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$Mn^{2+}/H_2O_2/O_3$, a high efficient advanced oxidation process in acidic solution

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ABSTRACT

$Mn^{2+}/H_2O_2/O_3$, an ozone-based advanced oxidation process, was investigated in acidic solution. Acetic acid (HAc) was selected as the target compound to be degraded because it is often the final product of macromolecules degraded by chemical oxidation. The results showed that only $Mn^{2+}/H_2O_2/O_3$ could effectively remove acetic acid at initial pH 1.0, while others like O_3, H_2O_2/O_3, Mn^{2+}/O_3 and Mn^{2+}/H_2O_2 almost had no removal ability, indicating that the coexistence of Mn^{2+}, H_2O_2 and O_3 was of great necessity to ensure the high removal rate of acetic acid in acidic solution. Optimized parameters suggested that there existed an optimal ratio of concentration of Mn^{2+} to concentration of H_2O_2 for acetic acid removal. The above results are of significance for effective treatment of acidic wastewater containing refractory pollutants. The mechanism study showed that $Mn^{2+}/H_2O_2/O_3$ in acidic solution was not associated with the generation of hydroxyl radicals, but with the generation of highly active intermediate Mn^{3+}.

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1. Introduction

Ozone, as a green oxidant, has been widely applied in the field of environmental sewage and drinking water treatment [1–4]. However, ozonation alone in general has low oxidative efficiency, especially for acidic solution. In order to effectively degrade some refractory organic compounds, some advanced oxidation processes based on ozone (AOPs-O_3) have been put forward, such as H_2O_2/O_3, UV/O_3, and catalytic ozonation, which have been received great attention [5,6]. According to the most popular views in AOPs-O_3 literatures, generation of hydroxyl radicals is always the key factor during ozonation, because hydroxyl radicals can react very quickly with many organic species without selectivity. The combined process of hydrogen peroxide with ozone (H_2O_2/O_3) is considered as a most promising process owing to its convenience and high efficiency [7]. However, the efficiency of H_2O_2/O_3 is strongly dependent on the pH value of solution, and the lower the pH is, the lower the degradation efficiency will be [8,9]. Considering the deprotonation of H_2O_2 is hard to occur in acidic solutions, many researchers [10–12] tried to bring in catalysts to promote the decomposition of H_2O_2 and improve the degradation efficiency of H_2O_2/O_3. In our previous studies, both TS-1 and Ti-MCM-41 showed good catalytic effects on the degradation of acetic acid in H_2O_2/O_3 process at initial pH 3.0 [13,14]. However, when solution acidity continued to increase, the activity of the catalyst greatly decreased. Therefore, it is very important to explore a kind of metal ion to improve efficiency of H_2O_2/O_3 even in strong acidic solution, which is very significant for the sustainable development of chemical engineering industry because it always discharges acidic wastewater containing refractory pollutants.

Mn(II) ion (Mn^{2+}), used as a homogeneous catalyst in ozonation, has been investigated a lot before [15–20]. In addition, Mn^{2+} can be easily removed through MnO_2 precipitation, so it has a great potential of application in ozonation. The existing literatures have provided several possible mechanisms for Mn(II) ion catalytic ozonation. Andreozzi et al. reported that the efficiency of manganese ion catalyzed ozonation process in acidic was enhanced by the generation of oxalate ion-Mn complex which can react with ozone more easily than oxalic acid [16,17]. However, Ma et al. indicated that the destruction rate of Atrazine by Mn^{2+}/O_3 in neutral solution was attributed to the formation of hydroxyl radicals [18,19]. Thus, scholars still cannot draw a unified conclusion on Mn(II) catalyzed ozonation. Therefore, the mechanism of manganese ion catalyzed ozonation needs to be further studied.

Due to the nature of stability, oxalic acid and acetic acid are often the final products of chemical oxidation of organic compounds, and these two organic acids are often selected as

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target compound to verify the oxidation efficiency of an AOP-O_3. Compared with oxalic acid (a usual reducing agent), acetic acid is more suitable to test the efficiency of an AOP-O_3 because oxalic acid may be oxidized by conventional oxidizing agent like $KMnO_4$. According to the above discussion, acetic acid was chosen as target compound to investigate the behavior of $Mn^{2+}/H_2O_2/O_3$ in acidic solution. Experimental factors such as pH, concentrations of Mn^{2+} and H_2O_2 were discussed in details. Acetophenone was also removed to verify the efficiency of $Mn^{2+}/H_2O_2/O_3$. Finally, a possible mechanism of $Mn^{2+}/H_2O_2/O_3$ was proposed. The experimental results are of significance for effective pretreatment of acidic wastewater containing refractory pollutants, especially for the reclamation of waste acid.

2. Experimental

2.1. Chemicals and reagents

All reagents (acetophenone, acetic acid, oxalic acid, *tert*-butanol (TBA) manganese (II) sulfate monohydrate, sodium pyrophosphate (PP)) were of analytical grade and used as received without any further purification. Mn^{2+} was added into aqueous solution in the form of sulfate. The content of hydrogen peroxide was 30% (w/w). All solutions were prepared with double distilled water.

2.2. Ozonation experiments

All experiments were carried out in a semi-continuous process [14]. Ozonation contactor was a 1.5 L cylindrical glass reactor (Fig. 1). Ozone was produced by a corona ozone generator (CFS-1A, Ozonia, Switzerland). Before the experimental operation, the reactor was pre-ozonated for 3 min and then was washed several times with double-distilled water to exclude possible side effects of the impurities. Oxygen gas was dried and purified through silica gel prior to get into the ozone generator. Ozone concentration was controlled by varying the voltage and a rotor flow-meter. The flow rate of oxidized oxygen was always 0.80 L/min and the rate of ozone input was 37.9 mg/min if without special instructions. Excess ozone was absorbed by two gas absorption bottles containing 2% KI solution before being emitted.

In a typical experiment of acetic acid removal, the reactor was filled with 500 mL acetic acid aqueous solution containing Mn^{2+} and hydrogen peroxide, and the temperature in the reactor was kept at room temperature (21 ± 0.5) °C. The required concentrations of manganese ion and hydrogen peroxide prepared in advance were added into the reactor. The sample was withdrawn for analysis at certain regular intervals, and dissolved ozone was removed by immediately bubbling nitrogen for 3 min after sampling to terminate oxidative reaction.

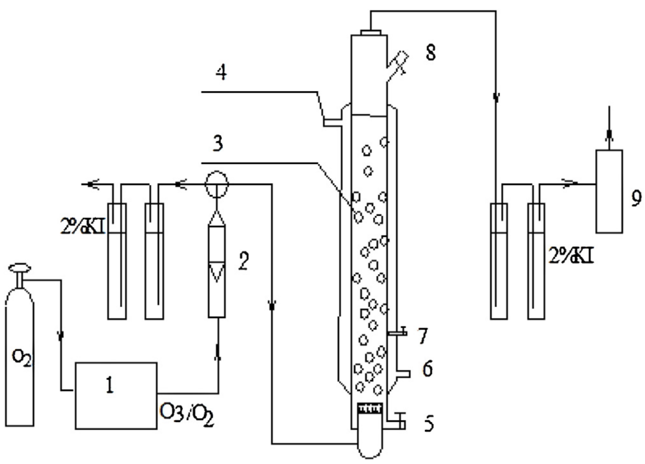

Fig. 1. Diagram of the experimental setup. (1) ozone generator; (2) flow-meter; (3) ozonation reactor; (4) outlet of circulation water; (5) outlet of material; (6) inlet of circulation water; (7) sampling; (8) inlet of material; (9) ozone destructor.

2.3. Analytical methods

The concentration of H_2O_2 was determined by potassium titanium (IV) oxalate method [21]. The presence of H_2O_2 did not interfere with the concentrations of ozone and acetic acid. The concentration of ozone dissolved in aqueous solution was analyzed by a spectrophotometer using the indigo method [22]. A high performance liquid chromatograph (ThermoFisher Dionex Ultimate 3000, USA) was used to assess the concentration of acetic acid and acetophenone. Hypersil Gold C18 column (250 × 4.6 mm, particle size 5 mm) was used as the analytical column. The operating conditions of HPLC for analysis of acetic acid concentration were described as follows: 0.0134 M phosphate buffer (pH = 3.0) and methanol (950:50, v/v) was the mobile phase, the flow rate was 1.2 mL/min and UV detector was set at 210 nm. The operating conditions of HPLC for analysis of acetophenone concentration were described as follows: the mixture of methanol and water (60:40, v/v) was the mobile phase, the flow rate was 1.0 mL/min and UV detector was set at 246 nm. The pH value of solution was recorded by a pH analyzer (PHS-3C, General Instrument Co., Ltd., Shanghai, China) and was controlled by adding 1.0 mol/L H_2SO_4 or NaOH. It was found that the solution pH almost unchanged during the whole experiment.

3. Results and discussions

3.1. Ozonation of acetic acid

At initial pH 1.0, 100 mg/L acetic acid was removed by O_3, H_2O_2/O_3, Mn^{2+}/O_3, Mn^{2+}/H_2O_2 and $Mn^{2+}/H_2O_2/O_3$ (as shown in Fig. 2). The results showed that acetic acid could hardly be removed by O_3, H_2O_2/O_3, Mn^{2+}/O_3 and Mn^{2+}/H_2O_2 at this pH value. The rate constant of acetic acid with ozone is 3×10^{-5} L/(mol s), so acetic acid cannot be removed by ozone alone. Acetic acid also could hardly be removed by H_2O_2/O_3 because of difficult deprotonation reaction of H_2O_2 in acidic solutions. The results of Mn^{2+}/O_3 and Mn^{2+}/H_2O_2 both indicated that Mn^{2+} alone could not promote the

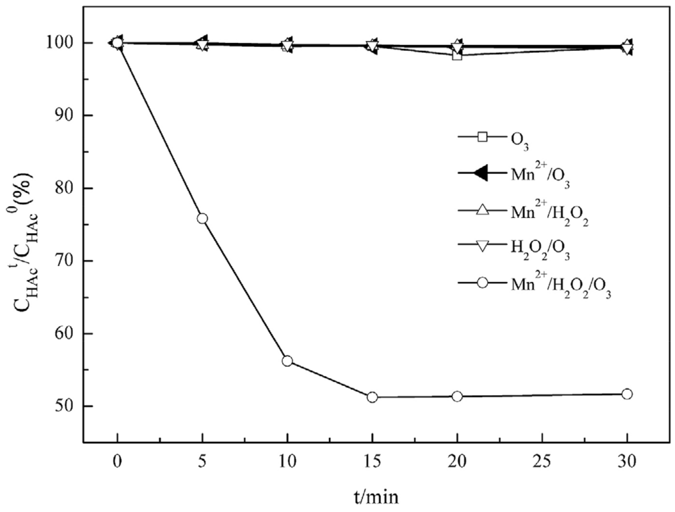

Fig. 2. Remaining rate of acetic acid by O_3, Mn^{2+}/O_3, Mn^{2+}/H_2O_2, H_2O_2/O_3, $Mn^{2+}/H_2O_2/O_3$. Experimental conditions: initial pH: 1.0; concentration of H_2O_2: 100 mg/L; concentration of HAc: 100 mg/L; concentration of Mn^{2+}: 1.0 mg/L; rate of ozonized oxygen: 0.80 L/min; rate of ozone input: 37.9 mg/min.

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