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Dual-frequency (20/40 kHz) ultrasonic assisted photocatalysis for degradation of methylene blue effluent: Synergistic effect and kinetic study

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ABSTRACT

Dual-frequency ultrasonic assisted photocatalysis (DUAP) was proposed to enhance the degradation efficiency of methylene blue (MB) solution. The influence of operational parameters, i.e., irradiation time, ultrasonic arrangement, TiO_2 concentration and power density, was studied. The results implied that the rapid degradation of MB solution was achieved in 18 min under DUAP with the dual frequencies of 20/40 kHz. Kinetic investigation of MB degradation for the DUAP process was conducted on the basis of first-order kinetic equation and the synergistic effect was assessed by examination of the apparent rate constant. The effect of ultrasonic arrangement was analyzed by comparison of the pressure amplitude of ultrasonic superposition field. The evolvement of intermediate products and the role of active species during DUAP were distinguished by UV–Vis spectra and the free radical scavenging experiment.

1. Introduction

Advanced oxidation processes (AOP), such as UV light/H_2O_2, UV/ozone and UV/TiO_2, have recently emerged as a promising technique to degrade organic dyes in the textile effluent due to its strong oxidizing power, non-toxic, and low cost [1–7]. However, it is difficult to completely mineralize the opaque or translucent wastewater by photocatalysis because of the low penetrating ability of light. In addition, it is confronted with the usual problems such as the aggregation of catalyst particles during photocatalysis, and sonochemical formation of stable H_2O_2 in the presence of low levels of pollutants [8].

One strategy to solve these problems is the degradation of dye effluent by coupling ultrasonic field with photocatalysis. The penetrating ability of ultrasound is very strong even for the opaque wastewater medium and its penetrating depth can ordinarily attain 15–20 cm [9,10]. Ultrasonic activation also contributes dye degradation via de-aggregating catalyst particles and acceleration of the splitting of H_2O_2 produced by both photocatalysis and sonolysis to form more ·OH and ·OOH free radicals [6,11–16].

Reports on the combination of ultrasonic irradiations with photocatalysis are available by examining the influencing factors including irradiation time, ultrasonic arrangement and ultrasonic power density [2,11–13,17–20].

On the other hand, the dual-frequency or multiple frequency ultrasonic processes have wide applications in the intensification of metal leaching process [21], sonolysis of organic pollutants [22–25] and combination with enzyme processing [26], etc. The corresponding results indicate that the dual-frequency ultrasonic process is more effective in the terms of improvement of the leaching or degradation efficiency, shortening of the processing time, etc. compared to the single frequency ultrasonic process. The single-frequency ultrasonic assisted photocatalysis process (SUAP) for the degradation of organic effluents has been reported in recent years. However, very little attention has been focused on the combination of dual-frequency ultrasound with photocatalysis for the treatment of industrial effluents.

The present work was aimed at investigating the synergistic effect and evaluating kinetic parameters of the DUAP process. The degradation efficiency of the DUAP process was compared to that of the SUAP process and the photocatalysis process (UV/TiO_2). In addition, the intermediate products were analyzed by UV–Vis spectra and the free radical scavenging experiment.

2. Experimental

2.1. Materials

Methylene blue (MB, AR, Tianjin Kaiyuan Reagent Corporation, China) were used as model organic pollutants. Degussa P-25 TiO_2

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(Nippon Aerosil) was used in all experiments as a standard photocatalyst.

Other chemicals were obtained as analytical reagents and used without further purification.

2.2. Experimental setup and process

The reactor consisted of a pyrex beaker and a temperature controllable water bath with a working volume of 3 L. The pyrex beaker containing 1 L MB solution of 10 mg L^{-1} was suspended in the water bath where its temperature was kept at 20 ± 1 °C by the circulation of cooling water. Photocatalyst powder (80 mg P25) was introduced into the beaker under each condition of UV/TiO_2 (without ultrasonic field), US/UV/TiO_2, as shown in Fig. 1(a) and (b) or dual-US/UV/TiO_2. The experimental schematic of the latter two processes was shown in Fig. 1. In view of the effect of arrangement of dual transducers on MB degradation efficiency in the DUAP process, the transducers are located in the opposite and orthogonal position as shown in Fig. 1(c) and (d).

A 36 W UV lamp with a maximum irradiation peak at 254 nm was employed as the central light source, which was sleeved in the center of a double-walled quartz cylinder. Besides, the coupled ultrasonic waves were produced by the CPS-3 probe type ultrasonic generator (20 kHz) and the bottom ultrasonic generator (40 kHz). The power density of ultrasound irradiation at 40 and 20 kHz was 100 W L^{-1} and adjustable in range of 0–250 W L^{-1}, respectively.

Air was simultaneously pumped in the MB solution for facilitation of scavenging electron excited by photocatalysis.

An aliquot of 10 mL was taken from the reactor at regular interval of time. The catalyst was filtered from the solution by Millipore filter (0.45 Lm) and the filtrate was analyzed for determining concentration of MB at k_{max} = 662 nm and identifying active mediates with a UV–Vis spectrophotometer (UV-2500PC). The degradation efficiency of MB with respect to its initial concentration was obtained at any time by the method. All the reported values are the average of the duplicate experimental results.

2.3. Analysis

The concentration of MB was determined by an UV–Vis spectrophotometer (Shimadzu UV2450, Japan). The concentration of hydroxyl (·OH) was identified by the free radical scavenging experiment with ethanol as ·OH scavenger.

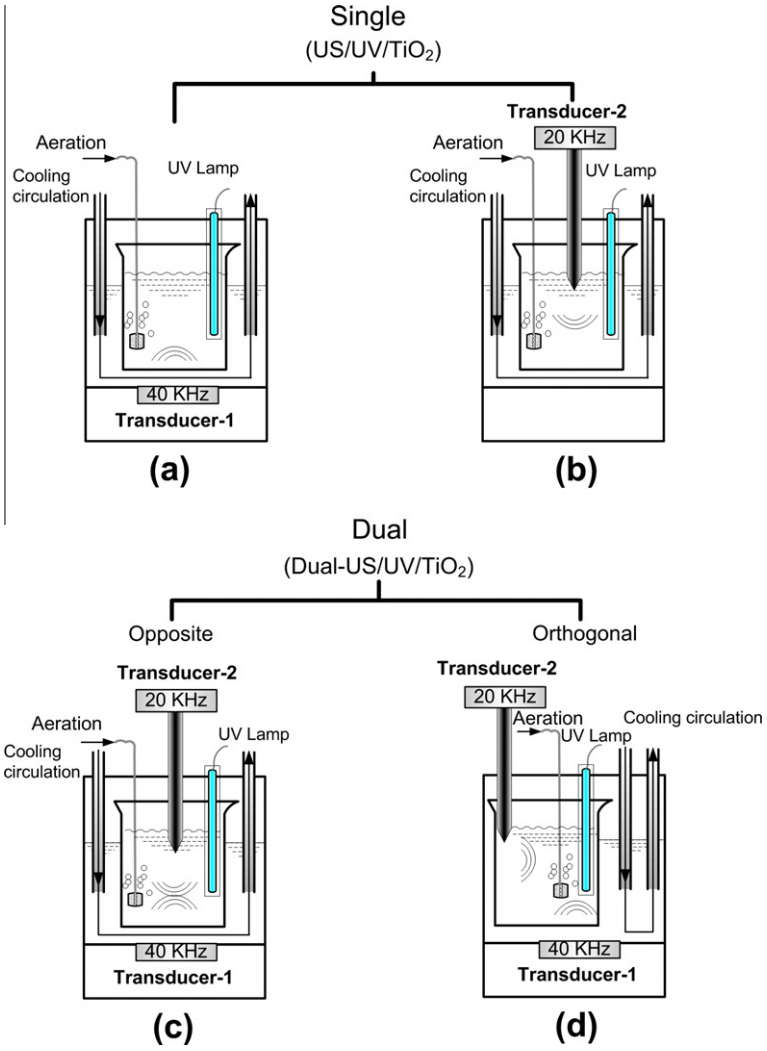

Fig. 1. Schematic of the ultrasound reactor. (a) US/UV/TiO_2, US: 40 kHz, (b) US/UV/TiO_2, US: 20 kHz, (c) and (d) dual-US/UV/TiO_2, dual transducers are arranged, respectively in the opposite and orthogonal position.