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Microwave-assisted catalytic degradation of methyl orange in aqueous solution by ferrihydrite/maghemite nanoparticles

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ABSTRACT

Six-line ferrihydrite was successfully prepared by precipitation method and characterized with XRD, SEM, TEM, BET and FTIR spectroscopy. The as-prepared ferrihydrite was used as catalyst for the degradation of methyl orange (MO) in an artificial dye wastewater without adding any oxidant. It was found that the ferrihydrite nanoparticles with average size of about 90–220 nm exhibited a high adsorption capability to MO and the dye molecules obey Langmuir type of adsorption. Batch degradation experiments show that the catalytic degradation of MO could be remarkably improved by coupling with microwave irradiation. The initial pH value of MO solution exerted notable influence on the degradation reaction and the optimal degradation efficiency was obtained under neutral conditions. Radical scavenger measurements indicated that •OH radicals could generate during the catalytic process even without adding oxidant. We proposed that the microwave irradiation facilitates the generation of active oxygen species derived from water and/or oxygen dissolved in water, which are responsible to the excellent performance of the MW-assisted catalytic process.

1. Introduction

Catalytic wet air oxidation (CWAO) is one of the most economical and environmental-friendly advanced oxidation processes and is considered to be a promising technology for the treatment of refractory organic pollutants in industrial wastewater [1]. In the three-phase CWAO process, the organic pollutants are oxidized by activated oxygen species in the presence of a heterogeneous catalyst into biodegradable intermediate products or mineralized into CO_2, water and associated inorganic salts [2]. However, CWAO suffers from the requirements of relatively high pressure (0.5–2.0 MPa) and high temperature (100–220 °C) to realize total mineralization of organic pollutants [3]. To overcome the limitations of a single method, it is viewed imperative to conceive technically and economically feasible wastewater treatment processes by coupling various promising technologies. Therefore, application of CWAO coupled with other techniques has been explored to reduce the reaction severity and/or improve the efficiency [4–6].

In the past decade, microwave (MW) irradiation technique has received wide attention as a means to improve the efficiency of the CWAO and other advanced oxidation processes [7,8]. Until now, numerous efforts have been made on the combination of MW with various catalytic materials including MFe_2O_4 [9], Pt/GAC [10], alumina-supported copper oxide [11], nano-NiO_2 [12] and Fe@Fe_2O_3/CNTs/PTFE [13] for eliminating a wide range of organic compounds in water. These studies demonstrated that the enhancement resulted by MW introduction is mainly due to the thermal and non-thermal effects of MW, i.e. superheating, polarization, dielectric properties, hot spot formation, nuclear spin rotation, and spin alignment [14].

Iron-containing nanomaterials have been proven promising for removing toxic organic pollutants from wastewater because of their low cost, natural abundance, strong adsorption capacity, easy separation, enhanced stability and environmentally friendly properties [15–17]. Ferrihydrites with the general formula of FeOOH•nH_2O are iron oxide hydroxides found in terrestrial systems such as soil and sediment. Owing to their large surface area and high reactivity, nanocrystalline ferrihydrites play an important role in controlling the toxicity and bioavailability of some contaminants and nutrients through adsorption and coprecipitation [18]. Recently, ferrihydrite [19,20], citrate modified ferrihydrite [21] and iron-maghemite mixture [22] were found to show excellent performance as heterogeneous Fenton catalysts for the treatment of pollutants.

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Despite previous research on MW irradiation of the CWAO reaction for degradation of organic compounds, investigations of ferrihydrite with respect to enhancement of MW have not been attempted in the combination of MW and CWAO. Methyl orange, a typical azo dye being widely used in many industries, is commonly used as a model pollutant of dye wastewater, thus an attempt is made for the first time to degrade MO in a microwave oven using ferrihydrite as the catalyst. *tert*-Butanol (*t*-butanol) was used as scavenger to check the generation of •OH free radicals during the CWAO reaction with and without MW irradiation.

2. Experimental

2.1. Chemicals

Methyl orange (4-[4-(dimethylamino) phenylazo] benzenesulfonic acid, MO) was obtained from Regent Chemicals. Iron (III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) was obtained from Tianjin BASF Chemical Reagent. Potassium borohydride (KBH_4) was obtained from Shanghai Aibi Chemical Preparation Co. Ltd. Ethanol and Hydrochloric acid were supplied by Yantai Sanhe Chemical Reagent. Sodium hydroxide was purchased from Tianjin Bodi Chemical Reagent. All chemicals mentioned above are of analytical grade.

2.2. Ferrihydrite synthesis

In a typical synthesis, a KBH_4 solution was prepared by dissolving 1.36 g of KBH_4 into a mixture of 35 mL of distilled water and 15 mL of ethanol. 5 mL of $Fe(NO_3)_3$ aqueous solution (0.3 M) was poured into 100 mL of boiling water to form a $Fe(OH)_3$ colloid. Then, KBH_4 solution was mixed with the formed colloid and stirred for 5 min. The above mixed solution was stabilized for another 30 min after stirring to obtain black product and subsequently washed repeatedly with distilled water and ethanol before being dried at 60 °C for 12 h.

2.3. Characterizations

A laboratory X-ray powder diffraction (XRD) pattern of the ferrihydrite sample was collected in a D/max-2500/PC X-ray diffractometer (Rigaku, Japan) using Cu Kα radiation operating at 40 kV and 30 mA. The morphology of the obtained-catalyst was studied by scanning electron microscopy (SEM, JSM 6700F, operating at 8 kV). Transmission electron microscopy (TEM) image was recorded using a JEM-1200EX microscope operating at 80 kV. BET specific surface area and pore size were determined from N_2 adsorption at 77 K using a Micromeritics ASAP 2020 instrument. Fourier transform infrared spectroscopy (FT-IR) was collected from 4000 to 400 cm^{-1} on a Bruker TENSOR27 IR spectrometer. All UV–vis absorption spectra were carried out using a UV752 spectrophotometer (Shanghai Yoke Instrument. Co., Ltd, China).

2.4. Adsorption experiments

The adsorption capacity of ferrihydrite to MO was evaluated in batch mode. A stock solution of MO (500 mg/L) was prepared by dissolving an appropriate amount of the dye in deionized water. The experimental solution was then obtained by diluting the stock solution with deionized water to the desired initial concentrations. In a typical procedure, 100 mg of the adsorbent was added to 50 mL of the dye solution with known initial concentrations and stirred for 2 h. The suspension was then centrifuged and the absorption spectra of the supernatant solution were collected using a UV–vis spectrophotometer. The equilibrium concentrations of MO were determined by monitoring the absorbance at the maximum wavelength (λ_{max} = 460) in relation to a previously prepared calibration plots.

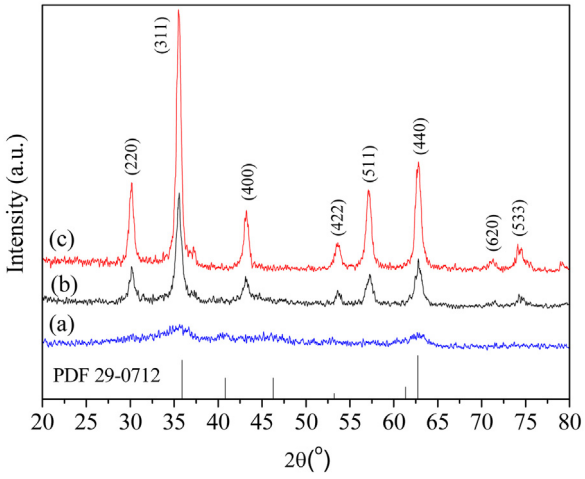

Fig. 1. XRD patterns of newly produced ferrihydrite nanoparticles (a) and the samples after treatment of MO in MW-assisted CWAO system (b) and CWAO system (c).

2.5. Degradation experiments

All batch MW-assisted degradation experiments were carried out in a house microwave apparatus (Meide household electrical appliances group Co., Ltd, China). Typically, 50 mL of MO solution (20 mg/L) was filled in a flask reactor, and then 0.1 g of catalyst was dispersed in the solution. For all experiments, the MO dye solution was adjusted by adding 1.0 M NaOH/HCl (aq) to the desired pH values. The reactor was put into the microwave oven operating at a fixed frequency of 2450 MHz with output power of 119 W and kept under irradiation for 4 min. In order to study the impact of MW on the system, conventional CWAO experiments were performed at 50 °C under atmospheric pressure by immersing the reactor in a water bath. After reaction, the catalyst particles were removed by magnetic separation and the clear supernatant was analyzed using UV–vis spectroscopy.

The MO degradation efficiency was calculated using the following formula:

$$\text{MO degradation\%} = \frac{C_0 - C_t}{C_0} \times 100\%$$

where C_0 (mg/L) is the initial concentration of MO in the solution, and C_t (mg/L) is the concentration of MO at *t* min.

All the above-mentioned tests were conducted in triplicate.

3. Results and discussion

3.1. Structural and morphology characterizations of ferrihydrite nanoparticles

Fig. 1 shows the XRD patterns of the ferrihydrite nanoparticles before and after treatment of MO in the simulated dye wastewater by both CWAO and MW-assisted CWAO processes. As shown in Fig. 1a, the newly produced nanoparticles exhibit poorly defined reflections featuring with board and coarse peaks, which match with the six-line ferrihydrite reference pattern (JCPDS 29-0712). Because of the lack of crystallinity associated with a particular Miller index, their width β cannot be used for a reliable measure of the crystallite sizes using the Scherrer equation. In contrast, the used samples show a well-defined XRD pattern independent of