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Synergistic degradation of methyl orange in an ultrasound intensified photocatalytic reactor

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ABSTRACT

An original ultrasound (US) directly intensified photocatalytic reactor was designed to degrade azo dye pollutant methyl orange (MeO) using Degussa TiO_2 as the photocatalyst. The sonolytic, photocatalytic and sonophotocatalytic degradation of MeO in the new reactor and the synergistic effect between sonolysis and photocatalysis were investigated. Effects of operation parameters i.e., US power, TiO_2 dosage, liquid circulation velocity and air flow rate on degradation efficiency were investigated and optimized. The results showed that all parameters have optimal values for the sonophotocatalytic degradation of MeO, and the optimum conditions for the new process are US power 600 W, TiO_2 dosage 3 g/L, liquid circulation velocity 4.05×10^{-2} m/s and air flow rate 0.2 L/min. Under the optimum conditions, 91.52% MeO had been degraded within 1 h, and the combination of sonolysis and TiO_2 photocatalysis exhibited an obvious synergetic effect.

1. Introduction

Water pollution due to colored effluents from textile industries has attracted much attention of scientists from all over the world, especially from China, because the large textile industry lies in its eastern coastal region. Azo dyes which contain one or more azo bonds (–N=N–) contribute 60% to 70% of total dyes used in textile industries [1]. However, many studies show that most azo dyes are carcinogenic, mutagenic and toxic, and resistant to the biological and other conventional treatments [2–5]. In this context, efforts have been devoted to find other effective treatment methods, among which are called Advanced Oxidation Processes (AOPs). AOPs are characterized by utilizing a strong oxidizing species such as ·OH radicals produced in situ, which causes the dye macromolecules to break down into smaller and less harmful substances and even to mineralize into the harmless products of water and carbon dioxide [6]. The AOPs applied in dye wastewater treatment include Fenton process [7], ozonation process [8], sonolysis [9], phtotocatalysis [10,11] and UV/H_2O_2 photolytic approach [12].

Although individual AOPs seem useful to treat the dyes, the critical limits are low efficiency for the degradation and complete mineralization of the pollutants due to technical or economical reasons [13]. Many researchers tried to enhance the efficiency of AOPs through forming hybrid systems from two or more techniques, among which the combination of sonolysis and photocatalysis is known as sonophotocatalysis receiving considerable attention [14–17].

Sonophotocatalysis not only achieves additive effect [18], but also obtains synergistic effect especially when employing relatively low frequency ultrasound (20–100 kHz) [16,19]. The observed synergistic effect is probably due to the following reasons: (i) for the ultrasonic process, photocatalyst particles enhances the cavitation phenomenon through breaking up the microbubbles into smaller ones; (ii) for the photocatalytic process, mechanical effects of ultrasonic waves cause the size of catalyst agglomerates to be reduced, increasing mass transfer and surface cleaning [20]. The enhancement of photocatalysis efficiency using ultrasound has been widely investigated, however, many researches are conducted in simply designed reactors, which may limit the efficiency of ultrasound intensification and is not suitable for industrial application [21–23].

This work attempts to find a more efficient intensification manner for the scale-up of sonophotocatalytic process by developing a new ultrasound intensified photocatalytic reactor. Methyl orange (MeO), a typical mono azo dye, was selected as a model pollutant in this study. The effects of process parameters were investigated and the synergistic effect between sonolysis and photocatalysis was also evaluated.

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2. Experimental

2.1. Photocatalyst and chemicals

The MeO used in the experiments was analytical grade and was provided by a local chemical company. Degussa P25 TiO_2 powder used as photocatalyst was purchased from Shanghai Haiyi Scientific & Trading Co., Ltd., which has an average particle size of about 30 nm and BET surface area of 50 m^2/g.

2.2. Design of the new sonophotocatalytic reactor

It was reported that in TiO_2 slurry photocatalytic system, the agglomeration of catalyst particles would reduce the efficiency of photocatalytic process [24,25]. However, the sonochemical process was found to be effective to deaggregate photocatalyst, resulting in photocatalytic efficiency improvement [20]. To utilize the deaggregation function of the ultrasound without affecting the photocatalytic process, the main design idea of the new reactor in this paper is to connect the individual sonolysis and photocatalysis through the circulating pump. In our previous work, we found that the annular photocatalytic reactor with an internal lamp has exhibited promising performance in azo dye wastewater treatment with high apparent quantum yield and low energy consumption. So we combined this annular photocatalytic reactor with sonolysis. The configuration and experimental setup of the newly designed reactor is shown in Fig. 1. The main body of the annulus photocatalytic reactor is a cylindrical PVC bed with an inside diameter of 65 mm and height of 250 mm. A UV lamp acrylic sheath with a diameter of 40 mm is fixed in the center of the cylindrical bed using a ring flange. An 11 W UV lamp with a peak wavelength of 360 nm is placed into the sheath as the UV light sources of the reactor. The UV lamp is immersed in the reaction system so that the UV light energy could be absorbed to the largest extent. A 20 kHz ultrasonic probe (diameter of 6 mm) of variable power was used as the source of ultrasound. As for ultrasonic reactor, a similar cylindrical polyvinylchloride (PVC) bed was manufactured, and the ultrasonic wave was emitted from the ultrasonic probe immersed in the slurry. As known, the dissolved oxygen in liquid phase is the electron acceptor in photocatalytic process, and as W. Nam et al. reported the air bubbles may promote the mass transfer, but a large number of bubbles may hinder the absorbance of UV light to the photocatalyst [26]. In this paper we directly introduced air into the sonochemical reactor to promote mass transfer without affecting the UV light irradiation. Besides, the air can also remove hydrogen that is always produced in the sonochemical process [27], and this benefits the production of hydrogen peroxide which improves the sonochemical degradation efficiency of MeO. The air volume is measured by an air flow meter. During experimental operation, the slurry is circulated between sonochemical reactor and photocatalytic reactor by a circulating pump.

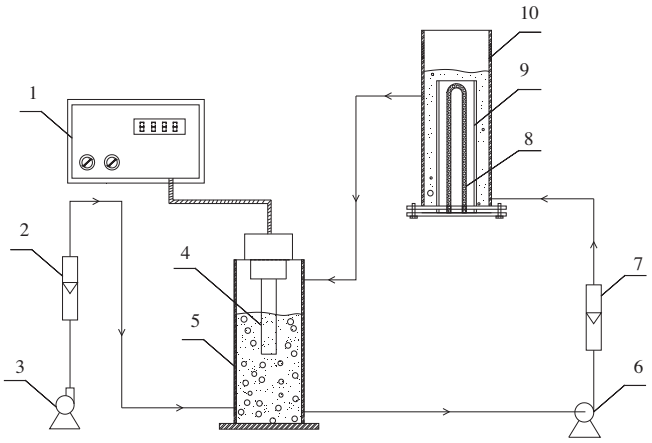

Fig. 1. The configuration and experimental setup of the sonophotocatalytic reactor for the MeO treatment. 1-ultrasound generator; 2-air flow meter; 3-air pump; 4-ultrasonic probe; 5-sonochemical reactor; 6-circulating pump; 7-slurry flow meter; 8-UV lamp; 9-UV lamp sheath; 10-annular photocatalytic reactor.

2.3. MeO degradation experiments

The whole experiment was carried out through two steps. Firstly a series of experiments of different treatment processes, i.e. ultrasound alone (sonolysis, labeled as US), TiO_2 photocatalyst alone (TiO_2), sonolysis in the presence of TiO_2 (sonocatalysis, US + - TiO_2), photoirradiation in the presence of TiO_2 (photocatalysis, UV + TiO_2), a combination of photocatalysis and sonolysis (sonophotocatalysis, US + UV + TiO_2) were carried out as preliminary studies to investigate the synergistic effect between sonochemical and photocatalytic treatment. After the preliminary studies, the effects of the process parameters, including US power, TiO_2 dosage, and liquid circulation velocity and air flow rate, on the degradation of MeO were examined and optimized. The comparative studies for the sonocatalysis and photocatalysis experiments were conducted through turning off the ultrasound or UV light under the same conditions as used in the sonophotocatalytic process.

For each experiment, an air pump was turned on firstly, and then 1.1 L 10 mg/L MeO aqueous solution was poured into the sonophotocatalytic reactor. The circulating pump was turned on when nearly half of the solution was poured. After all the solution was added, a different amount of P25 TiO_2 photocatalyst was added into the circulating solution. The suspension was circulated in the new system for 30 min in the dark to establish adsorption equilibrium, and then the UV light and ultrasound were turned on to begin sonophotocatalytic degradation of MeO. 10 ml of sample was taken out from the reaction system at internals. The suspension samples were centrifuged at 15,000 rpm for 5 min to obtain clear supernatant for analysis. The absorbance of MeO aqueous solution was detected using a UV-2000 UV–VIS spectrometer at 464 nm. Each degradation experiment was conducted in duplicate, and the averaged absorbance was used to calculate the concentration of the MeO, and the deviation of the measurement between the same experiments was controlled in ±5%. All experiments were conducted at room temperature and in batch mode.

3. Results and discussion

3.1. Preliminary study

The experiments in the preliminary study were carried out at a moderate condition according to our previous study. It was reported that sonolytic, phocatalytic and sonophotocatalytic reactions occurring at relatively low substrate concentrations can usually be described by a pseudo-first order kinetic expression as follows [22]:

$$\frac{dC}{dt} = kC \Longleftrightarrow \ln\frac{C_0}{C_t} = kt \tag{1}$$

where k represents the apparent MeO degradation rate constant, and C_0 and C_t are the MeO concentrations at the beginning and any time t, respectively. The good linear relationship of $\ln\frac{C_0}{C_t}$ with reaction time t shown in Fig. 2b verifies the degradation of MeO in different processes can be described by Eq. (1).

The results in Fig. 2 also show that sonolysis, TiO_2 photocatalyst alone and sonocatalysis processes show limited efficiency in the