Research Progress on degradation of Organic pollutants in Water Body by Iron-based Materials activated persulfate

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Abstract. The advanced persulfate oxidation technology has shown great potential in the efficient degradation of organic pollutants in water body, owing to its strong oxidation ability, easy operation and many other advantages. At present, the development of this technology focuses on the choice of activation mode of persulfate, and its essence lies in the cleavage of O-O bond in persulfate. Iron-based catalysts have been widely used in persulfate activation because of their advantages such as earth abundance, eco-friendliness and cost-effectiveness. In this paper, the methods and research progress of activating persulfate by iron-based materials (including nanometer zero-valent iron, common zero-valent iron, nanometer iron tetroxide) are reviewed. Finally, the existing problems and development direction of persulfate advanced oxidation technology in the current application are analyzed, in order to promote the development of related research work.

1. Introduction

With the development of China's economy, a large number of organic compounds have been synthesized and applied in the industries of printing and dyeing, pharmaceuticals, clothing and cosmetics. However, improper use and storage make organic pollutants enter the water environment and cause pollution, threatening the efficient utilization and protection of water resources. Organic pollutants were usually semi-volatile and would enter different environmental media such as soil, water and atmosphere¹⁻³, causing potential harm to aquatic organisms and human health. The persistence, long-distance migration and high toxicity of organic pollutants make organic pollution extremely difficult to control and remediation. The development of organic pollution control technology had become the problem that environmental scientists must face at present.

In recent years, advanced oxidation technology based on sulfate radical removal of organic pollutants had attracted much attention. Compared with Fenton oxidation method, ozone oxidation method, electrochemical oxidation method and other technologies, activated persulfate can produce sulfate radical (SO₄•⁻, E°=+2.50-3.10 V) with stronger oxidation capacity. In addition, SO₄•⁻ has a long half-life, a wide range of pH values, and is less affected by inorganic ions in water body⁴. Among the activated persulfate systems, the iron-based materials had attracted more and more attention and research due to their advantages of earth abundance, ecological friendliness and cost...
effectiveness. In this paper, the technology of activating persulfate by iron based materials to generate active free radicals were reviewed, and the reaction mechanism and recent research progress were introduced, in order to promote the further development of related research work.

2. Research status of persulfate advanced oxidation system
Activated persulfate technology is an advanced oxidation technology developed in recent years. Compared with other oxidants such as hydrogen peroxide, persulfate had the advantages of stable property, low cost and easy transportation. The solubility of sodium persulfate in water body is one order of magnitude higher than that of potassium persulfate, and the cost of sodium salt is relatively low, so it is the most commonly used oxidant for in-situ repair. When persulfate is used as oxidant alone, there is kinetic limitation\[5\], and the reaction is slow, but when persulfate anion is activated, sulfate radical (SO$_4$•, E°=+2.50-3.10V) can be formed, which is close to or even higher than the traditional active radical (•OH, E°= +2.60V). It has strong oxidation ability and can oxidize and degrade all kinds of organic pollutants in water body. In addition, SO$_4$• has a long half-life, a wide range of pH values and strong selectivity to pollutants, so it is not easy to be affected by inorganic ions in water body\[5\].

The activation of persulfate can be done in different ways, such as ultrasonic, thermal, optical, electrical and transition metal catalytic activation\[5\]. Among a series of activation methods, the energy consumption of ultrasonic, thermal and electric activation is relatively high, and there are still some limitations in its application to the treatment of polluted water in the actual polluted water. UV activation in photoactivation has the problems of energy consumption and the stability of UV lamp tube. Daylight activation mode needs to be further explored. The transition metal catalytic activation method does not need external heat source and light source, so it is relatively more economical and practical, but it is necessary to further explore the transition metal advanced oxidation system with low metal dissolution, low cost, high activation efficiency and good environmental protection performance. to investigate its treatment effect in the actual polluted water.

Fe$_2^+$ + SO$_4$•→2Fe$_3^+$ + SO$_4^{2-}$\hspace{1cm}(1)

Transition metal ions can provide electrons for persulfate and stimulate the production of sulfate radical. The activation of persulfate by transition metal ions such as Fe$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Co$^{2+}$ or Cu$^{2+}$ had been reported\[5\]. Fe$^{2+}$ was widely used to activate persulfate because of its low price, low toxicity and high catalytic efficiency, but Fe$^{2+}$ can combine with SO$_4$• to form Fe$_3^+$ and SO$_4^{2-}$, accompanied by the consumption of SO$_4$• with strong oxidation capacity. When the reaction rate is very high, adding excessive Fe$^{2+}$ will consume a large amount of SO$_4$•. Therefore, the amount and mode of adding Fe$^{2+}$ become the key point of activating persulfate. In order to overcome the difficulties in the process of homogeneous activation, researchers gradually focus on the heterogeneous research process, and develop iron-based catalysts to achieve high activation efficiency of persulfate. Iron-based materials mainly include nanometer zero-valent iron (NZVI), common zero-valent iron (ZVI), nano-iron trioxide (MNs) and so on\[6\].

3. Iron-based Materials activated persulfate

3.1. Zero-valent Iron Catalytic Materials
In the activated persulfate system, zero-valent iron (NZVI or ZVI) had been widely concerned and applied because of its less environmental pollution and slow release of Fe$^{2+}$. Zero-valent iron ((Eqs. (2-3) can slowly form Fe$^{2+}$, and activate persulfate to produce SO$_4$• (Eq.4).

\begin{align*}
2Fe^0 + O_2+ 2H_2O &\rightarrow 2Fe^{2+}+ 4OH^- \hspace{1cm}(2) \\
Fe^0 + 2H_2O &\rightarrow Fe^{2+}+2OH^-+H_2 \hspace{1cm}(3)
\end{align*}
Fe^{2+} + S_{2}O_{8}^{2-} \rightarrow Fe^{3+} + SO_{4}^{\bullet} + SO_{4}^{2-} \quad (4)

In recent years, zero-valent iron activated persulfate system had been widely used in the removal of organic pollutants in water body\cite{7-14}. Zhu et al. degraded DDT by NZVI/persulfate system, and EPR showed that the main active free radicals produced were SO_{4}^{\bullet} and •OH\cite{7}. Zhao et al studied the removal of bisphenol An and phosphate by ZVI/persulfate system, and considered that active free radical SO_{4}^{\bullet} degraded bisphenol A by electron transfer and hydrogen extraction, and the Fe^{3+} produced by the reaction could effectively remove phosphate\cite{8}. Dong et al used NZVI/persulfate to study the degradation of trichloroethylene, and found that the presence of EDTA could accelerate the degradation rate of TCE\cite{9}. Wei et al showed that ZVI/persulfate system could effectively degrade bentazon, and considered that low concentration of bentazon, low pH and high temperature were favorable for the reaction\cite{10}. Liu and others use ZVI/persulfate system to degrade fenitrothion efficiently, and the removal rate can reach 96%. Based on LC-MS/MS, the degradation intermediate of fenitrothasone is determined\cite{11}. Wang et al proposed a process of ultrasound-assisted ZVI activation of persulfate, in which the decolorization rate of acid orange 7 can reach 96.4%\cite{12}. Li et al used NZVI/persulfate system to carry out the degradation of dibutyl phthalate and found that the main active free radicals were different under different pH\cite{13}. Pan et al used ultrasound to assist ZVI/persulfate system and found that sulfamethazine could be efficiently removed when pH was neutral, and proposed a possible degradation pathway of sulfamethazine\cite{14}.

Compared with ordinary zero-valent iron (ZVI), nano-zero-valent iron (NZVI) has smaller particle size, high specific surface area and surface activity, so it shows greater potential advantages and development prospects in the remediation of organic pollutants in water body. However, it should also be noted that there are still the following shortcomings in the direct use of NZVI in the remediation of water PAHs pollution: first, it is poor stability, short existence time in the environment, easy to be oxidized, and poor maneuverability. Second, due to the small particles, it is easy to agglomerate in the water environment, thus reducing the specific surface area of the reaction and reducing the catalysis. Therefore, researchers load NZVI on various materials to facilitate the better dispersion of NZVI, which is used to activate persulfate. The loading materials are graphene, organic montmorillonite, biochar and activated carbon, and good results have been achieved in the removal of atrazine, sulfamethazine, trichloroethylene and tetracycline hydrochloride\cite{15-18}. Liang et al studied the oxidative degradation efficiency of naphthalene in water body by NZVI/persulfate system, and considered that the active free radical SO_{4}^{\bullet} in the reaction system could rapidly degrade naphthalene\cite{19}. Lu et al used NZVI-supported graphene/persulfate system to degrade phenanthrene in water body, and found that pH values between 7 and 8 could maintain a high removal rate, and that SO_{4}^{\bullet} and •OH were the main active free radicals produced by the system\cite{20}.

3.2. Nano-sized Iron tetroxide Catalytic Materials

In the activated persulfate system, nano-sized ferric oxide (MNP) has trans-spinel structure, and octahedral sites can stably hold Fe (II) and Fe (III). In recent years, MNP activated persulfate system has been widely used in the removal of toxic organic pollutants in water body\cite{21-25}. Yan et al use MNP to activate persulfate to degrade sulfamethoxine effectively, which can effectively remove sulfamethoxine\cite{21}. Ding et al prepared MNP activated persulfate to degrade norfloxacine by hydrothermal synthesis, and the degradation efficiency reached 90%; •OH was considered to be the main active substance for degradation under acidic conditions, while SO_{4}^{\bullet} and •OH were the main active substances for degradation under neutral conditions\cite{22}. Fang et al studied the process of degradation of trichlorobiphenyls by MNP activated persulfate and elucidated its potential degradation mechanism\cite{23}. Leng et al carried out the study on the degradation of rhodamine B by MNP activated persulfate, and found that the addition of polyhydroquinone improved the ability of reducing Fe^{3+}, accelerated the catalytic cycle rate, and increased the degradation ability of rhodamine B\cite{24}. Hu et al investigated the effects of humic acid and conventional inorganic anions on the
degradation of pollutants based on the oxidative degradation of p-nitrophenol by MNPs and microwave activated persulfate\cite{25}.

The activation of persulfate by heterogeneous transition metal catalysts had attracted more and more attention, but the slow electron transfer ability between $M^{n+}/M^{(n+1)+}$ limits its practical application. In order to overcome this defect, researchers have proposed many effective methods to assist the redox cycle of $M^{n+}/M^{(n+1)+}$. In homogeneous catalysis, electron donors such as hydroxylamine can be used as reducing agents to replace persulfate\cite{26}. However, the strategy of adding small organic molecules as reducing agents in heterogeneous systems is impossible. Therefore, the researchers tried to regulate the efficient activation of persulfate by adding foreign non-metallic heteroatoms (such as inorganic carbon, inorganic sulfur, etc.). Tang et al found that carbon-coated Mn$_3$O$_4$ composites can efficiently degrade dichlorophenol, Mn$_3$O$_4$ can enhance the electron transfer between persulfate and carbon shell, and the edge of carbon layer defects containing hydroxyl groups can be used as the active center of activated persulfate\cite{27}. Wang et al found that inorganic sulfur-doped Co/Co$_9$S$_8$@N-S-O-C composites can effectively activate persulfate to degrade sulfamethoxazole\cite{28}. Lan et al reported that inorganic sulfur-doped S-CuCoO composites have excellent catalytic activity, mainly due to the synergism of Cu (I) and Co (II) under the regulation of inorganic sulfur\cite{29}. Therefore, the performance of activated persulfate can be improved by the regulation of foreign non-metallic heteroatoms, which will provide a new clue for the design of new iron-based catalysts for activated persulfate.

4. Conclusions and prospects

Based on sulfate radical ($SO_4^{−}$, $E^0$=+2.50V-3.10V), it has a broad application prospect in the field of organic pollution treatment of water environment. Compared with other methods, the method of activating persulfate with iron is more economical and convenient, the energy consumption is lower, and the treatment efficiency is high, and the application range is very wide, but there are also the following problems:

1. There is a problem of slow redox cycle rate of Fe(II)/Fe(III) in the process of activating persulfate in iron-based materials, which limits the utilization efficiency of persulfate.

2. Although the catalyst can improve the treatment effect and reduce the loss, the preparation method of the catalyst is not easy, so it is necessary to develop a more easily available, efficient, environmentally friendly and reusable catalyst to reduce the threshold and cost of the technology.

3. Most of the studies are to simulate a single polluted water body for treatment, so it is necessary to carry out a variety of actual polluted water body research and develop related treatment processes to promote the industrialization of persulfate oxidation technology.

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