Research on Activating Persulfate by Co-based Multicomponent Catalysts

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Abstract. Persulfate (PS) is a hydrogen peroxide (H₂O₂) derivative, which can be catalyzed to produce sulfate radical. It can be activated in the following three ways: energy excitation, alkali activation and transition metal activation. Sulfate radical oxidation is an important advanced oxidation technology for wastewater treatment and advanced oxidation method is the main method for the treatment of refractory organic wastewater, mainly through the generation of hydroxyl radical (•OH) or sulfate radical (SO₄⁻•) and other free radicals to initiate a series of chain reactions. Co³⁺ activated persulfate (PMS) produces SO₄⁻• and Co³⁺ showing strong oxidation capacity. The preparation of catalysts prepared by "transition-metal, rare-earth-metal and noble-metal" can activate persulfate and produce SO₄⁻•, which can effectively degrade dyeing waste-water.

1. Introduction

Sulfate radical (SO₄⁻•) is a reaction intermediate with a REDOX potential of 2.5-3.1v and a half-life of up to 4 s, which is longer than that of conventional •OH and easier to make full contact with the target pollutant, thus making maximum use of SO₄⁻• [1]. The oxidation is stronger than •OH, which can lead to a series of chain reactions. Compared with some organic pollutants •OH, which cannot be oxidized and degraded, SO₄⁻• can be degraded [2]. Under acidic conditions, SO₄⁻• can exist stably. Under neutral or alkaline conditions, SO₄⁻• can react with OH⁻ to produce •OH. In contrast to •OH, SO₄⁻• can oxidize and decompose organic matter in a wide pH range [3]. Therefore, its application in the degradation of waste-water is more extensive, which is a hot research area of scholars.

At present, persulfate has a good treatment effect on refractory organic wastewater, so it has become a research hotspot in the field of water treatment [4-5]. At present, there are various researches on the activation of persulfate, mainly through light energy, heat energy, transition metal and alkali methods to achieve the activation of persulfate [6-8]. However, all of the above methods have their own disadvantages, such as high energy consumption and harsh technical conditions for energy-excited persulfate technology; The toxicity of transition metals introduced in transition metal activation technology may cause secondary pollution. Alkali activation technology requires a strong alkali environment and requires high requirements for instruments and equipment [9-12]. All these factors hinder the wide application of persulfate technology in organic wastewater treatment.

Therefore, the key of applying advanced oxidation technology of persulfate is how to activate persulfate efficiently and quickly to produce sulfate radical. Among them, the method of activating persulfate with transition metal has attracted a large number of researchers in this direction due to its mild reaction conditions and the need to add a large amount of energy consumption [13-15]. Due to
the excellent activation efficiency of Co\(^{2+}\) to PMS, the method of generating sulfate radical by activating persulfate with Co\(^{2+}\) has been paid attention to in the early stage. As early as 1956, Ball et al. [16-17] published the research results of using Co\(^{2+}\) to activate PMS.

2. Persulfate oxidation technology

2.1. Technical introduction

Persulfate (PS) is an H\(_2\)O\(_2\) derivative of hydrogen peroxide, which is the same as H\(_2\)O\(_2\) and has O-O bond in its molecular structure. These include Peroxodisulfate (PDS) and Peroxomonosulfate (PMS). Persulfate is a white powder solid state at room temperature and pressure, with high stability, easy storage and transportation, soluble in water, and lower price than pure H\(_2\)O\(_2\). Persulfate can exist in wastewater for months, with greater durability and stability. Its structure is shown in Figure 1, and the molecular structure of the three strong oxidized radical substances is shown in Figure 2.

![Figure 1. Structure chart of sulfate radical.](image)

![Figure 2. Molecular structure chart of PMS and PDS](image)

From the above structure diagram, permonosulfate PMS can be understood as one H atom in H\(_2\)O\(_2\) molecule is replaced by SO\(_3\), and perdisulfate PDS can be understood as two H atoms in H\(_2\)O\(_2\) molecule are replaced by SO\(_3\). Compared with the symmetric structure of PDS, the asymmetric structure of PMS is easier to excite, so this paper chooses the PMS system for research.

Sulfate radical has three different reaction modes with different kinds of organic compounds [18-19], and is mainly carried out with aromatic compounds through electron transfer. It reacts with unsaturated olefin compounds by addition. The reaction with alcohols, alkanes, ethers and lipids is mainly through hydrogen extraction, as shown in Table 1 below.

| Types of pollutants       | Mechanism of reaction | Response equation |
|---------------------------|-----------------------|-------------------|
| Aromatic compounds        | Electron transfer     | \( R\overset{-}{-} + SO_4\cdot \rightarrow R\overset{-}{-}SO_4\cdot \) |
| Unsaturated olefin        | Addition reaction     | \( SO_4^{2-} + H_2C = CHR \rightarrow OSOCH_2 - CHR\cdot \) |
2.2 methods of activating persulfate to obtain sulfate radical

There are various ways to obtain, mainly including the following ways:

2.2.1. Energy excitation. Energy is provided by heat, light, ultraviolet and microwave radiation to activate persulfate, break its O-O bond, generate sulfate radical to degrade organic pollutants and purify waste water. The basic principle is as follows Formula (1)-(2):

\[
\text{HSO}_5^- \xrightarrow{\text{UV/Heat ultrason}} \text{SO}_4^{2-} + \bullet \text{OH}
\]  

(1)

\[
\text{SO}_4^{2-} \xrightarrow{\text{UV/heat}} 2\text{SO}_4^{2-}
\]  

(2)

Thermal energy is one of the most direct forms of energy supply, and temperature is the key factor. Yang et al. [20] conducted a comparative study on the performance of thermal (25 °C~80 °C) activation of PDS, PMS and H₂O₂. The thermal energy required for the activation process was about 140.2kJ/mol, and the performance was ranked as: PDS > PMS > H₂O₂. It can be seen that under the action of thermal energy, O-O bond in PDS molecule is more prone to fracture and activation. Although many studies have shown that persulfate activation increases with temperature, it is not applicable to all organic pollutants. Hori et al. [21] stated in the literature that in the degradation of perfluorooctanoic acid by thermally activated PDS, the degradation efficiency at 150°C was lower than that at 80°C. Huang et al. [22] studied the degradation efficiency of 59 volatile organic compounds under thermally activated PDS, and found that 22 organic pollutants had better degradation efficiency at 30 °C than at 40 °C. This may be due to the quenching reaction between the generated SO₄•. The rapidly generated free radicals cannot touch the surface of organic pollutants in a short time, so they will be consumed during the transfer process, thus reducing the utilization efficiency of the oxidizer. In addition to thermal energy, ultraviolet light irradiation can also provide energy supply. Some studies have shown that in order to activate persulfate, ultraviolet light with a wavelength less than 270 nm is required, while thermal activation energy required to break the dioxygen bond is about 140.2 kJ/mol [23-24]. The above data show that although persulfate can be activated by energy provided by heat, light and other means, and has the advantages of fast reaction rate, no need to add chemical reality, no secondary pollution, etc., during activation, its huge energy demand and low light conversion efficiency greatly limit its application in practical situations.

2.2.2. Alkali Activation. Alkali activated persulfate technology is a common in situ chemical oxidation technology, its main principle is: under alkaline conditions, SO₄• can react with OH• to produce •OH, so as to achieve the purpose of degradation of wastewater. Furman et al. [25] attempted to degrade methyl ether by alkali activated persulfate, and the results showed that the degradation rate of organic methyl ether increased with the increase of pH value. In order to control the cost, alkali activation technology is mainly used to treat alkaline wastewater. The basic principle is as follows Formula (3)-(4):

\[
\text{SO}_4^{2-} + 2\text{H}_2\text{O} \xrightarrow{\text{alk}} 2\text{SO}_4^{2-} + \text{HO}_2^- + 3\text{H}^+
\]  

(3)

\[
\text{SO}_4^{2-} + \text{HO}_2^- \rightarrow \text{SO}_4^{2-} + \text{OH}^- + \text{H}^+
\]  

(4)

3. Ativation of Transition Metal

Transition metal ions can break the medium-o-o-bond by transferring an electron to PDS or PMS, thus activating persulfate and generating sulfate radical to degrade wastewater. The reaction mechanism is as follows Formula (5)-(6):
There are a variety of transition metal ions, commonly used transition metal ions are Co\textsuperscript{2+}, Fe\textsuperscript{2+}, Cu\textsuperscript{2+}, Ag\textsuperscript{+}, Ce\textsuperscript{2+}, Mn\textsuperscript{2+} and so on. Anipsitakis et al. [26] studied the comparison of catalytic activity of 9 common transition metal ions Ag\textsuperscript{+}, Co\textsuperscript{2+}, Ru\textsuperscript{3+}, Fe\textsuperscript{2+}, Fe\textsuperscript{3+} on oxidant PDS, PMS and H\textsubscript{2}O\textsubscript{2}, and found that Co\textsuperscript{2+} and Ru\textsuperscript{3+} had the best catalytic performance on PMS, and Ag\textsuperscript{+} had the highest catalytic activity on PDS, while for H\textsubscript{2}O\textsubscript{2}, Fe\textsuperscript{2+} and Fe\textsuperscript{3+} had the highest catalytic activity. Compared with other activation methods, mild reaction conditions of transition metal activation method under atmospheric pressure can be, do not need to add a lot of energy consumption, and some transition metal ions, such as Cu\textsuperscript{2+}, Fe\textsuperscript{2+}, Mn\textsuperscript{2+} in nature, there are also often have ore form, easy, cheap by everyone's attention, is a hot spot in current research.

4. Persulfate activated by Co-based multicomponent catalysts

To contrast Fenton and Co\textsuperscript{2+}/PMS system, Anipsitakis and Dionysiou [27] 2,4-dichlorophenol respectively for organic pollutants and atrazine degradation experiment was carried out in the two systems, the results show that these two kinds of pollutants in the Co\textsuperscript{2+}/PMS system degradation effect is better, and the difference in Fenton system defects of pH to demand higher, even under the Co\textsuperscript{2+}/PMS system pH for a wide range of 2.0~9.0 has good processing effect. Bandala et al. [28] also studied the degradation performance of 2,4-dichlorophenoxyacetic acid (2,4-D) in Fenton system and Co\textsuperscript{2+}/PMS system under light and dark conditions. The results showed that the removal rate of 2,4-D in the dark Co\textsuperscript{2+}/PMS system for 48 min was 86\%, and it was completely degraded in the light condition. Under the same conditions, the degradation rate of 2,4-D by Fenton system in the dark was only 17\%. The results prove that the advanced oxidation technology based on sulfate radical is superior to the traditional Fenton system. Regarding the dynamics and reaction mechanism of Co\textsuperscript{2+}/PMS system, people generally agree with the radical chain reaction mechanism proposed by Kim's team: Co\textsuperscript{2+} first activates PMS to produce SO\textsubscript{4}\textsuperscript{-}, and Co\textsuperscript{3+}, and the reaction generated Co\textsuperscript{3+} can be reduced by PMS to a catalytic cycle formed by Co\textsuperscript{2+} (seen in Figure 3) [29-31].

![Figure 3. Free radicalchain reaction mechanism in the system of Co/ PMS.](image)

Although Co\textsuperscript{2+}/PMS with all of these advantages, cobalt in water exists in the ionic Co\textsuperscript{2+}, Co\textsuperscript{3+} as a toxic heavy metal, human consumption will cause respiratory diseases such as asthma and pneumonia [32-34]. In order to reduce the dissolution of cobalt ionic, the preparation of the load type catalyst cobalt Quito components, and probes into the optimal preparation conditions optimization, in ensuring the degradation effect of reduced the dissolution of cobalt ions at the same time [35-36].

The results showed that the activation effect of Co\textsuperscript{2+} on monopersulfate was higher than that of other transition metals. The process of its activation to generate sulfate radical is shown in Formula (7)- (8):
Single metal activation is likely to lead to metal accumulation and aggregation, causing pollution to the environment. The composite metal catalyst activation method can reduce the use of metal Co, and improve the activation efficiency of sulfate radical and the degradation effect of wastewater. Therefore, the preparation technology of catalysts has been paid more and more attention.

5. Key technology research
In order to solve the problem of Co\(^{2+}\) dissolution in Co\(^{2+}\)/PMS system, Al\(_2\)O\(_3\) was selected as the carrier of the catalyst, and the supported cobalt-based multi-component catalyst was prepared by means of equal amount impregnation method. Taking rhodamine B (RhB), a simulated dye wastewater, as the actual water sample, the preparation conditions of the catalyst were optimized through the degradation effect of the wastewater, and the multi-component catalysts with high efficiency and good recycling performance were screened out and characterized to explore the reaction mechanism.

(1) Select shamrock pseudothion hydralite with convenient materials, low price and wide sources, and obtain a specific surface area and large pore diameter of \(\gamma\)-Al\(_2\)O\(_3\) carrier by calcination. The single-component metal salt catalyst of CO/\(\gamma\)-Al\(_2\)O\(_3\) was prepared by the same amount of impregnation method. The optimal single-component metal salt catalyst was screened by changing the carrier size, cobalt salt loading capacity, dynamic and static impregnation, impregnation time, impregnation temperature, calcination time and calcination temperature parameters.

(2) Rare-earth metals Ce and La were added to the above selected catalysts for modification, and the catalytic effect of the two rare-earth metals was compared, and the rare-earth metal Ce salt with better effect was selected as the catalytic assistant. On this basis, the influence of the ratio of Ce to cobalt salt, impregnation sequence, calcination time and calcination temperature on the performance of the catalyst was further investigated.

(3) The “transition metal-rare earth metal-noble metal” system was adopted, and the noble metal Ru was selected to modify the catalyst again. The optimum preparation conditions of the multi-component catalyst under the influence of metal salt proportion, impregnation sequence, calcination time and calcination temperature were investigated.

(4) By simulating the degradation effect of wastewater, the decolorization rate was used as the index. Under the PMS system, the degradation effect of wastewater under different reaction temperatures, catalyst dosage and oxidizer dosage was investigated. On the premise of ensuring the degradation effect of wastewater, ICP has been used as the evaluation index to detect the dissolution of Co ions in waste-water.

6. Conclusion
The methods of obtaining sulfate radical (SO\(_4^2\)•) include energy excitation, alkali activation and transition metal activation. Persulfate (PS) is a hydrogen peroxide (H\(_2\)O\(_2\)) derivative, which can be catalyzed to produce sulfate radical. Radical oxidation of sulfate is an important and advanced oxidation technology, which can achieve better wastewater treatment effect. Advanced oxidation is mainly through the production of hydroxyl radical (•OH) or sulfate radical reactions. The supported Co salt catalyst was prepared, which activated the SO\(_4^2\)• produced by persulfate and could effectively degrade the dye wastewater. The catalysts prepared by “transition-metal, rare-earth-metal and noble-metal”, which activates persulfate and produce SO\(_4^2\)•, so the dyeing waste-water can be degraded effectively.

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