Review on catalytic oxidation degradation of oil-contaminated soil by Fenton-like reagent

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Abstract: Petroleum-contaminated soil, whose soil availability is in rapid decrease and which also does great damage to other living things, is greatly different from the natural soil. Therefore, it is necessary and urgent to restore the oil-contaminated soil. In this paper, the current status of catalytic degradation of oil-contaminated soil using Fenton’s reagent is reviewed, including mechanism of traditional Fenton’s reagent, Fenton-like catalyst, photo-Fenton catalysis, and other modification.

1. Introduction

In industrial society, a large amount of petroleum is continuously extracted from onshore or offshore oil fields, and it is the key factor which maintains normal operation of our society. However, for certain reasons petroleum and the preliminary processed products (such as gasoline, kerosene, diesel, heavy oil, and lubricating oil, etc.) leak into the soil, and contaminate the soil during the soil exploitation, transportation and processing. The physical and chemical properties of the soil will change when it is polluted by oil [1]. Meanwhile the microbes, animals and plants in soil are significantly affected. Tang et al [2] found that the soil bacteria will be completely inhibited when the oil content in soil is above 1%. With the oil content of 3%, no worms can survive for more than 7 days. The germination inhibition of maize and wheat is 51.3% and 48.4%, respectively. Therefore, it is urgent to repair the oil-contaminated soils for soil availability and ecological health.

Remediation technology can be generally divided into the following categories: bioremediation, physical remediation and chemical remediation [1,3]. Bioremediation is a method which degrades pollutant via function of special organism, it is cheap, but takes a long time [4]. A common physical remediation is thermal treatment which repairs the contaminated soil by incineration or pyrolysis. It is quick, efficient but costly. The volume of thermal treatment is small and the secondary pollution may arise. The way repairs soil by using surfactants can in a short repair period, and can operate in situ, but the problem is that surfactants may remain in the soil that may cause secondary pollution. The chemical oxidation is a way destroying organic pollution in the soil by using oxidants such as hydrogen peroxide or ozone to achieve the purpose of repair. In this way, the repairing period is short...
and the repairing performs well, but there are some requirements for it and soil is easily to be affected. Representative method of chemical oxidation is Fenton's reagent or Fenton-like reagent method. The core of this method is the catalytic oxidation performance to rapidly generate a large number of free radicals. The high oxidizing free radicals can oxidize or even mineralize organic pollutants, thereby achieving the purpose of repair. In this paper, the current status of catalytic degradation of oil-contaminated soil using Fenton’s reagent is reviewed, including mechanism of traditional Fenton’s reagent, Fenton-like catalyst, photo-Fenton catalysis, and other modification.

2. Catalytic oxidation degradation of oil-contaminated soil by Fenton-like reagent

2.1 Mechanism of traditional Fenton’s reagent

The traditional Fenton reagent refers to an oxidation system composed of divalent iron salt and hydrogen peroxide. Hydrogen peroxide releases a large amount of hydroxyl radicals under the catalysis of divalent iron when hydrogen peroxide and divalent iron salt are mixed, and hydroxyl radical is a very effective non-selective oxidant, so the system is highly oxidizing for organic pollutants, and often used in water treatment as advanced oxidation technology. With the development of the soil remediation industry, it has gradually been applied to the repair of soil sites.

The main reaction mechanism of Fenton’s reagent is shown in Figure 1. and sees below equation:\n
\[ \text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{OH}^\bullet + \text{OH}^- + \text{Fe}^{3+} \]

\[ k_1 = 70 \text{M}^{-1} \text{s}^{-1} \] \hspace{1cm} (1)

Although the traditional Fenton’s reagent performs well in the degradation of oil contaminants in soil, it is difficult to be practically applied due to the following disadvantages:

1. Oxidation conditions are strict and need to be maintained near pH 3;
2. \( \text{Fe}^{2+} \) is easily consumed in the reaction that will affects the reaction;
3. Hydroxyl radical quenching is fast, organic matter may not fully oxidized.

Therefore, the researchers have modified the Fenton’s reagent to increase the applicability of Fenton's reagent, and the modified Fenton’s reagent is called the Fenton-like reagent. The following is a review of Fenton-like reagents and their repair mechanisms that have emerged in recent years.

2.2 Fenton-like catalyst

2.2.1 Homogeneous catalyst. The catalyst in the traditional Fenton’s reagent is \( \text{Fe}^{(II)} \), which consumes faster and reacts in a shorter time when reacting with hydrogen peroxide, while \( \text{Fe}^{(III)} \) reacts slower with hydrogen peroxide, and the reaction time is longer. Therefore, some researchers have used \( \text{Fe}^{(III)} \) instead of \( \text{Fe}^{(II)} \) as a catalyst. In the related research, \( \text{Fe}^{(III)} \) showed better repair effect than \( \text{Fe}^{(II)} \), which may be due to avoiding consumption of \( \text{H}_2\text{O}_2 \) and hydroxyl radicals that oxidize \( \text{Fe}^{(II)} \) to \( \text{Fe}^{(III)} \) at the beginning of the reaction. However, there are different catalytic effects when using the various iron salts as the source of \( \text{Fe}^{(III)} \). This is due to the different lifespan of hydroxyl radicals generated between different iron salts, in which perchlorate and nitrate as catalysts are better than sulfates and phosphates.

But, both \( \text{Fe}^{(II)} \) and \( \text{Fe}^{(III)} \) need to be carried out under the environment of pH 3, and the pH requirement of \( \text{Fe}^{(III)} \) is more strict, which will improve the difficulty and cost of repair, and will cause disadvantage to the site such as acidification of soils, changes in soil ecology that are not conducive to joint bioremediation techniques.
In order to avoid these problems, the researchers add chelating agents to the Fenton system. The role of the chelating agent is to make the catalytically active component in catalyst more stable, allowing the reaction to proceed under neutral conditions while prolonging the reaction time to improve the repairing effect. Chelating agents often used are ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), ethylenediamine disuccinic acid (EDDS), sodium N,N′-bis(carboxymethyl)glutamic acid (GLDA), ethylenediamine-N,N′-bis(o-hydroxyphenyl)acetic acid (EDDHA), sodium pyrophosphate (SP), sodium citrate (SC), oxalic acid, succinate, citric acid, citrate, cyclodextrin, etc.

Ferric or ferrous ion and chelating agent can form a chelate when the chelating agent is added to the oxidation system, and the iron in the chelate state has a lower reaction rate than the homogeneous Fenton system. Researchers use iron inorganic chelate, and its repairing effect is often superior to other organic chelating agents. Ma et al.[12] used EDDHA as a chelating agent combined with traditional Fenton’s reagent to repair polychlorinated biphenyl (PCB) in oily soil. The experimental results showed that the PCB removal rate in soil reached 77.1%. However, the soil pH dropped from the initial 7.6 to 7.2. This is due to the incomplete oxidation of organic matter leading to the production of organic acids, and compared to the Fenton system (Fe²⁺/SP/H₂O₂) using sodium pyrophosphate as a chelating agent, the Fe²⁺/EDDHA/H₂O₂ system produces too little OH⁻ to balance the acid, the combination of these two reasons lead to a drop in soil pH. In contrast, the pH of the soil treated by the sodium pyrophosphate system is only slightly decreased. The reason is the oxidized substance mainly produced by the Fe²⁺/SP/H₂O₂ system is a hydroxyl radical (accounting for 90%). Therefore, it has excess hydroxide to neutralize the acid produced.

Most of the chelating agents discussed above are organic, when organic chelating agents are added to the Fenton system, they usually compete with the oil components in the soil, causing a partial loss due to oxidation, while inorganic chelating agents do not react with hydroxyl radicals and therefore have higher oxidation efficiency relative to organic chelating agents[12]. Phosphate is a commonly used inorganic chelate, and its repairing effect is often superior to other organic chelating agents. Ma et al.[12] compared sodium pyrophosphate with other common organic chelating agents to improve Fenton’s reagent in repairing oily soil. The experimental results showed that sodium pyrophosphate modified Fenton’s reagent was the most effective.

2.2.2 Heterogeneous catalyst. Traditional Fenton’s reagent uses a homogeneous catalyst that has certain pH requirements and may cause soil acidification. In order to avoid these problems, some researchers use iron-containing minerals such as magnetite (Fe₃O₄), goethite (α-FeO(OH)), hematite (α-Fe₂O₃), ferrihydrite (α-Fe₁₀O₇·9H₂O) as heterogeneous catalysts to catalyze oxidants. And usually, the heterogeneous Fenton system has a lower reaction rate than the homogeneous Fenton system[12].

Goethite is a common iron-bearing mineral, and its catalytic mechanism is as follows and sees Figure 2:[13]:

\[
\begin{align*}
\text{Fe}^{III} \cdot \text{OH} + \text{H}_2\text{O} &\rightarrow \text{Fe}^\equiv \text{O}_2\text{H} + \text{H}_2\text{O} \quad (2) \\
\text{Fe}^{III} \cdot \text{O}_2\text{H} &\rightarrow \text{Fe}^\equiv \text{O}_2\text{H}^+ \quad (3) \\
\text{Fe}^\equiv + \text{H}_2\text{O} &\rightarrow \text{Fe}^{III} \cdot \text{OH} + \text{OH}^- + \text{H}_2\text{O} \quad (4) \\
\text{Fe}^{II} + \text{O}_2 &\rightarrow \text{Fe}^{III} \cdot \text{OH} + \text{HO}_2^- \quad (5) \\
\text{HO}_2^- &\rightarrow \text{H}^+ + \text{O}_2 \quad (6) \\
2\text{Fe}^{II} + 2\text{H}_2\text{O} + \text{HO}_2^-/\text{O}_2^- &\rightarrow 2\text{Fe}^{III} \cdot \text{OH} + \text{H}_2\text{O}/\text{OH}^- + \text{O}_2 \quad (7)
\end{align*}
\]
Figure 2. Schematic diagram of the catalytic mechanism of goethite catalyzed H$_2$O$_2$[13].

One advantage of heterogeneous catalysts is that they can be catalyzed under neutral conditions, Usman et al[14] treat weathered oil (WO) and fresh crude oil (CO) contaminated soil by magnetite catalyzed Fenton-like (FL) and activated persulfate (AP) oxidation at circumneutral pH. Experimental results indicated that approximately 70–80% of WO and 80–90% of CO removal respectively could be achieved by both H$_2$O$_2$ and persulfate treatments after one-week treatment, soluble Fe (II) as catalyst instead of magnetite and only 10–15% of degradation was achieved for oxidation experiments with or without soluble Fe (II) addition.

Different minerals have different catalytic effects, and Kong et al[15] used magnetite and goethite as catalysts in the Fenton system, the experimental results showed that magnetite as catalyst was better than goethite in the Fenton system to repair oil-contaminated soil. This may be due to the simultaneous presence of Fe(II) and Fe(III) in the magnetite, which dissolves into the liquid phase by the dissolution of the mineral, thereby increasing the catalytic efficiency of H$_2$O$_2$. But dissolved iron ions will partially precipitate on the mineral surface, gradually reducing the catalytic effect.

In addition to minerals, researchers also have used zero-valent iron as a catalyst. Jamialahmadi et al[16] used magnetite and zero-valent iron (ZVI) with a particle size of 10 microns as a catalyst to catalyze H$_2$O$_2$ to repair diesel-contaminated soil (5 000 mg/kg as initial TPH concentration). The experimental results showed that the removal rate of TPH by magnetite and zero-valent iron could reach 57% and 67%, respectively. Fenton reactions can noticeably enhance speed of the treatment process if the particle size of the heterogeneous catalyst is further reduced to the nanometer scale.

Mirzae et al[17] used synthetic nanomagnetite as a catalyst to catalyze H$_2$O$_2$ repair oil-contaminated soil from Mahshahr, result showed the highest TPH removal could reach 74.20% (32 030 mg/kg as initial TPH concentration) at pH 3.

It is also a modified way to develop novel catalysts by combining soil natural properties. Natural chelating agents such as humic acid and fulvic acid are present in soil organic matter (SOM). Iron ions can be combined with SOM in soil to form Fe-SOM catalyst through some special treatment[18]. Fe-SOM produces OH- by catalyzing H$_2$O$_2$ to achieve the purpose of oxidizing organic matter. Xu et al[18] combined iron ions with soils with different SOM contents to form Fe-SOM, then added Fe-SOM to artificially oil-contaminated soil, and used hydrogen peroxide as oxidant to repair artificially oil-contaminated soil. The experimental results showed that the TPH removal rate of the catalyst prepared by the soil with high SOM content was 67%, and the catalyst made by soil that without SOM removal rate was 6%. Iron ion’s ability to catalyze hydrogen peroxide is superior to that of iron ions alone when it combines with SOM. Xu et al[18] investigated the effect of bind Fe and SOM in Fenton system to repair crude oil contaminated soil. The results showed that the long-chain alkanes removal (C$_{21}$-C$_{30}$) in the Fenton system with Fe-SOM was 1.6 times higher than that achieved in the Fenton system with typical Fe (Fe unbound to SOM).
From the above research we can know that heterogeneous catalyst can catalyze hydrogen peroxide effectively under neural condition. Therefore, remediation cost can reduce and secondary pollution due to addition of other chemicals can be avoided if minerals are used as heterogeneous catalysts.

2.2.3 Photo-Fenton catalysis. When Fenton’s reagent is irradiated with ultraviolet or visible light while oxidizing organic matter, inorganic substances will be generated fastly. The Fenton’s reagent that enhanced by photo is a kind of Fenton-like, is also called photo-Fenton. The photo enhancement is mainly due to the photochemical properties of Fe(III)[19] that the Fe(III) complex excites ligand-to-metal charge transfer (LMCT) under light conditions, and the Fe(III) complex is converted into Fe(II) and oxidized ligand, $I_{ox}$, its reaction formula is as follows[20]:

$$Fe^{III}(L)_n + hv → Fe^{II}(L)_{n-1} + I_{ox}$$

(8)

The Fe(II) produced by photo enhancement can promote the Fenton reaction, and oxidation of the ligand may lead to further degradation of the target pollutant. And hydrogen peroxide is also catalyzed by ultraviolet light[21]:

$$H_2O_2 + hv → 2HO^*$$

(9)

Numerous studies have shown that photo-Fenton performed well in the treatment of oily water[22]. Therefore, this method applies in the treatment of oily soils is hopeful.

The oil-contaminated soil treatment process and remediation efficiency can be promoted by the synergistic use of ultraviolet light. Graciano et al [23] compared the remediation efficiency of photo-Fenton, Fenton’s reagent, and hydrogen peroxide for oil-contaminated soil (5 000mg/kg as initial TPH concentration). The results showed that the photo-Fenton could achieve 99% oil removal after 30 minutes treatment, and other methods couldn’t reach this removal rate even after 180 minutes treatment, and the best removal rate of Fenton’s reagent was 86.98%. The removal rate with hydrogen peroxide is 70.51%. Silva et al [24] performed photo-Fenton treatment on oil-contaminated soil with high endogenous iron concentration. The results indicated that 95% degradation rate could be achieved under the optimal conditions, in which polycyclic aromatic hydrocarbon (PAH) were removed more than 70%. And there without adjust the pH in the experiment, the natural light can be used to make the photo-Fenton process happen that can save cost and deuce the disturbance of microbial ecological environment caused by pH adjustment.

In summary, these attempts have proved that photo-Fenton is feasible for oil-contaminated soil remediation. However, many obstacles are still exist in the application of photo-Fenton. The biggest obstacle is that light can't penetrate the soil and can only effectively catalyze the soil layer with a few millimeters on the surface[25].

2.2.4 Other modification. There are some other ways to improve the repair efficiency, such as reducing the adsorption of oil on the soil that make oil easier to oxidize. Ahmadkalaei et al [26] added solvent ethyl lactate into traditional Fenton reagent in oil-contaminated soil treatment. The experimental results showed the addition of solvent ethyl lactate could reduce the time that reach the maximum TPH removal and increase the dissipation rate of TPH. Similarly, the addition of surfactants to soil will also increase the efficiency of oxidative repair. Yu et al [27] added a surfactant Tween 80 to enhance the desorption of petroleum hydrocarbons in the soil, which increased the recovery efficiency of activated sodium peroxodisulfate from 41.21% to 61.83%.

3. Conclusions
Fenton’s reagent has been widely used as an advanced oxidation technology in water treatment, but many difficulties arise when it applies in the soil. Therefore, the Fenton reagent needs to be modified for soil remediation. Many of the studies have shown that oil-contaminated soils can be repaired quickly and effectively by using Fenton-like reagents. And in soil remediation study, modification of Fenton-like reagents mainly focuses on the modification of catalysts. According to the current research, the heterogeneous catalyst has a lower reaction rate than the homogeneous catalyst. But, if minerals are used as a heterogeneous catalyst, the cost can be reduced.
Major of the current research is conducted on artificially contaminated soil or low TPH of actually contaminated soil. Therefore, in the future, we should make the research more realistic, conducting the experiment by using actually contaminated soil, high TPH soil and weathered oil soil etc. In summary, these studies suggest that modifications of Fenton’s reagent have great significance in reducing the cost and improving the efficiency of oil-contaminated soil restoration.

Acknowledgments
Supported by the Zhejiang Province Natural Science Foundation of China (No. Y4080247), the Zhejiang Province Natural Science Foundation of China (LY17E090001), the National Natural Science Foundation of China (No.21376213), and the Opening Project of Guanxi Key Laboratory of Petrochemical Resource Processing and Process Intensification Technology (No. K002), China.

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