RESEARCH ARTICLE

CATALYTICAL DEGRADATION OF DIESEL CONTAMINATED SOIL USING SMECTITE-Fe CATALYST WITH H_2O_2

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ABSTRACT

Currently, the types of treatment for oil-contaminated soil include soil vapor extraction (SVE), biological decomposition, solvent extraction, air stripping, activated carbon adsorption, and oxidation. Among these, solvent extraction, air stripping and activated carbon adsorption can only deal with the transfer between phases and must be supported with other types of treatment to complete remediation. Moreover, they are costly and could destroy local ecological systems. The objective of this study is to explore the fastest degradation rate of diesel contaminated soil and conditions needed for it through batch experiments, in which commercially available smectite is used as a catalyst carrier, modified into nano smectite-Fe catalyst using Fe^{+3}, and reacted with H_2O_2 to treat diesel contaminated soil. In terms of the basic properties of the test soil: the Lo series soil, it is characterized by high clay content, microscopic particles, relatively large specific surface area, extremely high cation exchange capacity, high soil density, and high organic matter content, which all contribute to the high diesel adsorption. As for the effects of smectite-Fe catalyst of various wt% and H_2O_2 of different concentrations on the degradation rate of diesel contaminated soil, the result shows that the higher the concentration of H_2O_2, the higher the degradation rate of diesel, since smectite-Fe catalyst facilitated the formation of •OH at high H_2O_2 concentration during the beginning of the reaction. However, the degradation rate of diesel declined, and the shielding effect occurred more often when H_2O_2 of more than 5~10% of the total weight and more smectite-Fe catalyst were added to the catalytic reaction. Hence, it can be inferred that excessive H_2O_2 and smectite-Fe catalyst will exhaust catalytic sites. Although more electrons and •OH were formed when H_2O_2 reacted with the smectite-Fe catalyst, the amount of formed •OH decreased when the two reacted in the Lo series soil, signifying a decline in the catalytic activity.

INTRODUCTION

The reaction between Fe(II) and H_2O_2 (the Fenton reaction) occurs naturally in aquatic environments (White *et al.*, 2003), biological systems (Jomova *et al.*, 2012; Lee *et al.*, 2012), and is also employed in water treatment applications (von Sonntag, 2008). Although ubiquitous and an important source of reactive oxygen species (ROS), if $HO^•$ is indeed produced, the identity of the intermediate formed in this reaction has long been the subject of debate (Dunford, 2002; Remucal Keenan and Sedlak, 2011). It is generally accepted that •OH is formed under acidic conditions and in the absence of ligands. However, an alternative mechanism invoking higher valent Fe complexes such as Fe(IV), first proposed by Bray and Gorin (1932), is also consistent with many findings (Kremer, 1999).

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Under circumneutral conditions the mechanism is particularly controversial (Remucal Keenan and Sedlak, 2011), with recent studies now mostly in agreement that at higher pH the product of the Fenton reaction with inorganic Fe(II) shifts to a species other than $HO^•$, possibly to a high-valent Fe species such as Fe(IV) (Hug and Leupin, 2003; Keenan and Sedlak, 2008; Bataineh *et al.*, 2012; Lee *et al.*, 2013). The underlying cause of this is not clear. The presence of organic ligands that are important to the speciation of Fe(II) in natural waters (Hopwood *et al.*, 2015), as well as those employed to solubilize Fe under circumneutral conditions in industrial practices, complicates this further. In the present study the oxidation of inorganic Fe(II) and Fe(II)L by H_2O_2 was examined under oxic conditions at low micromolar concentrations of Fe(II), combining measurements of Fe(II) oxidation kinetics, $HO^•$ production kinetics, and competition between well-defined competitive $HO^•$ scavengers and the $HO^•$ trapping agent phthalhydrazide (Phth). Kinetic modeling was then used to quantitatively examine whether $HO^•$ was the

key intermediate formed. By employing oxic conditions with relatively low concentrations of Fe and H_2O_2, the fate of intermediate organic radicals was determined by well-defined O_2-mediated pathways, resulting in minimal interference to the $Fe(II)L-H_2O_2$ system under study. This approach, combined with quantitative kinetic modeling incorporating the fate and further interaction of intermediate organic radical species, has allowed the $Fe(II)L-H_2O_2$ reaction to be effectively isolated and studied. A critical aspect of this approach is being able to reasonably predict the actual fate of any oxidizing radical formed, as well as the kinetics and mechanism of Fe(II) oxidation [and potentially Fe(III) reduction] in the presence of the ligand (Fujii *et al.*, 2008; Miller *et al.*, 2012). This study examined the effects of smectite-Fe catalyst on the degradation rate of diesel in contaminated soil by conducting catalytic degradation with H_2O_2 of different concentrations and smectite-Fe catalyst of different wt% using the self-synthesized smectite-Fe catalyst. It is hoped that this study can provide not only a fast and effective treatment for contaminated soil, but also serve as reference for soil remediation in the future.

MATERIALS AND METHODS

Sources of test soils: The sample soil was obtained from Neipu Township in Pingtung County, Taiwan. It is a kind of oxidized diluvium soil containing abundant iron and aluminum oxides and is characterized by fine texture. Its high iron and aluminum oxide content makes it an ideal catalyst carrier. The Lo series soil was dried at room temperature for 2 d after being collected. After impurities were removed, the soil was ground with glass bottles and run through 2mm sieves before being stored in boxes, pending an analysis on its basic properties.

Preparation of diesel contaminated soil: After preconditioning (drying, breaking down, grinding, and sieving), the Lo series soil was used to concoct 0.4% diesel contaminated soil. The contaminated soil was later placed in an ethane-acetone (1:1, v/v) solvent and shaken for 2 h at room temperature. After putting the mixture aside for 2 d, the diesel contaminated soil for our experiment was obtained.

Purification and preparation of sodium saturated smectite: Put 60 g commercially available smectite into a 2-liter beaker, and add 1.8 liters of deionized water to it. After stirring, soak it for days to fully expand it. After it is expanded, take 250 ml of the smectite suspension out of the beaker. Filter sand using the wet sieving method with a 300-mesh sieve. Transfer the filtrate to a 1-liter sedimentation cylinder, and add deionized water to make 1 liter. Leave it to naturally sediment after stirring it rigorously with a stirring rod. Siphon the suspension at the top of the sedimentation cylinder by 10 cm 8 hours later. Use an 18000 rpm high-speed centrifuge to have the suspension centrifuged. Perform sodium saturation of the smectite obtained after centrifugation with 1 M NaCl solution. Next, grind the saturated smectite into powder with an agate mortar after freeze drying it, and obtain the sodium saturated smectite.

Preparation of smectite-Fe catalyst: We mixed ferric chloride ($FeCl_3$) and sodium hydroxide (NaOH) in the mole ratio of 2:1 and added 2 wt% of sodium saturated smectite into the mixture. The mixture was stirred for 48 h under 40℃. After setting it aside for several hours, we removed the chloride ions from it with 95% ethanol.

The modified smectite-Fe catalyst was then freeze-dried before being sintered at 350°C for 2 to 3 h. It was then stored after cooling to room temperature.

Fourier-transform infrared spectroscopy (FT-IR) of smectite and smectite-Fe catalyst: The principle of FT-IR is using rotations or vibrations of molecules to absorb radiation at the same frequency. The fingerprint and Eigen areas in FT-IR can help to determine the existence of isomorphous replacement structure or organic molecules in the smectite and smectite-Fe catalyst. Put the smectite and smectite-Fe catalyst and KBr powders in an oven. After heating them up and drying them for 48 hours, mix them evenly in a 1:10 ratio, and then grind the mixture with an agate mortar. Use a hydraulic press to press the mixture at 10 tons/hour, making it into a transparent foil. Put the foil in a spectrometer and perform an analysis with a scan range of 4,000 cm^{-1} to 400 cm^{-1}.

Field emission scanning electron microscope (FE-SEM) analysis of zero-valent iron: With a scanning electron microscope (SEM), this study observes the size of smectite and smectite-Fe catalyst and their distribution. The model in use is JEOL-6330, and its emitting energy comes from the field emission filament with high space and energy resolution.

The effects of various wt% smectite-Fe catalyst and H_2O_2 concentrations on the degradation rate of diesel contaminated soil at room temperature. We took 4.0 g of the Lo series soil and concocted 0.4% diesel contaminated soil, to which smectite-Fe of three wt% (0.2 wt%, 0.5 wt%, and 1 wt%) were added as catalysts. We then added H_2O_2 of eight concentrations to the soil to study the catalytic degradation rate of diesel in the contaminated Lo series soil at room temperature.

RESULTS AND DISCUSSION

Analysis of the basic properties of the Lo series soil: Table 1 shows that the Lo series soil is high in iron and aluminum oxides, but low in sand grains, which only takes up 14.6% of the composition. In terms of texture, the Lo series soil has extremely high clay content of up to 53%. It also has particularly small particles, relatively large specific surface area, impressively high cation exchange capacity, high soil density, and high organic matter content. The mentioned properties all contribute to its high diesel adsorption.

Results of FT-IR analysis of smectite and smectite-Fe catalyst: Figures 1 and 2 show the infrared spectroscopy analysis results of the smectite and smectite-Fe catalyst, respectively. Figure 1 shows many significant and complex wave crests in the following wavenumber sections in the fingerprint area: 415~600 cm^{-1} and 750~1170 cm^{-1}; they represent strong bonds between impure silicates (Si-O) and silicates (O-Si-O) within the silicate mineral. Since a part of Si^{4+} within the silicates layer (tetrahedral layer) is replaced by Al^{3+} and many metal ions within the metal ion layer (octahedral layer) can go into the metal ion layer, various absorption characteristics of the octahedron's OH bending vibrations will be formed. If the octahedron contains aluminum only, its absorption peak is approximately 920 cm^{-1}; if it contains iron only, its absorption peak is approximately 820 cm^{-1}; if it contains both iron and magnesium, its absorption peak is approximately between 820~920 cm^{-1}. A further interpretation of the absorption area suggests that a split and

Table 1. Results of an Analysis on the Basic Properties of the Lo Series Soil

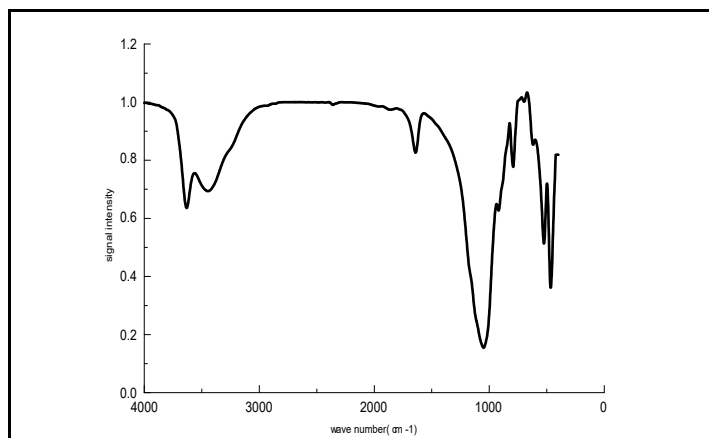| soil	Water content %	pH	CO_3^{2-} %	CEC cmole/kg	Particle Size (%)			texture	organic matter content
					sand	silt	clay		
Lo series soil	3.33	4.21	0.63	11.96	14.6	32.4	53.0	clay	1.28

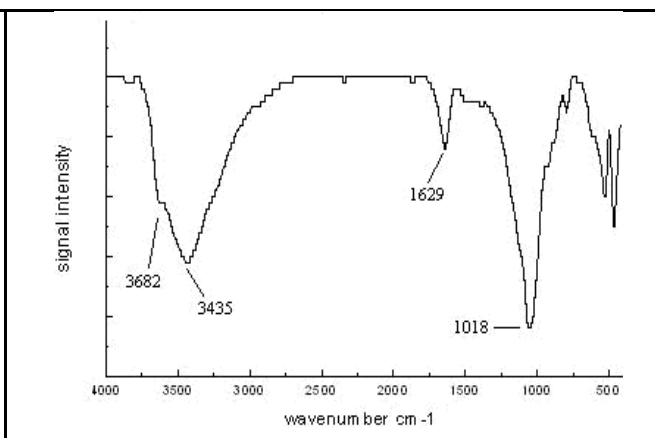**Figure 1. FT-IR spectrum of the smectite (before being sintered at [] temperature**

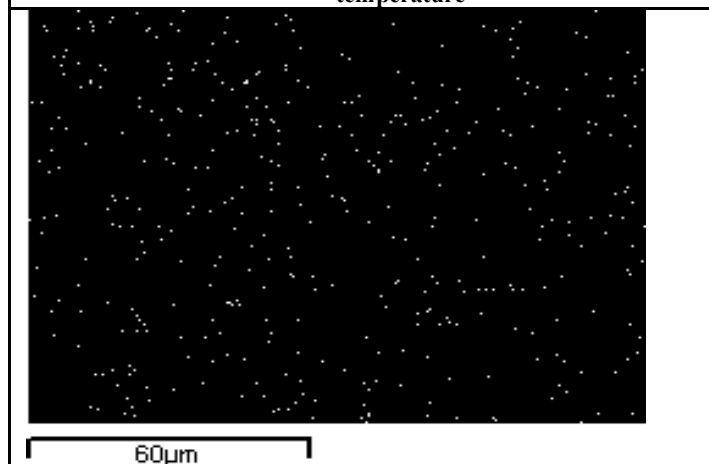**Figure 2. FT-IR spectrum of the smectite-Fe catalyst (sintered at 350°C)**

60μm

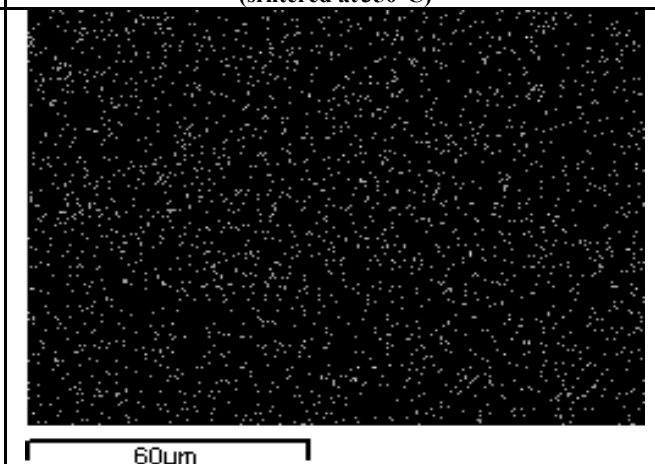**Figure 3. FE-SEM analysis of the smectite**

60μm

Figure 4. FE-SEM analysis of the smectite-Fe catalyst

shift occurs in the OH absorption peak between 3200 cm^{-1}~3700 cm^{-1}; the silicon within the tetrahedron will also be replaced by aluminum. Figure 2 shows that the structure of smectite-Fe catalyst remains intact after being sintered at 350°C for 2 hours; it still keeps the absorption band of clay minerals with inherent characteristics. As such, a catalyst carrier will still have a good clay structure via complex modification and sintering, whereby it can be used as a good catalyst.

FE-SEM analysis of smectite and smectite-Fe catalyst: Figures 3 and 4 show the elemental mapping of the smectite and the smectite-Fe catalyst via SEM-EDS. White spots represent the iron content in the minerals. From Figure 3, we can see that saturated smectite clay mineral has low iron content. On the other hand, Figure 4 indicates that the iron content in the smectite clay increased after Fe^{3+} was transferred to the mineral. Also, the size of all particles in the smectite-Fe catalyst was at the nano level. 3.4Effects of smectite-Fe catalyst of various wt% and H_2O_2 of different concentrations on the degradation rate of diesel contaminated soil. Figures 5 and 6 present the diesel degradation rate after the smectite-Fe catalyst of three wt% (0.2 wt%, 0.5 wt%, and 1wt %) and H_2O_2 of eight concentrations (0.05%, 0.1%, 0.2%, 0.3%, 0.5%, 1%,

5%,10%) reacted in the diesel-contaminated Lo series soil. Since oxidation of H_2O_2 is non-selective, the dose of oxidant used in this kind of experiment varies based on the basic properties of soils because it reacts with other reducing agents or oxidizable materials before reacting with target contaminants. Hence, the amount of H_2O_2, as well as the amount and type of catalyst, can largely influence the degradation rate of target contaminants (Pecchi *et al*., 2001). Figures 5 and 6 show that during the early stage of the reaction, the diesel degradation rate reached the highest level of 58% when 1 wt% smectite-Fe catalyst and 0.3% H_2O_2 were added at the 12th h into the reaction, and that the concentration of formed •OH was the highest. The diesel degradation rate rose when more H_2O_2 was added because H_2O_2 at high concentrations also decomposed to form more •OH. A study by Mueller *et al*. (2012), in which chlorophenol was degraded with goethite, demonstrates that while 0.4 g/L of goethite eliminated chlorophenol, an increased amount of goethite would decrease the amount of chlorophenol being removed. This result occurred because goethite at high concentrations hampered iron from dissolving, thus forming less ferrous ions; it was unable to produce •OH, which in turn resulted in a decreased degradation rate. The Lo series soil did not cause the degradation rate to drop because it consisted
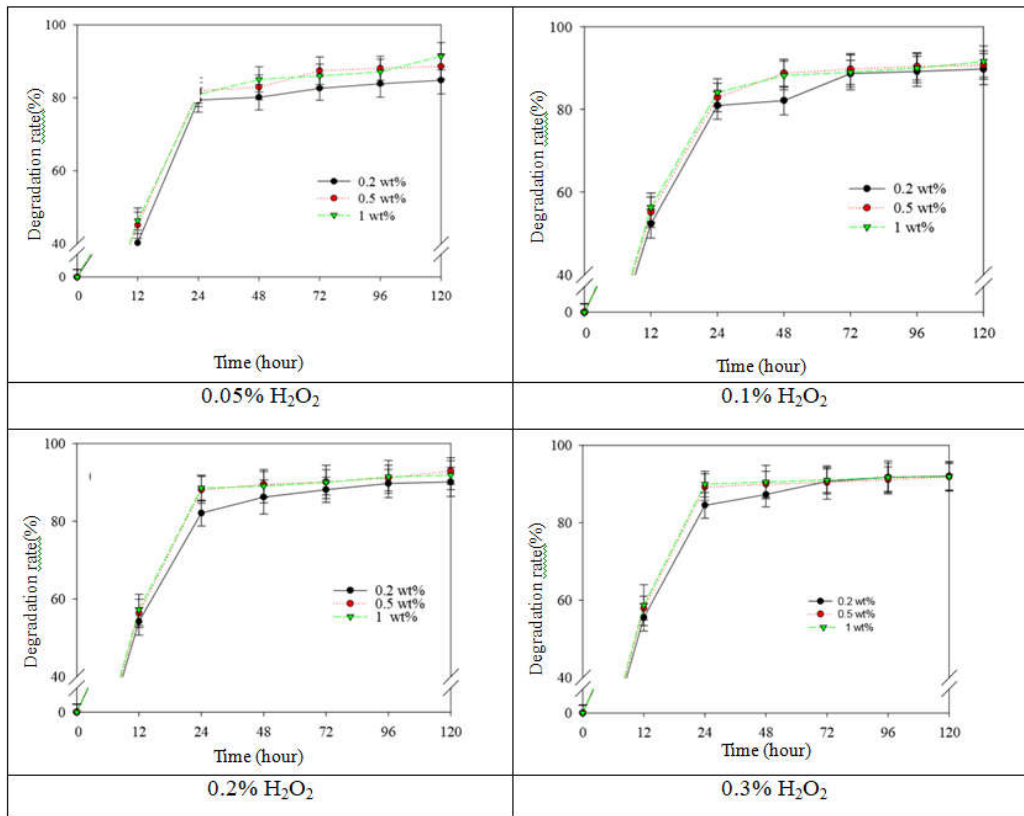
Figure 5. Effects of H_2O_2 of different concentrations and s mectite-Fe catalyst on the degradation rate of diesel contaminated soil (0.05~0.3%)
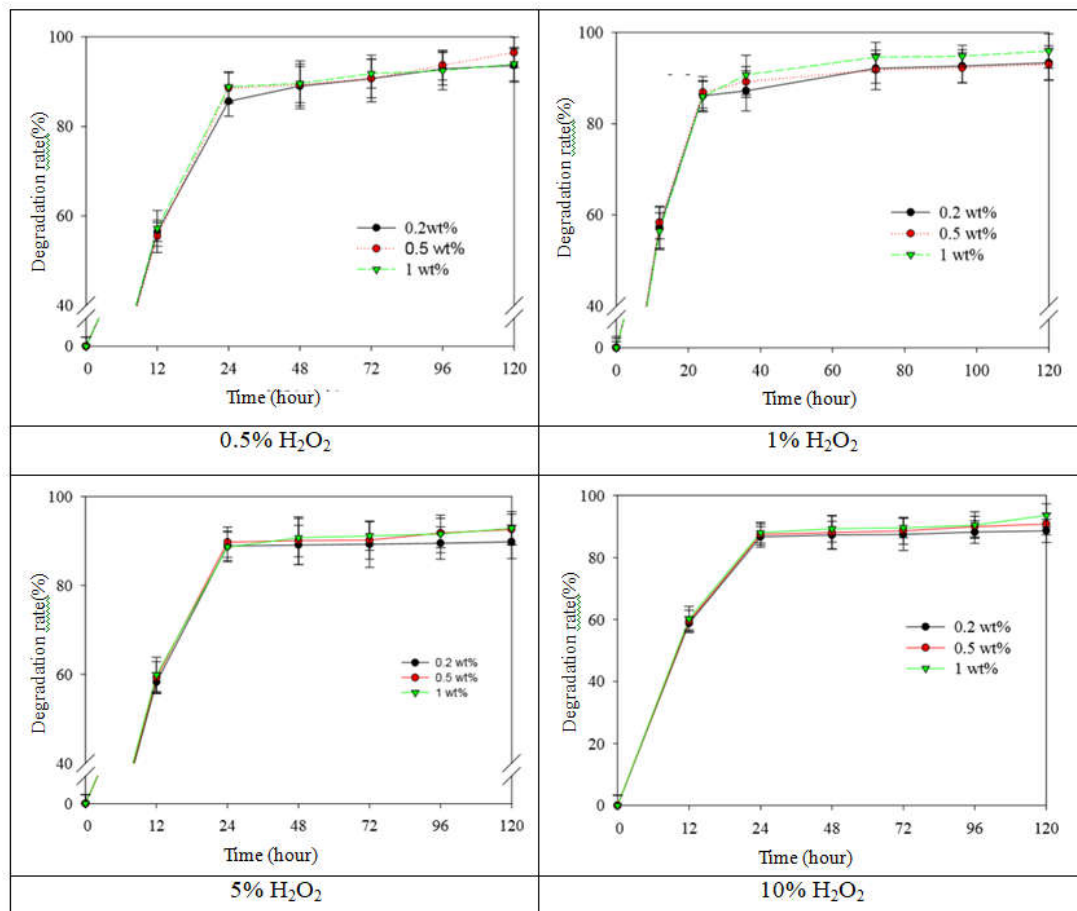

Figure 6. Effects of H_2O_2 of different concentrations and smectite-Fe catalyst on the degradation rate of diesel contaminated soil (0.5~10%)

mostly of clay and was low in goethite content, as shown in Table 1, meaning that it did not impede iron from dissolving (Adeleye *et al.*, 2016). However, Figure 6 shows that the diesel degradation rate declined as more smectite-Fe catalyst and H_2O_2 exceeding 5~10% of the total weight were added to the reaction, suggesting that the occurrence of shielding effect increased as the percentages of H_2O_2 and smectite-Fe catalyst in the soil increased (Wu *et al.*, 2009). This means that excessive H_2O_2 and smectite-Fe catalyst took up too many catalytic sites. Although more electrons and •OH were formed when H_2O_2 reacted with smectite-Fe catalyst, fewer •OH were formed when the two reacted in the Lo series soil. This outcome reflects a decline in catalytic activity. Furthermore, since H_2O_2 also reacted with •OH, it reduced the amount of formed •OH that could react with diesel.

An increase in the amount of H_2O_2 will lead to lower degradation rate.

Conclusion

This study explored the highest degradation rate of dieselcontaminated soil using commercially available smectite as a catalyst carrier, modifying it into nano smectite-Fe catalyst with Fe^{+3}, and having it reacted with H_2O_2 to treat diesel contaminated soil. An observation of the self-synthesized smectite-Fe catalyst under an FE-SEM indicates that iron content in the sodium-saturated smectite decreased, while iron content in the smectite that underwent Fe^{3+} exchange increased. Furthermore, the size of all smectite-Fe catalyst particles was at the nano level. We studied how smectite-Fe catalyst of various wt% and H_2O_2 of eight different concentrations influenced the degradation rate of diesel in the contaminated Lo series soil at room temperature. The results indicate that the shielding effect occurred more easily when H_2O_2 of more than 5~10% of the total weight and more smectite-Fe catalyst were added to the reaction because excessive H_2O_2 and smectite-Fe catalyst at high concentrations take up more catalytic sites. While more electrons and •OH were formed when H_2O_2 reacted with smectite-Fe catalyst, less •OH was formed when the two reacted in the Lo series soil, signifying a decrease in the catalytic activity. Nano-level smectite-Fe catalyst has been widely applied to a variety of environmental remediation works; they appear to be especially effective when it comes to the remediation and restoration of soil and groundwater pollution control sites.

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