Research Progress on the Removal of Organic Pollutants Removal by Sodium Persulfate and Calcium Peroxide

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Abstract. In situ chemical oxidation has the advantages of simplicity, rapidity and thoroughness in removing some biodegradable pollutants (such as trichloroethylene). This paper reviews the research progress of three environmentally friendly oxidants, hydrogen peroxide, calcium peroxide and sodium persulfate, in environmental remediation. This paper mainly traces back the literature from two aspects and summarizes the following: on the one hand, the mechanism of free radicals generated by catalytic activation of hydrogen peroxide, calcium peroxide and sodium persulfate; on the other hand, the main factors affecting the removal of groundwater chlorinated hydrocarbons and other organic pollutants by these three oxidants.

Introduction

In recent years, along with our country economic and accelerating process of industrialization, "half astern into three", "city back into the garden" policy of further implement, a large number of polluting enterprises were forced to move, the transformation or even shut down production, lead to the city and its surrounding areas appear a large number of industrial pollution of legacy abandoned field[1], causing serious pollution of groundwater and soil, especially with trichloroethylene serious, and the organic pollutant has the "three" effect, a serious threat to human body health[2-4], people urgently need to take quick and effective measures to governance.

Method for In-situ Remediation of Chlorinated Hydrocarbon Pollution

The treatment of chlorinated hydrocarbon pollution represented by TCE and PCE in groundwater has been studied abroad for decades. The treatment methods include ectopic remediation and in situ remediation. Ectopic remediation requires turning over and excavating the soil, so that the soil structure is damaged and the cost is high, which is suitable for the treatment of areas with small contaminated areas[5].In-situ remediation USES a variety of techniques to degrade or remove contaminants in the source area (aerated zone, groundwater). At present, existing in situ remediation technologies are mainly permeable reactive barrier (PRB) and other technologies that integrate biology, chemistry and physics[7]. In situ chemical oxidation (ISCO) is a method of feeding chemical oxidants into the contaminated in-situ regions to remove pollutants. This method relies on the strong oxidation of oxidants to break the chemical bonds of organic compounds such as chlorinated hydrocarbons and make them into harmless substances such as chloride ions, carbon dioxide and water. The chemical oxidants used must have little harm to the environment and be able to effectively destroy pollutants and make the generated oxidation products harmless[8].

Generally speaking, oxidants in ISCO should follow the following principles[9]: first, the reaction must be strong enough to remove pollutants through degradation, evaporation and precipitation, and eliminate or reduce the toxicity of pollutants; Secondly, the oxidants and reaction products should be harmless to human body. Finally, the restoration process should be practical and economical[10]. Common chemical oxidants are potassium permanganate (KMnO4), ozone (O3), hydrogen peroxide (H2O2), sodium persulfate (Na2S2O8) and calcium peroxide (CaO2).
Characteristics of in Situ Chemical Oxidation

Sodium Persulfate

Sodium persulfate was originally used to test the total nitrogen and total phosphorus in water samples [11]. It was later found that under thermal activation and transition metal activation, it can produce strongly oxidizing sulfate radical (SO$_4^-$·, E=2.6v) [12].

The sulfuric radical and hydroxyl radical produced by activation oxidize the pollutant. Such as Liang activated by heating method, sodium persulfate was studied in 20, 40, 50, 60°C down in addition to the efficiency of TCE and 1,1,1-trichloroethane, found in 20°C when sodium persulfate degradation of small amounts of TCE, rather than 1,1,1-trichloroethane degradation; But in 40, 50, 60°C when sodium persulfate can quickly degradation of TCE and 1,1,1-trichloroethane (13-14). Transition metal catalysis, Liang et al. added ferric ions to sodium persulfate solution and studied the effect of one-time addition and batch addition on the removal efficiency of TCE, and concluded that the removal efficiency of TCE by batch addition of ferric ions was higher than that by one-time addition. In addition, Liang et al. [15] also used zero-valent iron and ferric iron to activate sodium persulfate, and found that TCE can be removed as well, and the higher the pH value, the better the TCE removal [16].

Regarding the mechanism of the generation of free radicals by sodium persulfate to remove pollutants, the results of the Liang experiment are as follows [17-23]:

\[
S_2O_8^{2-} + \text{heat} \rightarrow SO_4^-·. \tag{1}
\]

or

\[
S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^-· + SO_4^- + Fe^{3+}. \tag{2}
\]

alkaline pH

\[
SO_4^-· + OH^- \rightarrow SO_4^- + HO^-. \tag{3}
\]

all pH

\[
SO_4^-· + H_2O \rightarrow SO_4^- + HO^- + H^+. \tag{4}
\]

Other scholars have also discussed the chain reaction process in the reaction process [24-25]:

\[
SO_4^- + RH \rightarrow SO_4^{2-} + R^- + H^+. \tag{5}
\]

\[
SO_4^-· + H_2O \rightarrow HSO_3^- + HO^-. \tag{6}
\]

\[
SO_4^-· + HO^- \rightarrow HSO_4^- + 1/2O_2. \tag{7}
\]

The acidic pH

\[
S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^-·. \tag{8}
\]

\[
S_2O_8^{2-} \rightarrow SO_4^-· + SO_4^{2-} + H^+. \tag{9}
\]

Sodium persulfate under 20 °C is very stable, it is both its advantages and its disadvantages. On the plus side, sodium persulfate may travel farther underground than hydrogen peroxide. Its disadvantage is that it is too stable to react with the pollutant, thus failing to achieve the purpose of removing the pollutant.

Fenton Technology

The Reaction of removal of pollution by hydrogen peroxide decomposition catalyzed by ferric ions is known as traditional Fenton Reaction. Ferric iron, first discovered by fenton in 1894, can greatly improve the efficiency of H$_2$O$_2$ in oxidizing malic acid [26]. In 1934, Haber and Weiss pointed out that the hydroxyl radical (HO•) was the dominant free radical in this reaction. The main action mechanism of the reaction is as follows [27]:

\[
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\[ H_2O_2 + Fe^{2+} \rightarrow HO + HO^- + Fe^{3+} \]  \hspace{1cm} (10)

\[ H_2O_2 + Fe^{3+} \rightarrow HO_2^- + H^+ + Fe^{2+} \]  \hspace{1cm} (11)

\[ HO^- + RH \rightarrow RH^- + H_2O \]  \hspace{1cm} (12)

\[ HO^- + H_2O_2 \rightarrow HO_2^- + H_2O \]  \hspace{1cm} (13)

\[ HO_2^- \rightarrow O_2^- + H^+ \]  \hspace{1cm} (14)

\[ HO_2^- + Fe^{2+} + H^+ \rightarrow H_2O_2 + Fe^{3+} \]  \hspace{1cm} (15)

\[ H_2O_2 \rightarrow HO_2^- + H^+ \]  \hspace{1cm} (16)

HO• produced by catalytic decomposition of \( H_2O_2 \) has no selectivity in pollutant removal and can quickly repair most of the chlorinated hydrocarbon pollution including TCE and various pollutants.

**Calcium Peroxide**

Calcium peroxide is a new oxidant for remediation of contaminated soil and groundwater. Calcium peroxide dissolves in water to produce hydrogen peroxide with a maximum release rate of 0.47g·HP/g·CP. Calcium peroxide is considered as "solid" hydrogen peroxide [28]. Compared with hydrogen peroxide, calcium peroxide is relatively stable and can release hydrogen peroxide slowly by controlling its solubility. Therefore, calcium peroxide can prolong the reaction time and make full use of calcium peroxide in repair. As an environmentally friendly oxidant, calcium peroxide also provides oxygen to microorganisms and promotes their bioremediation. In previous studies, Viisimaa et al. reported the use of calcium peroxide as a high-pressure carrier for ISCO to overcome the rapid release of hydrogen peroxide and oxygen caused by liquid hydrogen peroxide. In their study, calcium peroxide increased the bioremediation efficiency of PCBS [29]. Other applications of calcium peroxide in environmental remediation, including toluene oxide, tetrachloroethylene and polycyclic aromatic hydrocarbons, have also been demonstrated in some studies to promote bioremediation of soil contaminated with di-(2-ethylhexyl) phthalate and underground sewage contaminated with methyl tert-butyl ether [28,29,30-32]. Nano-CaO, in particular, has been widely concerned by researchers in recent years due to its characteristics of small particle size and large specific surface area, high reactivity and easy dispersion and migration in the underground environment [33]. In 2007, the United States Continental Remediations System took advantage of the nanometer CaO\(_2\) grout to remediate the oil tank leaks. After six months of treatment, the number of detectable pollutants in the plume dropped from 13 to one, with an average 94 percent reduction.

**Summary**

With the increasingly serious groundwater and soil pollution, it is urgent to find efficient and economical remediation technology. Calcium peroxide can be used as an activator of sodium persulfate, which has good remediation effect on contaminated groundwater and soil.

**References**


