

Photodegradation of Diesel Oil in Aqueous Solutions

P. Zhong,¹ L. R. Kong,¹ Z. F. Lin,² G. M. Liu¹

¹ State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210093, People's Republic of China

² South China Sea Institute of Oceanology, Chinese Academy of Sciences, Guangzhou 510301, People's Republic of China

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A large number of petroleum pollutants are discharged into the natural and wastewater from various processes. Diesel oils have many complex components, such as asphalt, carbon residue and ash. Therefore, their release into the environment, whether as a solid or a liquid, will produce pollution and be a potential health hazard to living organisms. Diesel oils are sometimes refractory to degradation by available effluent treatment technologies, such as biological treatment processes (Balba et al. 1998; Delille and Delille 2000). The photo-Fenton method, which can treat wastewater effectively with Fenton reagent and light, has attracted interest and become a serious alternative compared with conventional wastewater treatment methods (McGinnis et al. 2000; Shimoda et al. 1997). With this method, a highly reactive intermediate, the hydroxyl radicals ($\text{OH}\cdot$, which has high oxidation potential, i.e., $E^0=+2.80\text{ V}$), can be generated. The $\text{OH}\cdot$ attacks and destroys toxic organic pollutants non-selectively in wastewater (Halliwell 1978; Wu et al. 1999). The spin-trapping electron paramagnetic resonance (EPR) spectroscopy technique is one of the direct methods in detecting $\text{OH}\cdot$, especially short-lived free radicals intermediates (He et al. 1998). In order to investigate the mechanism of photo-Fenton reactions, it is important to monitor intermediate radicals. In the present work, EPR was utilized to investigate $\text{OH}\cdot$ generation via the reaction between ferrous iron and H_2O_2 .

Our objective in this study was to determine the effect of different reaction conditions on the efficiency of the Fenton reagent for photodegradation of diesel oil in wastewater. The results should help to find the optimal conditions, in a cost-effective way, to treat petroleum pollution in aquatic environments.

MATERIALS AND METHODS

Commercial reagents H_2O_2 (30%), $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO})_3\cdot 9\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3\cdot \text{XH}_2\text{O}$, $\text{K}_2\text{C}_2\text{O}_4\cdot \text{H}_2\text{O}$, H_2SO_4 , Na_2SO_3 , diesel oil and petroleum ether were of analytical grades used as purchased, without further purification. The

spin trap, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), was purchased from Aldrich Chemical Co. Distilled deionized water was used to prepare all solutions.

The DMPO stock solutions were prepared under nitrogen, stored at 273 °K, and protected against light.

Photodegradation experiments were performed in a bath equipped with a gas inlet. A 500 W (250 mm long and 22 mm in diameter) mercury lamp source was employed in such a way that its center was positioned inside a cylindrical Pyrex vessel surrounded by a circulating water jacket (Pyrex) to cool the lamp. The lamp radiation was centered at $\lambda = 365$ nm and the output intensity between 240-400 nm, 40% of its total. A 300 W mercury lamp (230 mm long and 18 mm in diameter) with the same radiation center, was used to compare the effect of the variation of light intensity on the degradation efficiency. The initial pH of the solutions was adjusted to 3 (Delaat et al. 1999) by adding H_2SO_4 . Then $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added and mixed using pumped air. The solution was then put into the reaction tube, immediately after the light source was stabilized and purged with pumped air. Degradation was started by addition of H_2O_2 . The samples were withdrawn from reactors every 3 minutes with sampling volume 50 ml. Stable reagent Na_2SO_3 was then added to the samples to stop further reactions. The initial diesel oil concentration was kept at 50 ppm and its residue was analyzed by UV spectrophotometry.

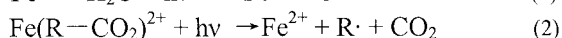
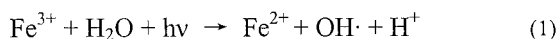
Several experiments were performed to determine the effects of irradiation wavelength, H_2O_2 and Fe^{2+} concentrations and the effect of differing Fe valence by examining Fe^{3+} -complexing anions.

All samples were freshly prepared, mixed, immediately transferred into a quartz sample cell, and immediately measured by EPR. EPR was performed at room temperature in a cavity with a 180 W mercury lamp used as the irradiation sources in all samples. EPR operated at 9.77 GHz with a modulation frequency of 100 KHz. A Bruker ER-200D-SRC spectrometer was used to record spectra. The concentrations of the reagents used, including DMPO, H_2O_2 and FeSO_4 , were 50 mM, 6 mM and 0.3 mM respectively.

RESULTS AND DISCUSSION

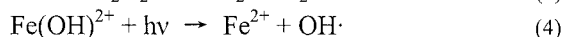
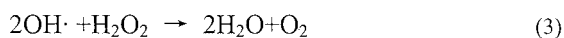
The photodegradation of diesel oil wastewater was studied as a function of different irradiation sources. The reaction time was kept as short as possible because diesel oil is volatile. As shown in Figure 1, the degradation efficiency of the Fenton reaction ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) system, using light irradiation, was improved compared with a dark control and was about 76%~82%. The improvement can

be explained by the appearance of highly reactive intermediates. With light irradiation, the Fe^{3+} complexes can be photoreduced into Fe^{2+} and yield oxidative $\text{OH}\cdot$. The regenerated Fe^{2+} then reacted with H_2O_2 to form $\text{OH}\cdot$ [see reaction (1)]. The organic reactive intermediate was produced through the photolysis of $[\text{Fe}^{3+} - \text{L}_\pi]$ complexes ($\text{L}=\text{R}-\text{OH}$, $\text{R}-\text{CO}_2\text{H}$). During this procedure, Fe^{2+} complexes were formed, and then they were photolyzed into Fe^{2+} as seen in reaction (2) (Nadtochenko and Kiwi 1997). At the same time a higher intensity accelerates the degradation efficiency. Under irradiation, lower Fe-sludge would be formed after treatment with beneficial effects during the disposal and redissolution of the iron in solution.



The photodegradation efficiency of diesel oil at different H_2O_2 concentrations has been measured (Fig. 2). A lower H_2O_2 addition did not afford sufficient oxidant concentration in solution for the reaction to proceed favorably. The concentrations of oxidant higher than 6 mM, as shown in Figure 2, were observed to be detrimental for an adequate degradation since the propagation step was hindered by excess H_2O_2 acting as a hydroxyl radical scavenger. Hence H_2O_2 should be added at a proper concentration.

Iron under appropriate conditions can catalyze degradation of toxic organics in the environments. When Fe^{2+} (0.3 mM) was added with 6 mM H_2O_2 , 82.0% photodegradation of diesel oil was observed within 18 min as shown in Figure 3. A controlled experiment was conducted in pure water under the same conditions in this study. Results indicated that the loss of diesel oil by volatilization and direct photolysis mineralization was less than 29.5% after 18 min. The influence of Fe^{2+} concentration on photodegradation of diesel oil was tested (see Fig. 4). Photodegradation efficiency increased with the catalyst concentration, but reached a plateau. In case of diesel oil, the plateau seemed already reached at 0.3 mM Fe^{2+} . As excess Fe^{2+} was added, the reaction was hindered by excess H_2O_2 produced [see reaction (3)]. The curves in Figure 5 showed that the photodegradation efficiency of diesel oil was much faster by $\text{Fe}^{2+}/\text{H}_2\text{O}_2/500$ WUV than by $\text{Fe}^{3+}/\text{H}_2\text{O}_2/500$ WUV because the rate of formation of $\text{OH}\cdot$ in the $\text{Fe}^{3+}/\text{H}_2\text{O}_2/500$ WUV process was kinetically controlled by the rate of formation of Fe^{2+} (Gallard 1998). For the reaction to progress, Fe^{3+} was reduced to Fe^{2+} [see reaction (4)] which was the homolytic cleavage of the $\text{Fe}^{3+}-\text{OH}$ bond:

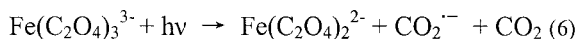


Several reactions can occur in this system to oxidize Fe^{2+} back to Fe^{3+} such as :



This indicated that although Fe^{3+} may be regenerated, it was not truly catalytic. The Fe^{3+} -ions in aqueous solutions containing inorganic anionic ligands showed a tendency to form ion pairs of the type $\text{Fe}^{3+}\cdot\text{X}^-$ (where $\text{X}=\text{Cl}, \text{Br}, \text{OH}, \text{SO}_4, \text{NCS}$, etc.). When solutions containing weak anionic ligands, such as NO_3^- , the principle ion pair was $\text{Fe}^{3+}\cdot\text{OH}^-$, formed by hydrolysis (Uri and Evans 1949).

The influence of Fe^{3+} -complexing chloride, nitrate, sulphate and oxalate anions on the photodegradation efficiency of diesel oil is shown in Figure 6. The degradation efficiencies decreased in the following order of iron salts: $\text{Fe}_2(\text{SO}_4)_3 < \text{FeCl}_3 < \text{Fe}(\text{NO}_3)_3 < \text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$. The addition of chloride resulted in an increase of absorption of photons generated by the 500 W mercury lamp (240-400 nm wavelength) because the $\text{Fe}^{3+}\text{Cl}^{2+}$ species had an absorption peak at 340 nm. In contrast to chloride, the effect of sulphate on photodegradation efficiency was less. Emmett and Khoe (2001) reported that Fe^{3+} -sulphate complex can absorb near ultraviolet light strongly with an absorption peak at 310 nm. More photons are absorbed, yet a reactive sulphate free-radical cannot be produced by this complex, because sulphate was doubly charged, and the energies required to transfer the electron to the iron are much greater than can be supplied by a near-UV photon. The $\text{Fe}^{3+}\cdot\text{OH}^-$ in the nitrate anion solution, which had a charge-transfer maximum at 300 nm (Richards and Sykes 1960; Turner and Miles 1957), rather than $\text{Fe}^{3+}\cdot\text{Cl}^-$, was the photoactive species (David and David 1976). When $\text{C}_2\text{O}_4^{2-}$ at 0.9 mM concentration was added to a reaction mixture containing FeCl_3 there was a large increase in the efficiency of diesel oil. The results showed (Fig.6) that the high quantum efficiency of reaction (6) increased the degradation rate, while the intermediate radical $\text{CO}_2^{\cdot-}$ should be able to attack organic contamination, such as diesel oil wastewater (Huston and Pignatello 1996). The degradation resulted from increased photon absorption, as generated by the 500 W mercury lamp. When Ferrioxalate absorbed over a broad range of wavelengths (300-400 nm), the UV-VIS radiation was more efficiently utilized. The quantum yield of Fe^{2+} is 1.0-1.2. However that of Fe^{2+} is decreased in the photo-Fenton process to 0.14 at 313 nm and to 0.017 at 360 nm (Andreozzi et al. 1999). The ferrioxalate/ H_2O_2 /UV system was more efficient than photo-Fenton for the abatement of organic pollutants:



It was known that the Fenton system ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) produced the $\text{OH}\cdot$. Figure 7a shows that the DMPO solutions did not contain any EPR detectable impurities. We found the four-line EPR spectrum of hydroxyl radical adducts [spectrum (b-e) of Fig. 7], whose intensity ratio was 1:2:2:1 during this experiment, in the presence of DMPO. A spectrum showed that hyperfine splitting constants are

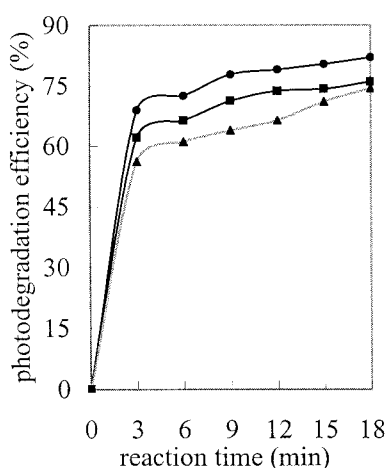


Figure 1. Effect of the wavelength of irradiation on diesel oil photodegradation ($[\text{Fe}^{2+}] = 0.3 \text{ mM}$, $[\text{H}_2\text{O}_2] = 6 \text{ mM}$)

● $\text{Fe}^{2+}/\text{H}_2\text{O}_2/500\text{WUV}$
 ■ $\text{Fe}^{2+}/\text{H}_2\text{O}_2/300\text{WUV}$ ▲ dark control

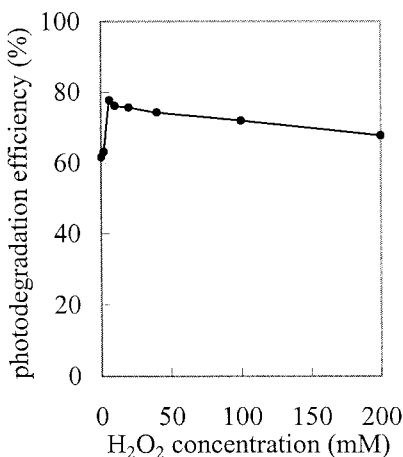


Figure 2. Effect of H_2O_2 concentration on diesel oil photodegradation ($[\text{Fe}^{2+}] = 0.3 \text{ mM}$, 500 WUV)

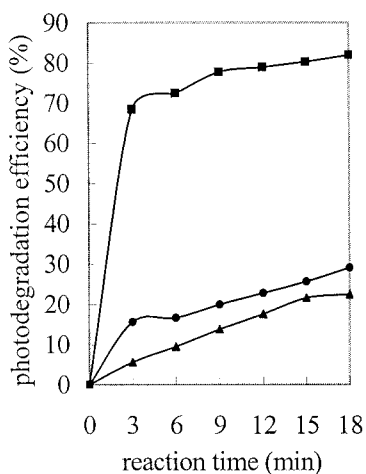


Figure 3. Effect of direct photolysis and volatilization on diesel oil photodegradation

■ $\text{Fe}^{2+}/\text{H}_2\text{O}_2/500\text{WUV}$ ● direct photolysis
 ▲ volatilization

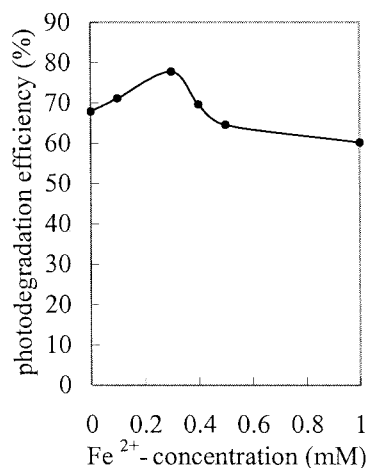


Figure 4. Effect of Fe^{2+} Concentration on diesel oil Photodegradation after 9 min reaction ($[\text{H}_2\text{O}_2] = 6 \text{ mM}$, 500 W UV)

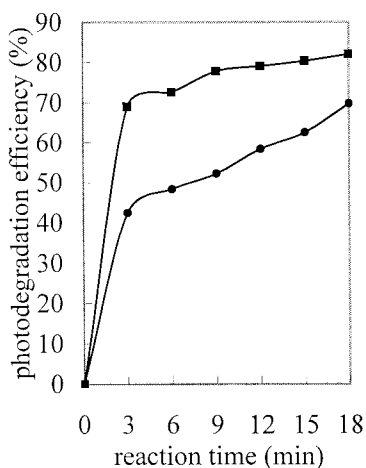


Figure 5. Effect of differing iron Valence on diesel oil photodegradation ($[\text{Fe}]=0.3\text{ mM}/[\text{H}_2\text{O}_2]=6\text{ mM}$)
 —■— FeSO_4 —●— $\text{Fe}_2(\text{SO}_4)_3$

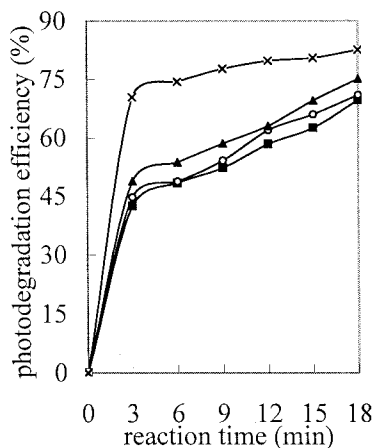


Figure 6. Effect of addition of different Fe^{3+} -complexing anions on diesel oil Photodegradation ($[\text{Fe}^{3+}]=0.3\text{ mM}/[\text{H}_2\text{O}_2]=6\text{ mM}$)
 —×— $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$ —▲— $\text{Fe}(\text{NO}_3)_3$ —○— FeCl_3
 —■— $\text{Fe}_2(\text{SO}_4)_3$

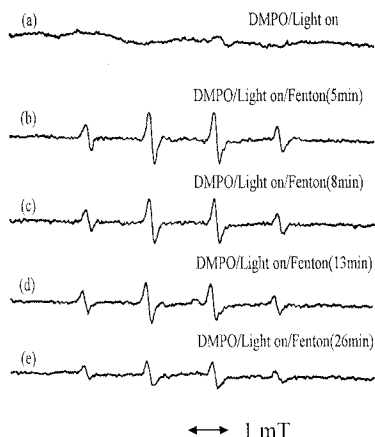


Figure 7. (a) EPR spectrum, recorded 50 mM DMPO with 180 W mercury lamp irradiation; (b) same as (a) but with Fenton after irradiation 5 min; (c) same as (a) but with Fenton after irradiation 8 min; (d) same as (a) but with Fenton after irradiation 13 min; (e) same as (a) but with Fenton after irradiation 26 min

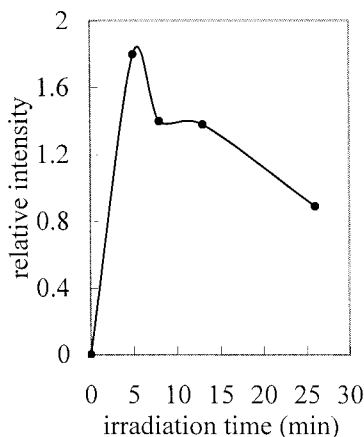


Figure 8. Relative intensity of DMPO-OH vs irradiation time

$a_N=a_H=14.9$ G, typical of the spin adduct DMPO-OH (Janzen et al. 1978). For the Fe^{2+}/H_2O_2 system, the intensity of the four characteristic peaks changed with increasing time after 180 W mercury lamp irradiation. The hydroxylation of DMPO by $OH\cdot$ creation was started by addition of 0.3 mM Fe^{2+} and 6 mM H_2O_2 to the incubation medium containing 50 mM DMPO.

The time dependence of the radical concentrations was traced in order to investigate the reaction behaviors of the spin adducts. The signal intensities (peak height) in Figure 8 were obtained from the amplitude of the second line for each 4-lined signals (in Fig.7). It was possible to obtain the growth of DMPO-OH signal as a function of the irradiation time which showed the intensity increased with the irradiation time and leveled off as it proceeded.

Using a radical-based theory of Fenton catalysis and direct evidence obtained from EPR, it was possible to postulate all photolytic reactions that may contribute indirectly or directly to $OH\cdot$.

In conclusion, the photo-Fenton process proved to be very powerful in treating wastewater containing diesel oil. Under optimal conditions: 0.3 mM Fe^{2+} , 6 mM H_2O_2 , pH=3 and 500 W mercury lamp irradiation, the initial concentration (50 ppm) of diesel oil solutions was reduced by about 82% within 18 min. The importance of individual reactions depend on the concentration of H_2O_2 and the light intensity. The appropriate amount of Fe^{2+} catalyzed and accelerated the reaction. The final photodegradation efficiency of diesel oil was affected by differing iron valence and Fe^{3+} -complexing anions. Photodegradation efficiencies decreased in the following order for iron salts: $Fe_2(SO_4)_3 < FeCl_3 < Fe(NO_3)_3 < FeSO_4 < Fe(C_2O_4)_3^{3-}$. The photodegradation of diesel oil by the advanced oxidation processes (AOPs) studied in this work can therefore be attributed to a radical mechanism initiated by the reaction between hydroxyl radicals and diesel oil.

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