxidant composites for samples A and B; A – solely persulfate (PS), B – PS + ferrous sulfate, C – PS + magnetite, D – PS + ferrous sulfate + MnO_2 , E – PS + magnetite + MnO_2

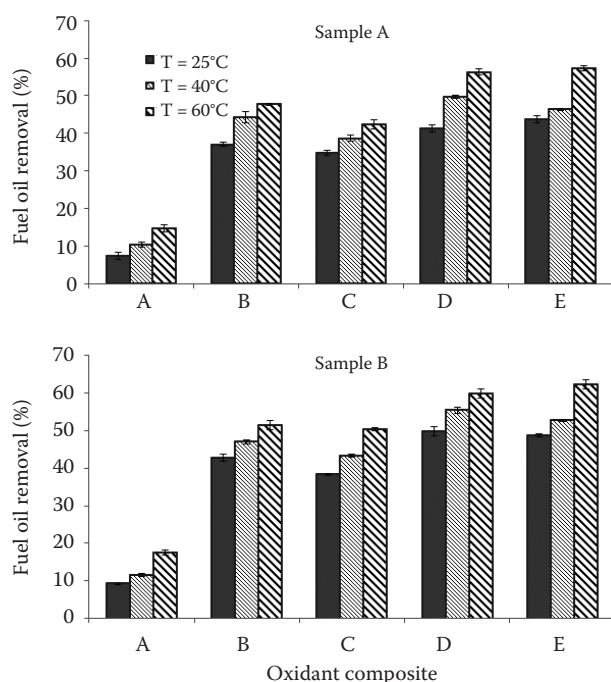
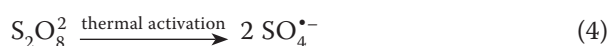


Figure 5. Fuel oil degradation at pH 3 by different oxidant composites and temperature for samples A and B; A – solely persulfate (PS), B – PS + ferrous sulfate, C – PS + magnetite, D – PS + ferrous sulfate + MnO_2 , E – PS + magnetite + MnO_2

Effect of temperature. Thermal activation of PS is an approach to produce sulfate radical (Eq. (4)) (OLMEZ-HANCI *et al.* 2013). The influence of temperature (25–60°C), initial pH (pH = 3) at the best PS: Fe^{2+} molar concentrations (400:2 for soil sample A, 250:1 for soil sample B) on fuel oil removal was examined. In all experiments, increasing the temperature from 25 to 60°C led to increasing fuel

oil removal. When PS was used solely for the fuel oil degradation ($T = 60^\circ\text{C}$), the removal efficiency was low (16 and 19% for sample A and B, respectively), while the highest efficiencies were obtained when MnO_2 and magnetite were used together for PS activation at pH = 3 under 60°C treatment, being 58 and 64% for sample A and B, respectively (Figure 5).



Other studies proved that by increasing temperature in heat-activated PS, oxidant consumption and redox potential (E_h) values increased (ZHAO *et al.* 2013). Rising the temperature from 20 to 40°C led to increasing naphthalene degradation from 50.6 to 98.3% (HUANG *et al.* 2005), and most of the chlorinated ethenes were completely dechlorinated involving thermal PS activation at 30–70°C (WALDEMER *et al.* 2007). However, increasing the temperature may decrease the removal efficiency of some volatile organic pollutants (ZHAO *et al.* 2013). Oxidative capability of PS can be improved by thermal activation which can get by producing a large numbers of oxygen radicals with a higher oxidative activity (ZHAO *et al.* 2013). Sulfate radicals are the predominant generated radicals in a thermal activated PS system (pH= 2–7) (OLMEZ-HANCI *et al.* 2013).

All oxidation process systems were effective for the removal of lighter petroleum components (Figure 6). As the comparison of Figure 1 and Figure 6 shows, although the oxidation processes by PS did not cause a complete degradation of higher carbon ranges ($> C_{12}$), their ability to remove these compounds was remarkable. It was proved that PS is a

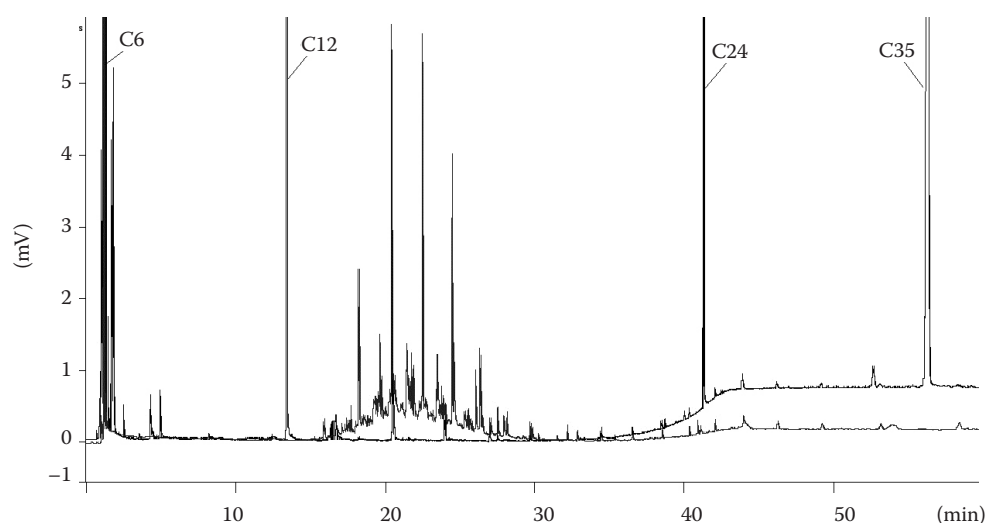


Figure 6. Fuel oil degradation at pH 3 when persulfate is activated by a simultaneous use of ferrous sulfate and MnO_2

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very strong oxidant for removing these components from contaminated soils.

Statistical analysis results. Before ANOVA testing, the homogeneity of variances assumption (pH and temperature data) was proved using Levene's test. The results of one-way ANOVA of pH showed that in all reactions except when the PS was used alone, the degradation of petroleum compounds was remarkable at different pH values ($P < 0.05$). By changing pH value from 9 to 3, a significant change in the efficiency of petroleum compounds degradation was observed ($P < 0.05$). The results of ANOVA showed that in all reactions by changing temperature from 25 to 60°C, a significant difference between average removal efficiencies of fuel oil components was observed ($P < 0.05$).

CONCLUSIONS

In this study, PS was used as a chemical oxidant for the treatment of fuel oil contaminated soils. Well-known activators, magnetite and sulfate heptahydrate together with MnO_2 were tested to determine their activation ability for increasing PS reactivity in fuel oil degradation. Proper molar ratios of PS to ferrous ions were the most important factors in fuel oil degradation. Higher pH values resulted in lower removal efficiency of fuel oil degradation. Acidic condition was more effective in PS activation. Using MnO_2 along with a metal activator increased the degradation of fuel oil in contaminated soils. Increasing temperature from 25 to 60°C had a positive role in fuel oil degradation.

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