

Application of Advanced Oxidation Technology in Remediation of Petroleum Contaminated Soil

Yuhu Luo ^{1, 2, 3, 4, a, *}, Na Wang ^{1, 2, 3, 4, b}

¹Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Xi'an 710075, China

²Institute of Land Engineering & Technology, Shaanxi Provincial Land Engineering Construction
Group Co., Ltd., Xi'an 710075, China

³Key Laboratory of Degraded and Unused Land Consolidation Engineering, the Ministry of Natural
Resources, Xi'an 710075, China

⁴Shaanxi Provincial Land Consolidation Engineering Technology Research Center, Xi'an 710075,
China

^ayuhu_luo@163.com, ^b1370199046@qq.com

Abstract: As an important chemical raw material, petroleum has caused serious harm to the soil environment in the process of utilization. This article introduces the main advanced oxidation technologies such as Fenton oxidation technology, Fenton-like oxidation technology, persulfate oxidation technology, ozone oxidation technology, and permanganate oxidation technology, as well as these technologies in the remediation of petroleum contaminated soil In the application.

Keywords: petroleum pollution, soil remediation, advanced oxidation technology

1. INTRODUCTION

As the blood of modern industry, petroleum is an important industrial raw material and plays a vital role in the fields of energy, materials, and chemicals. However, the abnormal leakage of oil in the mining, processing, storage and transportation links often causes soil oil pollution. The oil that enters the soil and then enters the human body through the food chain causes harm to human health, causing a series of economic, environmental and social issues [1-3].

At present, soil oil pollution remediation technologies mainly include physical remediation technology, chemical remediation technology, and biological remediation technology. However, because petroleum contains a large amount of long-chain alkanes, cycloalkanes, and aromatic hydrocarbons and other difficult-to-degrade organic substances, it is difficult to degrade them by

conventional methods after these substances enter the soil. The advanced oxidation technology can produce groups with strong redox potentials, which are extremely active and can oxidize macromolecular organic matter into small molecules, even water and carbon dioxide, and cause less harm to the environment. It is the current stage of soil oil pollution control popular technology.

2. ADVANCED OXIDATION TECHNOLOGY

Advanced oxidation technologies mainly include Fenton oxidation technology, Fenton-like oxidation technology, persulfate oxidation technology, ozone oxidation technology, permanganate oxidation technology, and photocatalytic oxidation technology.

2.1 Fenton and Fenton-like oxidation technology

Fenton oxidation technology was discovered by French chemist Fenton HJ 1893. The mixed solution of hydrogen peroxide (H_2O_2) and ferrous ions has strong oxidizing properties. This is because Fenton's reagent can produce strong oxidizing carboxyl radicals $\cdot OH$ under normal temperature and pressure. Its activity is extremely strong ($E=2.80 V$), which is 1.35 times that of ozone, second only to chlorine, and can be indistinguishable. Oxidizing the organic matter in the soil can oxidize many organic compounds such as carboxylic acids, alcohols, and esters to an inorganic state, even water and carbon dioxide, which has a significant effect on removing pollutants.

Because traditional Fenton reagents have many limitations, such as high pH requirements, low catalytic efficiency of catalysts and other shortcomings. Therefore, later generations improved Fenton's reagent and appeared Fenton-like reagent. Facing the increasingly serious problem of soil oil pollution, the use of Fenton-like oxidation method to degrade oil pollution in the soil has received more and more attention. With the continuous improvement of Fenton-like technology, it has gradually been used in actual projects to treat organic pollution on the site and achieved good results [4].

2.2 Persulfate oxidation technology

The reaction mechanism of persulfate is to cause its own O-O cleavage to produce strong oxidizing sulfate radicals ($SO_4^{\cdot -}$) through activation, and then react with target pollutants through electron transfer to oxidize organic pollutants. The activation methods of persulfate mainly include homogeneous activation and heterogeneous activation. The activator used in homogeneous activation is transition metal ion, and the activator of heterogeneous activation is solid metal ion. The ions that can be used to activate persulfate to generate free radicals mainly include Fe^{2+} , Cu^{2+} , Co^{2+} , Ag^+ , Mn^{2+} and so on. Fe^{2+} is often used as a persulfate activation catalyst because of its ubiquity, good activation effect and no toxic effect on the environment.

2.3 Ozone oxidation technology

Ozone is a highly oxidizing oxidant. Its oxidizing property is second only to F. It can oxidize and decompose organic matter to achieve the effect of decontamination. However, under normal temperature conditions, ozone alone has a slow degradation effect on organic matter. Therefore, under normal circumstances, ozone is catalyzed to produce hydroxyl radicals ($\cdot OH$) with strong oxidizing ability, so as to achieve higher oxidation efficiency. Ozone catalysts can also be divided into homogeneous catalysts and heterogeneous catalysts. Homogeneous catalysts mainly include

various metal ions and complexes, mainly Fe^{2+} , Fe^{3+} , and Mn^{2+} . Heterogeneous catalysts mainly include solid metals, metal oxides, and metals and metal oxides supported on supports. At the same time, activated carbon can also be used as a catalyst to catalyze ozone production OH .

Ozone oxidation technology has little impact on the soil environment. When ozone oxidation technology is used to degrade oil pollution in the soil, it will not be toxic to the microorganisms in the soil. After a week of use, the microorganisms in the soil return to normal. When ozone is used to repair oil pollution in the soil, it is related to the content of pollutants in the soil, the particle size of the soil, the moisture content, and the content of organic matter in the soil [5].

2.4 Permanganate oxidation technology

Compared with Fenton's reagent and persulfate, permanganate has lower oxidation and its redox potential is only $E^0=1.7\text{V}$, and the oxidation process is relatively gentle. During the oxidation process, O^- and HO_2 groups interact with oxygen ions to break the hydrogen bonds on the organic matter to achieve the removal of the organic matter. Commonly used permanganates are NaMnO_4 and KMnO_4 , but because of the high cost of NaMnO_4 , in actual engineering, KMnO_4 is often used as an oxidant to remove petroleum pollution in the soil.

In the process of removing petroleum in the soil, permanganate has lower requirements for pH, Therefore, compared with Fenton's reagent, it can be used in a wider range of soil remediation fields. Studies have shown that when permanganate removes diesel contaminated soil from soil, its removal rate is higher than Fenton's reagent and lower than persulfate reagent [6]. However, in the process of oxidizing soil organic pollution, MnO_2 will be produced, because its solubility is low, which reduces soil permeability, and also causes the pH of the soil to decrease, causing secondary pollution to the soil [7].

3. CONCLUSIONS AND PROSPECTS

In actual engineering, advanced oxidation technology is simple and convenient in operation and can save a lot of cost economically. Secondly, advanced oxidation remediation technology can greatly improve the efficiency of soil remediation. In addition, advanced oxidation technology has mild reaction conditions but high reaction efficiency, which can shorten the time of soil remediation and improve the anti-pollution ability of the soil after remediation. Therefore, advanced oxidation technology is of great significance in the remediation of petroleum-contaminated soil. However, the current research on the remediation of petroleum-contaminated soil by advanced oxidation technology is not perfect in practical application, and there are many problems that need to be solved urgently. Therefore, some suggestions are put forward for the problems existing in the application of advanced oxidation technology in practical engineering. (1) From the perspective of repair technology, it is an urgent need to seek a technology with simple operation and low cost. (2) From the perspective of environmental protection, soil remediation technology that is green and environmentally friendly and does not cause secondary pollution is more in line with the concept of harmonious development between man and nature. (3) From the perspective of scientific research, advanced oxidation technologies need to be studied in depth to fundamentally enhance the soil's own resistance to pollutants.

ACKNOWLEDGEMENTS

This paper was financially supported by the Research Project of Shaanxi Provincial Land Engineering Construction Group in China (DJNY2021-19).

REFERENCES

- [1] Wenxia Liu, Xiangyuan Meng, Jiancan Feng, et al., “Analysis of Cultivated Land Pollution in Zhongyuan Oil Field”, *Agricultural Environmental Protection*, 2002, Vol. 21 (1), p56-59
- [2] Kunlun, “The painful lesson of the oil pipeline explosion”, *Cities and Disaster Reduction*, 2010, Vol. (05), p46-47
- [3] P. W. Sammarco, S. R. Kolian, R. A. Warby, et al., “Distribution and Concentrations of Petroleum Hydrocarbons associated with the BP/Deepwater Horizon Oil Spill, Gulf of Mexico”, *Marine Pollution Bulletin*, 2013, Vol. 73 (1), p129-143
- [4] Ganglian Song, Jianbin Jiang, and Kecheng Zhu, “Application of Fenton oxidation method to repair an industrial site in Shanghai”, *Geological Hazard and Environmental Protection*, 2017, Vol. 28 (02), p106-110
- [5] Lu Ji, “Treatment of polycyclic aromatic hydrocarbons in simulated soil by in-situ ozonation method”, *Wuhan University*, 2004
- [6] K. F. Chen, Y. C. Chang, and W. T. Chiou, “Remediation of diesel-contaminated soil using in situ chemical oxidation (ISCO) and the effects of common oxidants on the indigenous microbial community: A comparison study”, *Journal of Chemical Technology & Biotechnology*, 2016, Vol. 91 (6), p1877-1888
- [7] R. L. Siegrist, M. Crimi, and T. J. Simpkin, “In situ chemical oxidation for groundwater remediation”, *New York: Springer*, 2011