Research article

The effect on ozone catalytic performance of prepared-FeOOH by different precursors

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A B S T R A C T

In this study, different precursors were used to prepare FeOOH and the ozonation catalytic activity was s investigate by using ibuprofen as the degradation substrate. It could be found that FeOOH prepared from ferric sulfate performed higher activity. Subsequently, the catalysts were characterized by X-ray diffraction, Fourier transform infrared spectrometer, scanning electron microscope and N_2 adsorption-desorption techniques. X-ray diffraction and Fourier transform infrared spectrometer showed that the synthesized FeOOH consisted of α-FeOOH and β-FeOOH mainly. Scanning electron microscope showed that their appearance and morphology were significantly different, and the FeOOH prepared from ferric sulfate had a larger specific surface area, resulting in its better catalytic activity. Finally, the hydroxyl groups and pH_{zpc} of the catalyst surface were measured. It was also found that the FeOOH prepared from ferric sulfate owned more hydroxyl groups and the pH_{zpc} of the surface was closer to the pH of the degradation substrate, which illustrated the reasons for the increased catalytic activity. In addition, the degradation kinetics conformed to the pseudo first-order kinetic model and the hydroxyl radicals played an important role in the reaction process.

1. Introduction

With the development of social economy, the environmental pollution problem had become more serious. In particular, untreated industrial and agricultural waste water and domestic sewage were discharged directly into the rivers and lakes, which had led to a serious decline in water quality (Jiang, 2009; Wang et al., 2008). In recent years, pharmaceutical and personal care products (PPCPs) as a new pollutant are attracting increasing attention. Ibuprofen is widely used in medicine. Small amounts of ibuprofen entering water will pose a threat to drinking water, reuse water, reclaimed water and aquatic ecosystems, as well as human health (Quero-Pastor et al., 2014). Advanced oxidation processes (AOPs) had been widely studied for water and wastewater treatment. Among them, ozonation and photocatalysis had attracted the attention of many researchers. Ozone (O₃) had been shown to be a valid method by chemical oxidant in drinking water and wastewater treatment (Broséus et al., 2009). Due to its excellent oxidation capacity, ozone oxidation had been widely applied for disinfection (Xu et al., 2002), decolorization (Hadavifar et al., 2016), odor removal (Antonopoulou et al., 2014), and also successful elimination of refractory contaminants (Ikhlaq et al., 2015). Ozone could react directly with pollutants through its own molecules, or indirect oxidation

with hydroxyl radical (OH·) which could be generated spontaneously through ozone in water (De Vera et al., 2015; Tripathi et al., 2011). The direct oxidation of organic matter in water by ozone, there were two ways: (I) the dipole addition reaction, which was because ozone had dipole structure, could led to ozone molecules and organic matter containing unsaturated bond addition reaction; (II) the substitution reaction, which mainly had occurred in the high density of electron cloud in organic molecular structure, especially aromatic compounds (Sudhakaran and Amy, 2013; Zhu et al., 2014). Thus, the reaction between ozone and organic matter was highly selective. For some organic compounds, ozone could have a high removal rate, such as diclofenac (García-Araya et al., 2010), microcystin-LR (Liu et al., 2010), and sulfamethoxazole (Del Mar Gómez-Ramos et al., 2011). However, direct ozonation could not effectively remove organic compounds consisting of saturated ring systems or electron-withdrawing groups, such as geosmin (Schrader et al., 2010), endrin and atrazine (Zhu et al., 2017). Therefore, ozone had usually been combined with other technologies of water-treatment, so that generating more OH· in removing the organic compounds which could not been treated by only ozone (Chen et al., 2010; Nawrocki and Kasprzyk-Hordern, 2010). Regarding photocatalysis, a large number of reports had been published during the last decades, for example, the commercial titanium dioxide was used to

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remove the 2,4-dichlorophenol in water solution (Favier et al., 2016) and the caffeine was degraded by the Ag-ZnO-Al$_2$O$_3$ nanocomposite in aqueous solutions under UV irradiation (Elhalil et al., 2017). However, photocatalysis still had some disadvantages. First of all, the light energy efficiency is low, and its efficiency will be limited by the catalyst property, ultraviolet wavelength and reactor. Secondly, photocatalysis need to solve the problem of transmittance, because some suspended substances and deep chroma in some wastewater (such as printing and dyeing wastewater) had been not conducive to the transmission of light, which will affect the photocatalytic effect. Finally, the duration of the light source was also a problem. The above problems restricted its application in practical engineering. Ozone oxidation started early, and catalytic ozonation did not have the above problems.

Recently, catalytic ozonation had appeared as a powerful technology for the treatment of pollutants in water, even for refractory compounds by producing more active groups, especially OH· (Einaga et al., 2013; Zhao et al., 2012). It has been reported that many synthesized catalysts, including metal oxides (Zhu et al., 2017), metal oxides attached on support (Lv et al., 2012), and porous materials (Ren et al., 2012), have been studied in the catalytic ozonation processes. They were found to improve removal by promotion of hydroxyl radical formation through the ozone decomposition. Among these known catalysts, the most widely used catalysts in heterogeneous catalytic ozonation are metal oxides (Zhu et al., 2017), metals on supports and activated carbon (Zhuang et al., 2014).

Among these widely used catalysts, Fe-based catalysts have received increasing attention due to their some advantages, such as, (1) they are abundant in nature and can be easily synthesized; (2) they are almost non-toxic; (3) some Fe-based catalysts own special characteristics, for example, magnetite (Fe$_3$O$_4$) own magnetic properties (Zhu et al., 2017) and iron oxyhydroxide (FeOOH) has high density of hydroxyl group. In addition, FeOOH catalysts show a high catalytic activity in catalytic ozonation system. Sui M et al. (Sui et al., 2010) used α- FeOOH to catalyze ozone degradation of oxalic acid and found that the α-FeOOH catalyst had been effective in promoting the decomposition of ozone in acidic (pH = 4) and neutral (pH = 7) conditions. When pH = 4, the degradation efficiency of oxalic acid was increased from 7% with ozone alone to 42% with catalyst, and when pH = 7, the degradation efficiency of oxalic acid was increased from 22% with ozone alone to 54% with catalyst. Oputu (Oputu et al., 2015) made use of hydrothermal synthesis of artificial β-FeOOH nanorods with diameters of 2–6 nm, catalytic ozonation for chlorine phenol (4-CP), ozone oxidation alone, compared the removal rate of 4-CP increased from 67% to 99%, and beta FeOOH nanorods basic 4-CP no adsorption. Using β-FeOOH as a catalyst, Yang (Yang et al., 2010) compared the degradation and mineralization of ibuprofen (IBU) with individual ozone oxidation, and the TOC degradation rate increased from 20% to 40%.

As was known to all, the synthesis of conventional FeOOH was made of iron chloride, iron nitrate and iron sulfate. However, due to the difference of experimental precursors and methods, and used to degrade different pollutants, the catalytic performance of the prepared FeOOH could not be effectively evaluated. In this study, the different FeOOH catalysts were synthesized from different precursors (iron chloride, iron nitrate and iron sulfate) by the same experimental methods, and ibuprofen (IBU) was selected as a target pollutant. And that was concluded that which precursor had been used as the raw material to manufacture FeOOH, which could obtain better ozone catalytic activity, so that the reference could be provided for the preparation of FeOOH in practical engineering. The main objective of this study was to investigate the catalytic performance of the prepared-FeOOH by different precursors in the heterogeneous catalytic ozonation, and explored the causes. The morphology and physico-chemical properties of different prepared-FeOOH catalysts were characterized by XRD, FT-IR, SEM and N$_2$ adsorption-desorption techniques. Additionally, the kinetics of reaction was discussed in degradation. Finally, the stability and possible catalytic mechanism were also

studied.

2. Experimental

2.1. Synthesis of catalyst

All chemicals were in analytical grade and used as received without purification. Synthesis of Cl$^-$-FeOOH: in a typical synthesis, FeCl$_3$·6H$_2$O (2.7 g) was completely dissolved in distilled water in a beaker at 25 °C under magnetic stirring. Then, an aqueous solution of NaOH (1.2 g) was added dropwise to the beaker and the color of the solution immediately turned yellow. After continuous stirring for 30 min, increasing the temperature to 60 °C and stopping stirring, ageing 24 h. Finally, the products were collected by centrifugation and washed several times with distilled water and ethanol, and then dried at 50 °C for 12 h. Likewise, The use of ferric sulfate and ferric nitrate as precursors for the synthesis of catalysts was described above.

2.2. Characterization of catalyst

The crystalline phases of as-prepared catalysts were analyzed by XRD in the range of 2θ = 10–80° (X'TRA, Swiss ARL). The morphology and structure of the as-prepared samples were examined with SEM by S-3400N II (Hitachi, Japan). Infrared spectra of the resins in the range of 4000–400 cm^{-1} were collected using Nexus870 spectrophotometer (Nicolet, USA). The BET surface area and pore diameter of catalysts were determined using an automatic analyzer (Micromeritics ASAP-2010C, USA) with N$_2$ as the adsorbate.

2.3. Experiments on ozonation and catalytic ozonation

In a typical catalytic ozonation procedure, 0.5 g catalyst was mixed with 500 mL ibuprofen solution (20 mg/L, pH = 7) in a flask under magnetic stirring, which made the catalyst concentration keeping 1 g/L. The flowing rate of O$_3$ during ozonation process was kept at 0.5 L/min and the concentration was 4.0 mg/L. During the reaction process, 5 mL solution was taken out from the reactor for analysis in each 2 min interval. The similar experimental process was carried out by only ozone. Then, the filtrates were analyzed by recording variations of the absorption band maximum (273 nm) in the UV–vis spectra of ibuprofen by using a Shimadzu UV-1800 spectrophotometer. TOC was measured with a TOC analyzer (Aurora 1030C, OI Analytical Co., Ltd., United States) with autosampler (Model 1088, OI Analytical Co., Ltd., America) The catalytic degradation efficiency (E) of ibuprofen was obtained by the following formula (Eq. (1)):

$$E = \left(1 - \frac{C}{C_0}\right) \times 100\% = \left(1 - \frac{A}{A_0}\right) \times 100\% \tag{1}$$

where C was the concentration of the ibuprofen solution at reaction time t, C$_0$ was the adsorption/desorption equilibrium concentration of ibuprofen (at reaction time 0); A and A$_0$ were the corresponding values for the absorbance.

2.4. LC-MS analysis

Liquid Chromatography Mass Spectra (LC-MS) (LXQ Linear Ion Trap Mass Spectrometer) were used to analyze the degrade products. The LC setup was equipped with two Varian ProStar210 pumps, an Agilent TC-C (18) column, and a Varian ProStar325 UV–vis Detector at 220 nm. A solution of methanol and H$_2$O in the ratio 50:50 (v/v) was used as the mobile phase at 1 mL/min, and 20 μL of the sample solution was injected. The column oven temperature was 35 °C. The MS spectrometer was operated in negative polarity.