Study on the Transformation of I\(^-\) in Fe\(^{2+}\) Activated PMS System

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Abstract. In order to solve the problem of more and more iodinated by-products in water, the advanced oxidation system of peroxymonosulfate (PMS) activated by ferrous (Fe\(^{2+}\)) was used to study the transformation process and principle of iodine ion (I\(^-\)) as the initial target under different influencing factors in this system. The results showed that when the pH value was 3, the molar concentration ratio of Fe\(^{2+}\) and PMS was 0.8:1, the conversion effect was the best. When the concentration of I\(^-\) was 20 μmol/L, the conversion rate of I\(^-\) was 94%. Under the action of sulfate radical (SO\(_4\)^{\cdot-}\)), the final conversion product of I\(^-\) is only iodate (IO\(_3\)^\(\cdot\)). With the increase of pH value, the conversion effect will also decrease. The concentration of I\(^-\) itself also affects the reaction.

1. Introduction
In recent years, a large number of iodine-related products have been found in the process of drinking water treatment [1]. These products have strong cytotoxicity and genetic toxicity, and there is a huge potential risk for human health, which has begun to attract in the academic community [2]. In water, halogen ions are common, and I\(^-\) are often detected, with the content of about 10~20 μg/L. Although iodates do not cause harm to the human body, I\(^-\) reacts with certain organic compounds in water under the action of some strong oxidants to produce harmful iodinated organic by-products [3].

Peroxymonosulfate (PMS) has strong oxidizing property, which can be used as an oxidant and is easily soluble in water. Ionization will produce persulfate ions (HSO\(_5\)^\(\cdot\)), and its redox potential is higher than that of permanganate and hydrogen peroxide. Its oxidizing property is mainly derived from peroxy (O-O) [4]. Peroxymonosulfate (PMS) can generate sulfate radical (SO\(_4\)^{\cdot-}\) with high activity under the action of light, heat, transition metal and so on. SO\(_4\)^{\cdot-}\) has a strong oxidation effect, can make many refractory organic matter is decomposed, thus forming an innovative advanced oxidation process (AOP). Among them, the transition metal activated PMS has the advantages of fast and high efficiency, low energy consumption, low cost, and no secondary pollution to water body, which has a good application prospect [5].

At present, there is no specific theoretical foundation for the transformation law of iodine in the advanced oxidation system. Therefore, in order to better explore the transformation law of I\(^-\) in the water treatment process, the advanced oxidation system of ferrous (Fe\(^{2+}\))/peroxymonosulfate (PMS) was used in this experiment. By changing the molar concentration ratio of Fe\(^{2+}\) to PMS, pH value and I\(^-\) concentration, the yield and change trend of the generated products were observed and the law was analyzed. It is expected that this study will lay a theoretical foundation for the transformation of iodine substances in the practical application of Fe\(^{2+}\)/PMS advanced oxidation system in water treatment.
2. Experiment

2.1. Agents and instruments
Main reagents: ferrous sulfate heptahydrate, sodium persulfate (PMS), potassium iodide, potassium iodate, glacial acetic acid, disodium hydrogen phosphate, potassium dihydrogen phosphate, sodium tetraborate, dilute sulfuric acid, sodium hydroxide, 2,6-dichlorophenol, sodium sulfite, methanol, acetonitrile, anhydrous sodium carbonate. All analytically pure.

Main instruments: high performance liquid chromatograph (waters7980), ion chromatograph (ICS1500), pH meter (pH730), water bath thermostatic oscillator (SHZ-B), electronic balance (ME204E), liquid gun (freshman), magnetic stirrer (squid), ultrapure water preparation system (Z00Q0V0CN).

2.2. Preparation of main reagents
Configure a certain amount of main solution, are dissolved with MililQ water configuration. 50 mmol/L sodium persulfate (PMS), 100 mmol/L ferrous sulfate heptahydrate (FeSO₄·7H₂O), 10 mmol/L potassium iodide (KI), 5 mmol/L 2,6-dichlorophenol, 200 mmol/L sodium sulfite (Na₂SO₃), 10 mmol/L acetic acid buffer, and 10 mmol/L phosphate buffer.

2.3. Experimental method
Add 100 mL ultrapure water into 250 mL iodine bottle, and then add the calculated volume or I⁻ to the solution to prepare the required concentration. Adjust the pH value of the solution to the required value with dilute sulfuric acid or sodium hydroxide solution. This process needs to be carried out on a magnetic stirrer to ensure uniform diffusion of the solution. Then add the calculated concentration of Fe²⁺ and the corresponding molar ratio concentration of PMS, and use the timer to start timing. At the set time point, 6 mL of the sample was taken with a syringe, and the NaOH solution with the calculated volume of the alkaline solution and 200 μL of 2,6-dichlorophenol were immediately added to the sample. The sample was shaken for 10~15 s, to capture the intermediate active substance hypoiodous acid (IO⁻), and then 50 μL of sodium sulfite (Na₂SO₃) and 100 μL of methanol were added to terminate the reaction. 1 mL sample was injected into the liquid bottle, and IO⁻ was determined by liquid chromatography. The remaining 5 mL sample was injected into the ion chromatography tube to determine the corresponding ions.

2.4. Analysis method
In the experiment, the content of IO⁻ in the experiment was detected by the reaction of IO⁻ with 2,6-dichlorophenol to generate 4-I-2,6-dichlorophenol. 4-I-2,6-dichlorophenol was determined by Waters HPLC. The mobile phase was V (acetonitrile): V (water) = 7:3, the UV detection wavelength was 225 nm, the flow rate was 1 mL/min, and the injection volume was 10 μL. I⁻ and IO₃⁻ were determined by ion chromatography (ICS1500) with 9 mmol/L anhydrous sodium carbonate solution as the eluent at a flow rate of 1 mL/min. The injection volume was 1000 μg/L. The detection limit of the method was 0.3 μg/L.

3. Result and discussion

3.1. Effect of pH on I⁻ transformation
Fe²⁺/PMS system is Fenton-like system, so the system is greatly affected by pH value. The oxidation effect is the best under acidic conditions, and the effect is poor under neutral or alkaline conditions [6]. In this experiment, under the conditions of reaction temperature of 25 °C, Fe²⁺ concentration of 160 μmol/L, PMS concentration of 200 μmol/L and I⁻ concentration of 20 μmol/L, the transformation of I⁻ under pH values of 3, 4, 5, 6 and 7 was observed and analyzed. The results are shown in Fig.1.
It can be seen from Fig. 1 that when pH value was 3, the conversion effect of I⁻ was the best, and 94% of I⁻ was oxidized. With the increase of pH value, when pH value was 7, the conversion efficiency of I⁻ continued to drop to 39%. The main reason may be that in neutral or alkaline environment, Fe²⁺ is prone to hydrolysis and precipitation, so that the effective Fe²⁺ concentration involved in Fe²⁺/PMS is reduced, and SO₄²⁻ is easy to react with OH⁻ under alkaline conditions. So that the conversion efficiency of I⁻ is reduced. Under acidic conditions, and when pH value is 3, most Fe²⁺ can participate in activation, and the number of effective SO₄²⁻ can also be maximized. So in the actual water treatment system, we should always pay attention to the change of pH value, control the pH value of water, so that the treatment effect is the best.

3.2. Effect of concentration ratio of Fe²⁺ to PMS on I⁻ transformation

PMS can produce more concentrations of active substances faster through the activation of Fe²⁺. In this experiment, the molar concentration ratio of Fe²⁺ to PMS was changed by changing the concentration of Fe²⁺. Under the conditions of reaction temperature of 25 °C, pH value of 3, PMS concentration of 200 μmol/L and I⁻ concentration of 20 μmol/L, the transformation of I⁻ was observed and analyzed when the concentration of Fe²⁺ was 100 μmol/L, 160 μmol/L, 200 μmol/L, 240 μmol/L and 300 μmol/L. The concentration ratio of Fe²⁺ to PMS was 0.5:1, 0.8:1, 1:1, 1.2:1 and 1.5:1, as shown in figure 2.

As shown in Fig. 2, when Fe²⁺ increased from 100 μmol/L to 300 μmol/L, the conversion rate of I⁻ increased from 59 % to 94 %, and then decreased to 70 %. It can be seen that when the concentration of Fe²⁺ was 160 μmol/L, namely the concentration ratio of Fe²⁺ to PMS was 0.8:1, the conversion
effect was the best. The main reason for this result is that when the concentration of Fe²⁺ is low, it can’t play a good activation role, but it is not the more the better. Excessive Fe²⁺ will compete with the SO₄⁻ which plays a major oxidation role in the system. The content of effective SO₄⁻ in the reaction is reduced, and the content of Fe³⁺ is increased, which reduces the reaction efficiency. Therefore, in the relevant experiments, it is necessary to control the dosage of Fe²⁺, taking into account the processing cost and environmental protection and other issues, so that the concentration ratio of Fe²⁺ and PMS is kept at about 0.8:1, and the cost performance is higher, which can maintain the maximum activation effect and oxidation effect [7].

3.3. Transformation of different concentrations of I⁻
The content of I⁻ in waters of different regions is different, so it is necessary to find out the rules and appropriate schemes according to different regions. According to this phenomenon, under the conditions of reaction temperature of 25 °C, pH value of 3, Fe²⁺ concentration of 160 μmol/L, and PMS concentration of 200 μmol/L, the conversion efficiency of I⁻ was observed and analyzed when I⁻ concentration was 10 μmol/L, 15 μmol/L, 20 μmol/L, 25 μmol/L, and 30 μmol/L. The results are shown in Fig. 3.

![Figure 3](image)

As shown in Fig. 3, when I⁻ concentration increased from 10 μmol/L to 30 μmol/L, the conversion rate of I⁻ decreased from 97 % to 67 %. I⁻ will react with SO₄⁻ in Fe²⁺/PMS system, and SO₄⁻ will react with other active substances in the whole reaction process [8]. When the concentrations of Fe²⁺ and PMS remain unchanged, the conversion efficiency of I⁻ will not be improved by continuously increasing the concentration of I⁻. Therefore, in the water with known I⁻ concentration, the concentration relationship between Fe²⁺/PMS and I⁻ should be appropriately adjusted to achieve the best response.

3.4. Analysis of transformation products of I⁻
I⁻ is already in the lowest valence state and has a certain degree of reduction, which can be oxidized by the system to produce compounds with high valence state. In this experiment, the optimal reaction conditions were as follows. Temperature was 25 °C, pH value was 3, the concentration of Fe²⁺ was 160 μmol/L, the concentration of PMS was 200 μmol/L, and the concentration of I⁻ was 20 μmol/L. The reaction results are shown in Fig. 4.
Figure 4 Change process of Fe<sup>2+</sup>/PMS oxidized I<sup>−</sup> under optimal conditions

As shown in Figure 4, because of the strong reducibility of I<sup>−</sup>, the reaction rate in the first 30 minutes was faster and the conversion rate was higher. Finally, 18.82 μmol/L I<sup>−</sup> was oxidized, and all the oxidized parts generated IO<sub>3</sub><sup>−</sup>, and no IO<sup>−</sup> was detected. The reason for this phenomenon may be that the iodine active substances produced during the reaction are more active, difficult to capture, and the reaction rate is very fast, directly forming the final product IO<sub>3</sub><sup>−</sup>.

3.5. Effect of PMS alone on I<sup>−</sup>

From the above results, it can be seen that Fe<sup>2+</sup> is very important for the activation of I<sup>−</sup> transformation. In order to more intuitively and accurately see the specific role of Fe<sup>2+</sup> in the system of I<sup>−</sup> transformation, this section did a set of blank test for comparison. Only PMS was used to oxidize I<sup>−</sup>, without adding Fe<sup>2+</sup>, under the optimal conditions, namely the temperature was 25 °C, pH value was 3, PMS was 200 μmol/L, I<sup>−</sup> concentration was 20 μmol/L. The transformation of I<sup>−</sup> was observed and analyzed, and compared with the Fe<sup>2+</sup>/PMS system under the optimal conditions. The reasons for the differences between the two conditions were analyzed, as shown in Figure 5.

Figure 5 Changing process of PMS oxidized I<sup>−</sup> under the best conditions

As shown in Figure 5, PMS itself has a certain oxidation effect, but the effect is relatively poor. Compared with the 94 % conversion of I<sup>−</sup> in the Fe<sup>2+</sup>/PMS system under the optimum conditions, only 86 % of I<sup>−</sup> is converted and only IO<sub>3</sub><sup>−</sup> is generated, and IO<sup>−</sup> is still not detected. It can be seen from the results that, under the same optimal conditions, the direction of action and reaction trend of PMS alone and Fe<sup>2+</sup>/PMS system on I<sup>−</sup> are generally consistent. However, under the activation of Fe<sup>2+</sup>, the
conversion rate of the target substance and the formation rate of the product have been improved to some extent. In addition, it can also be seen that under the optimal conditions, the reaction of Fe\(^{2+}\)/PMS system to I\(^-\) is very fast in the first 10 min, and tends to be gentle after 30 min, while the reaction of PMS alone to I\(^-\) is relatively slow, and tends to be gentle after 90 min. This shows that the activation of Fe\(^{2+}\) in the reaction of I\(^-\) is mainly to accelerate the reaction rate, and the effect is very significant. And Fe\(^{2+}\) cost is low, pollution-free, can be considered to be applied to the actual water treatment.

4. Conclusion
1. The reaction rate and reaction effect of I\(^-\) were affected by Fe\(^{2+}\) concentration, pH value and its own concentration. The conversion of I\(^-\) was the best under acidic conditions close to pH value of 3. The molar ratio of Fe\(^{2+}\) to PMS was adjusted to 0.8:1, and then the specific system concentration was determined according to the concentration of the target substance, which was maintained at the best treatment conditions.
2. After the whole redox reaction, the final product is only IO\(_3\)\(^-\).
3. Fe\(^{2+}\) plays a major role in catalysis and activation, which can greatly improve the conversion of I\(^-\), the formation rate and reaction rate of related products.

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