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Ultrasound irritation enhanced heterogeneous activation of peroxymonosulfate with Fe_3O_4 for degradation of azo dye

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ABSTRACT

Magnetic Fe_3O_4 nanoparticles were synthesized and used as peroxymonosulfate (PMS) activator in the presence of ultrasound (US) irritation for azo dye degradation in this study. At pH 7.0 and temperature 298 K, Fe_3O_4 nanoparticles were able to activate PMS under ultrasound irritation to produce sulfate radicals for acid orange 7 (AO7) removal in 30 min. Higher catalysts dosage, neutral pH as well as optimum values of PMS dosage and ultrasound power favored the AO7 degradation. Fe_3O_4 displayed excellent stability and reusability in the US/PMS system. Both of the sulfate radicals and hydroxyl radicals were produced in the reaction and sulfate radicals were the dominant according to the scavenging tests and electron paramagnetic resonance (ESR) tests. The mechanisms of ultrasound irritation enhanced PMS activation in the presence of Fe_3O_4 were proposed based on the results and literatures.

1. Introduction

Discharge of refractory organic matters to the water body is a great threat to the environment. However, conventional wastewater treatment can hardly degrade the refractory organic matters efficiently, which is needed to be solved urgently [1]. As an alternative technology, advanced oxidation process based on hydroxyl radicals ($^{\cdot}OH$) can oxidized the refractory organic matters into small molecular [2], or even carbon dioxide and water [3], which is mainly attribute to the high redox potential of $^{\cdot}OH$ [4].

Recently, advanced oxidation process based on sulfate radicals have been received extensive attentions for the degradation of refractory organic matters owing to the longer half-life, higher selectivity towards organic matters oxidation and redox potential ($E_0 = 2.6$ V vs. NHE) of $SO_4^{\cdot-}$ in comparison with $^{\cdot}OH$ [5]. $SO_4^{\cdot-}$ can be generated by means of the decomposition of persulfate or PMS [6–8]. In addition, PMS could be catalytic decomposed more easily than persulfate due to the shorter bond length of O—O in PMS [9]. Heterogeneous activation of PMS with magnetic metal oxides cannot only reduce the leaching of metal ion, but also separate the catalysts conveniently with external magnetic field, receiving more attentions currently. Magnetic spinel ferrites including $CuFe_2O_4$ [10–12], $MnFe_2O_4$ [13], $CoFe_2O_4$ [14], $ZnFe_2O_4$ [15] can catalytic decomposed PMS to generate $SO_4^{\cdot-}$ efficiently. However, complicated synthesis route of these solids limit their application in the practical engineering.

Fe_3O_4 with inverse spinel cubic structure could activate the O—O in the H_2O_2 [16], persulfate [17] and PMS [18] to generate strong oxidizing radicals efficiently. Moreover, easy preparation process, stable physiochemical structure, low preparation cost and sensitive magnetic response of Fe_3O_4 [19] make itself a promising catalyst for the PMS activation.

In addition, ultrasonic irritation could enhance the catalytic activity of Fe_3O_4 significantly because of the decreasing mass transfer limitations and cavitation effect [20]. All of US/Fe_3O_4/oxidants systems, including US/Fe_3O_4/persulfate [21], US/Fe_3O_4/H_2O_2 [22] and US/Fe_3O_4/O_3 [23] system were used to remove the refractory organic matters. Nevertheless, enhancement of the PMS activation capacity of Fe_3O_4 with ultrasonic irritation for pollutants degradation has not been reported.

In this study, Fe_3O_4 nanoparticles were synthesized and applied as PMS activator under ultrasound irritation for enhanced degradation of AO7, a typical organic pollutant of azo dye. Some important factors affecting on the removal efficiency were investigated. Meanwhile, the effect of ultrasound irritation on the reusability and stability of catalysts was evaluated. At last, the mechanism of generation of oxidizing radicals was proposed.

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2. Materials and methods

2.1. Materials

All of the reagents were purchased from Aladdin Co. Ltd and of analytical grade as well as without purification before use. AO7 and 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO) was obtained from Sigma–Aldrich.

2.2. Synthesis and characterization of Fe_3O_4

In brief, 100 mL deioned water containing 12 mmol NaOH was heated to 363 K with stirring. And then, 20 mL solution containing 6 mmol $FeSO_4$ was added into the heated solution. The mixture was maintained at 363 K for 2 h with stirring and cooled naturally. After that, the solids washed 3 times with deioned water were dried in a vacuum drying oven at 333 K for 6 h.

The crystal structure of solids was determined with X-ray diffractometer (D8 Advance, Bruker, Germany) with CuKα radiation. The morphology of the catalysts was measured transmission electron microscopy (TEM, F-20, Tecnai, USA) operated at 200 kV. The valence of element in the solids was demonstrated with X-ray photoelectron spectroscopy (XPS, PHI 5000C ESCA System, USA). The special surface area ($m^2 \cdot g^{-1}$) of the catalyst were obtained with the Brunauer-Emmett-Teller (BET) method measured on an accelerated surface area and porosometry system (ASAP2020, USA) at 77 K by N_2. The magnetic properties of the synthesized catalyst were acquired by means of the vibrating sample magnetometer (VSM, JDM-13, China). The zero-point charge of solids were measured through potentiometric titrations method.

2.3. Experimental procedures

The degradation of AO7 in various systems was operated at 25 °C. 200 mL mixture containing the Fe_3O_4 and pollutants was added into 500 ml Erlenmeyer flasks and shaked for 20 min for adsorption balance. Then, the flask was immersed into the ultrasonic bath (400 W, 20 kHz, NingBo Xinzhi Technology Co., Ltd., China). After the addition of PMS, about 0.5 ml solution was sampled at fixed interval time and filtered through 0.22 μm membrane, and then added into a vial containing 0.5 mL ethanol to quench the PMS for analysis. The adjustment of the solution pH from 3.0 to 12.0 was through the addition of borate buffer solution. In the successive catalytic experiments, the separated catalysts were washed using pure water and ethanol several times and then added into the 200 mL containing AO7 and PMS.

2.4. Analytical methods

AO7 analysis was determined by means of the UV spectrometer with wavelength at $\lambda = 556$ nm. Leakage of Fe was conducted on an inductively coupled plasma mass spectrometry (ICP-MS, Angilent 7700s, USA).

3. Results and discussions

3.1. Physicochemical properties of the Fe_3O_4

The structure of as-synthesized samples was examined by powder X-ray diffraction (XRD) technology. As is shown in Fig. 1a, all of obvious characteristic diffraction peaks could be identified as the crystal faces of the cubic phase of Fe_3O_4. The morphology of the Fe_3O_4 were obtained through TEM (Fig. 1b) images. It can be seen that all of nanoparticles were in sphere shape. The hysteresis curve (Fig. 1c) obtained through the vibrating sample magnetometer showed the ferromagnetic property of Fe_3O_4. The surface area and pore structure of Fe_3O_4 were measured by means of N_2 adsorption–desorption isotherms. The results showed that the BET surface areas calculated from Fig. 1d was 20.17 m^2/g while the corresponding pore volume was 0.19 cm^3/g.

3.2. AO7 degradation in different systems

The degradation of AO7 in different systems was evaluated and displayed in Fig. 2. It can be seen that adsorption affinity is not existed between AO7 and Fe_3O_4. In addition, the addition of PMS alone in the solution did not induce the large increase of decomposition of AO7, which may be due to the stable chemical property of PMS at ambient condition. Meanwhile no obvious degradation of AO7 appeared in the US/ Fe_3O_4 system, also. On the other hands, the decomposition of AO7 was increased to an extent in both of Fe_3O_4/PMS and US/PMS system, about 31% of AO7 degraded. These results demonstrated that Fe_3O_4 or ultrasound irritation can activate PMS to generate radicals. In the Fe_3O_4/PMS system, the $SO_4^{\cdot -}$ and $^{\cdot}OH$ can be formed on the surface of Fe_3O_4, which can attack the AO7 molecular [18]. For US/PMS system, the removal efficiency of AO7 is 39.6%, which may be induced by the acceleration of HSO_5^- decomposition to form $SO_4^{\cdot -}$ and $^{\cdot}OH$ by cavitation [24].

Interestingly, the degradation efficiency of AO7 was significantly enhanced in the US/Fe_3O_4/PMS system in comparison with US/PMS and Fe_3O_4/PMS system, up to 90%, which displayed that a strong synergistic effect existed between the sonochemical and catalytic degradation of AO7. This phenomena may be due to the follow reasons: ultrasound irritation accelerated the decomposition of HSO_5^- at the surface of Fe_3O_4 to generate $SO_4^{-\cdot}$ and $^{\cdot}OH$ and increases the mass transfer rate of the system [25].

3.3. Effect of other parameters on the AO7 degradation

In order to meet the need of practical application, the effect of operational parameters of the catalytic experiment such as PMS concentration, catalysts dosage, initial pH of the solution, anions and temperature was evaluated.

3.3.1. Effect of PMS concentration

Fig. 3 showed the effect of PMS concentration on the degradation of AO7. It can be seen that as the molar ratio of PMS/AO7 increased from 30 to 50 the k_{obv} inceased from 0.037 min^{-1} to 0.078 min^{-1}. Meanwhile, no obvious change for k_{obv} appeared at 50–70 M ratio. At the low concentration of PMS, the increase of the PMS concentration may induce the production of more radicals, which means the limited factor is the PMS concentration. However, at higher PMS concentration, number of active site on the catalysts determined by the fixed amount of catalysts in the solution limited the amount of radical generated, leading to the no change of the reaction kinetics, which demonstrated the independent relationship between radical yield and PMS concentration.

3.3.2. Effect of catalysts amount

The active sites on catalyst surface is critical for catalytic oxidation. More active sites could make more oxidants decompose to generate radical in a given time, favorable the promotion of pollutants degradation. Fig. 4a displayed the effect of catalysts dosage on the performance of the US/Fe_3O_4/PMS system. It can be seen that the reaction rate of US/Fe_3O_4/PMS system increased along with the increase of the catalysts dosage. The reaction rate is related linearly to the Fe_3O_4 dosage (Fig. 4b). The equation can be established as list, which is similar to other reports [18].

$$k_{obv} = 0.0516\ \text{min}^{-1} + m(Fe_3O_4)_0 \times 0.067\ \text{L}/(\text{g min})$$