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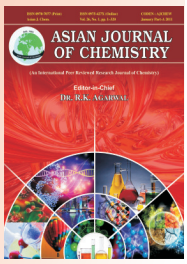

Radial Sonophotocatalytic Device and Degradation of Organic Pollutant†

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Sonophotocatalysis is extensively used in the treatment of wastewater in recent years. A new type of sonophotocatalytic reactor based on the radial ultrasonic technology was designed. The experimental results showed a synergistic enhancement effect of radial sonolysis and photocatalysis on the degradation of organic pollutants. The optimum conditions for the process are initial methylene blue concentration 10 mg L^{-1}, the added P25 catalyst concentration 0.1 g L^{-1} and ultrasonic intensity 200 W, ultraviolet (UV) lamp intensity 100 W. Under the optimum conditions, the degradation rate can achieved 90 %. The results showed that the distribution of radial ultrasound wave was more uniformity than other sonophotocatalytic reactors. It improved the efficiency of the degradation of organic pollutants. The radial sonophotocatalytic degradation of methylene blue followed pseudo-first order kinetics. The application of radial ultrasonic technology holds a promising future on the treatment of high concentration of persistent organic pollutants.

Keywords: Radial ultrasound, Photocatalysis, Synergistic effect, Organic pollutant, Sonophotocatalytic reactor.

INTRODUCTION

In recent years, with the rapid industrial development, a large number of persistent organic pollutants (POPs) are continuously emitted into the environment, which leads to heavy pollution. Persistent organic pollutants have been arousing concerns worldwide due to their high toxicities and bioaccumulation[1,2]. With the development of the wastewater treatment technologies, advanced oxidation processes (AOPs) have been extensively studied, such as ultraviolet (UV) photolysis, UV/H_2O_2 photolysis, UV/O_3 photolysis, UV/US photolysis and UV/Fenton photolysis[3]. Among advanced oxidation technology, sonophotocatalysis has attracted considerable interest and has been studied as a more effective method for the treatment of POPs[4].

The development of photocatalytic reactors has received considerable attention. Photocatalytic reactors can be classified into two types of systems such as slurry reactors and fixed bed reactors[5]. The photocatalyst powders in slurry reactor exist as a suspended state, which contribute to obtain strong oxidation activities with photogenerated holes on the surface, resulting in high photocatalytic efficiency. However, the suspended catalyst tends to aggregate and the separation of the catalyst is difficult. Moreover, the suspended catalyst is hard to be used in the continuous mode. Generally, the catalyst is supported on a carrier in the fixed bed reactor, which reducing the aggression of catalyst[6,7], but the photocatalytic activity also decreases.

In general, the ultrasonic sources of sonophotocatalytic reactor are flat-type ultrasonic transducer[8] and the probe-type axial power ultrasonic[9]. In recent years, the radial ultrasonic transducer has emerged as an attractive alternative to conventional ultrasonic transducers[10]. A very promising alternative was coupling the photocatalysis with radial ultrasound technology. The radial sonophotocatalytic technique in environmental remediation holds a promising future. By contrast to conventional sonophotocatalytic technique, radial sonophotocatalytic technique could be more suitable for the degradation of high concentration POPs in water. The radial sonophotocatalytic technique can enhance the degradation rate and reduce the reaction time than other treatment methods.

Previous studies[11-14] had indicated that the combination of UV and ultrasound can generate a synergistic effect. The observed synergistic effect is probably due to the fact that ultrasound enhances the chemical reactivity through the phenomenon of cavitation. Meanwhile, the mechanical effects

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of ultrasound reduced the agglomerating of the catalysts, increased mass transfer and surface cleaning. The enhancement of photocatalytic efficiency using ultrasound had been widely investigated. However, the radial sonolysis as well as radial sonophotocatalytic degradation of organic compounds has not reported in the treatment of wastewater.

To overcome the drawbacks of the conventional reactor, a new type of radial sonophotocatalytic reactor was designed. Methylene blue (MB) was selected as a model pollutant. Some parameters, such as the photocatalyst and reagents, the light intensity, the ultrasonic intensity, the volume of reactor and the distribution of ultrasound field were studied in radial sonophotocatalytic reactor. The synergistic effect between the sonolysis and photocatalysis on degradation rate was also studied.

EXPERIMENTAL

Commercial TiO_2 powder (P25, AR., Sigma-Aldrich), methylene blue (AR, Shanghai Chemical Reagent Company) were used as model compounds.

Experiments were performed in a self-made radial sonophotocatalytic reactor. Fig. 1 shows the apparatus and schematic diagram of the process for the oxidative degradation of methylene blue using TiO_2 as catalyst and recovering photocatalysts through filtration at the same time. The main body of the annulus radial photocatalytic reactor is a cylindrical stainless steel vessel with the diameter of 300 mm and the height of 400 mm. A radial ultrasound generator (3) with a fixed frequency of 20 kHz and a variable nominal power in the range 200-600 W was employed. The radial ultrasonic irradiation was produced by an immersed ultrasonic probe (1). Four UV lamps (16) were fixed around the radial ultrasonic probe. A 15 W UV lamp with a peak wavelength of 254 nm was inserted into a quartz cold trap (15) to provide light energy. The cold trap was utilized to maintain reaction temperature by circulating water through the reactor. The air was introduced into the radial sonophotocatalytic reactor through an aeration pipe. The micro and well-dispersed bubbles were obtained to promote the mass transfer without affecting the UV light irradiation and the absorbance of the photocatalyst[15,16]. The air volume was measured by air flow meter (2). During experimental operation, the slurry was circulated in radial sonophotocatalytic reactor by a circulating pump (10).

Experimental method: The novel reactor designs for large volume operations can be used in the batch mode and the continuous mode. The batch mode, a certain amount of aqueous solution of methylene blue was poured into the radial sonophotocatalytic reactor and then an air pump was turned on. After all the solution was added, a different amount of P25 photocatalyst was added into the solution and then the UV light and ultrasound were turned on. About 10 mL of the suspension samples were taken out from the reactor and centrifuged at 8000 rpm for 10 min to obtain clear supernatant for analysis. The absorbance of methylene blue solution was detected using a UV-VIS spectrometer (UV-2000) at 664 nm. The degradation experiment was conducted in twice. All experiments were conducted at room temperature.

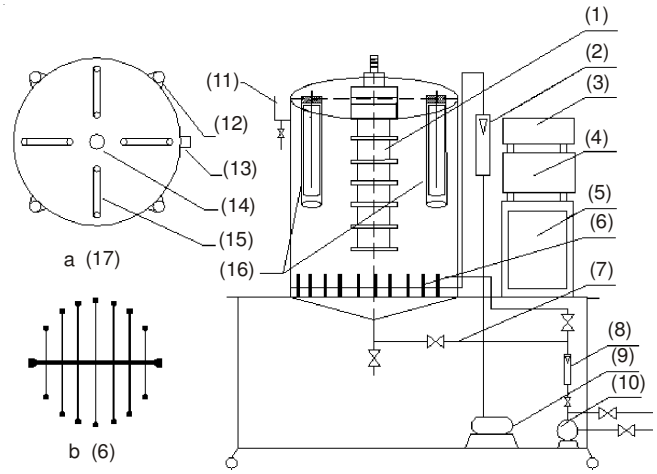

Fig. 1. Schematic of radial sonophotcatalytic reactor: (a) schematic diagram of the aeration tank cover, (b) schematic diagram of the aeration pipe; (1) radial ultrasonic probe, (2) air flow meter, (3) radial ultrasound generator, (4) UV light trigger ballast, (5) electric cabinet, (6) aeration pipe, (7) water inlet, (8) liquid flow meter, (9) draught fan, (10) water pump, (11) overflow gutter, (12) the pothook of aeration tank cover, (13) the hand shank of aeration tank cover, (14) ultrasonic probe mounting hole, (15) quartz tube, (16) UV lamp (17) aeration tank cover

RESULTS AND DISCUSSION

Influence of UV lamp power: The effect of UV lamp power on degradation of methylene blue was investigated in our self-made reactor with 100 L reaction volume. All of these experiments were undertaken in the presence of 0.05 g L^{-1} TiO_2 and the ultrasound power of 200 W. Fig. 2 shows the comparison of degradation rate between different UV lamp power (60 and 200 W). Namely, 50 % degradation of methylene blue within 3 h under 200 W UV lamp, while only 10 % degradation of methylene blue within 180 min using 60 W UV lamp. In the process of degradation of methylene blue, the irradiation of TiO_2 with UV light energy greater than the band gap energy of the semiconductor ($h\nu > E_g = 3.2$ EV) generates holes in the valence band (h^+) and the conduction band electrons (e^-)[9]. However, the hole-electron recombination limits the use of TiO_2 photocatalytic system in wastewater treatment. Whereas the electrons are consumed during the reaction with oxygen to convert it to the superoxide radical ($O_2^{\bullet-}$), the holes can react with hydroxide ion or H_2O on the TiO_2 surface to form hydroxyl radical. $OH^\bullet$ attack on the dye molecules[17,18]. During the whole degradation process, the production of $OH^\bullet$ radicals remained constant and reacted with the organic pollutant molecules. Thus, the UV light played an important role on the catalyst. Low UV power was unfavourable to the propagation of the UV light, which resulted in the decreased effect on the degradation rates.

Effect of the amount of TiO_2: The effect of the amount of TiO_2 on methylene blue degradation was shown in Fig. 3. It was observed that the degradation rate increased with the irradiation time. As the amount of TiO_2 was 0.1 g L^{-1}, complete degradation of methylene blue was achieved after 100 min. The results showed that the optimum catalyst concentration was 0.1 g L^{-1}. The degradation rate observably increased till the concentration of TiO_2 increased to 0.1 g L^{-1}. However, high

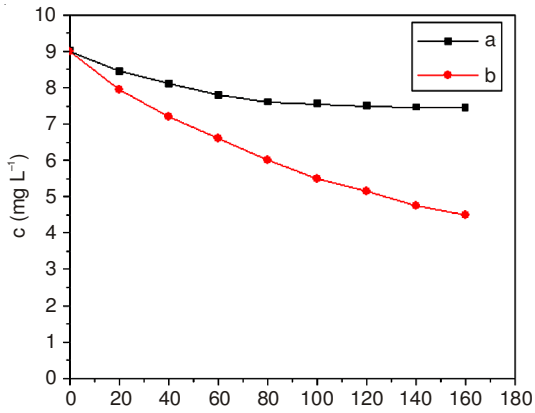

Fig. 2. Radial sonophotocatalysis of methylene blue with different UV power: (a) 60 W, (b) 200 W

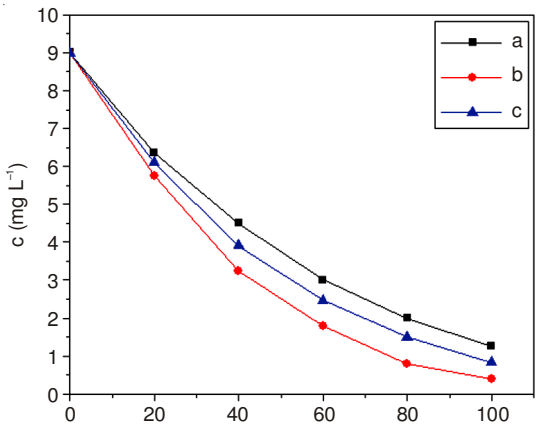

Fig. 3. Radial sonophotocatalytic degradation of methylene blue with different P25 concentration (a) 0.05 g L^{-1}; (b) 0.1 g L^{-1}; (c) 0.2 g L^{-1}; ultrasound power 200 W

catalyst concentration was unfavourable to light transmitting in water suspension, resulting in the reduction of the degradation efficiency. Meanwhile, at the optimum catalyst concentration, ultrasound was facile to the mass transport of pollutants on the catalyst surface, which improved the degradation efficiency.

The changes of the photocatalytic degradation of methylene blue were shown in Fig. 4, which was described by Langmuir-Hinshelwood (L-H) model according to the following formula[19,20].

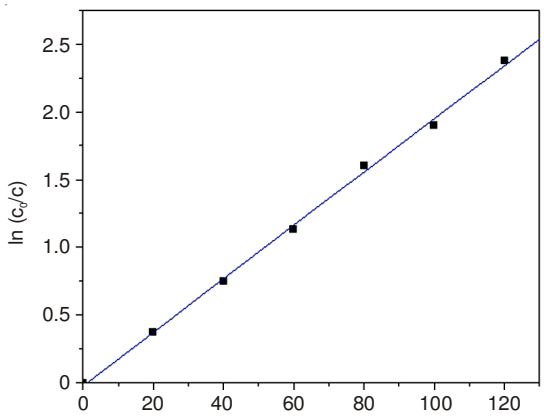

Fig. 4. Kinetics of the degradation of methylene blue using 0.05 g L^{-1} P25

$$\ln\left(\frac{c_0}{c}\right) = k_{L-H}K_{ad}t = kt \quad (1)$$

where c_o is the initial concentration, c is the variable concentration at any time t, k_{L-H} is the reaction rate constant, K_{ad} is the adsorption coefficient of methylene blue on photocatalyst and $k = k_{L-H}K_{ad}$ is the pseudo-first-order reaction rate constant. The values of linear fitting variance of methylene blue degradation with different photocatalyst concentration are shown in Table-1 and the value of R are in 0.9925-0.9997. It is also evident that sonophotocatalytic degradation of methylene blue follows pesudo-first order kinetics.

TABLE-1
THE VALUES OF RATE CONSTANT K AND REGRESSION COEFFICIENTS R OF METHYLENE BLUE DEGRADATION

Amount of P25 (g/L)	Curve fitting equation	Rate constant k (min^{-1})	R
0.05	y = -0.01381 + 0.02021x	0.02021	0.99962
0.10	y = -0.00904 + 0.02773x	0.02773	0.99285
0.20	y = 0.06196 + 0.02109x	0.02109	0.99630

Study on the synergistic effect: The degradation of methylene blue was performed under experimental conditions, including sonolysis, photocatalysis and radial sonophotocatalysis. As shown in Fig. 5, 9.5 % degradation of methylene blue was achieved within 80 min under radial ultrasound, 46 % under UV irradiation in the presence of TiO_2 and 80 % under radial sonophotocatalytic conditions. The results showed that radial sonophotocatalytic mode was more effective than solo sonolysis or photocatalysis, due to the synergistic effect between ultrasonication and UV irradiation. Several reasons should be taken into account to explain the synergistic effect. First of all, the radial ultrasound enhanced the mass transport of reagents to the surface of TiO_2. Moreover, radial ultrasound irradiation provided an extra source of hydroxyl radicals, which undergo decomposition of methylene blue. Importantly, the distribution of radial ultrasonic intensity was more uniform than other ultrasonic modes, which was suitable for large-scale operations.

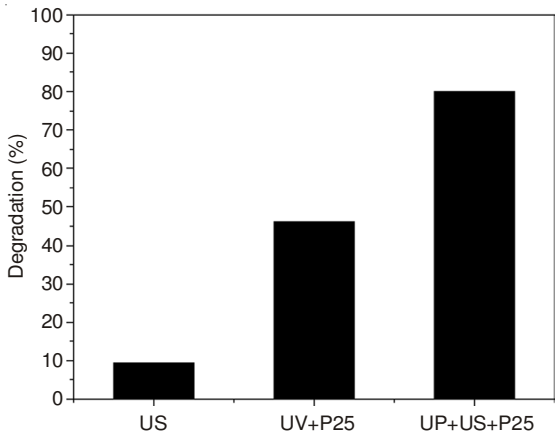

Fig. 5. Comparison of the degradation rate in different processes (ultrasonic power: 200 W, UV power: 200 W, 10 L, P25: 0.1 g L^{-1}, reaction time: 80 min)

Effect of the volume of reactor: The effect of reaction volume on the radial sonophotocatalytic degradation of methylene

blue was further studied. The different reaction volume (10 and 100 L) were used to study the influence on degradation rates. As seen in Fig. 6, methylene blue solution in 10 L reactor was completely degraded at 2 h. While no significant degradation was observed in 100 L reactor. The increased volume attenuated the UV intensity through the whole reaction solution, resulting in the decreased degradation efficiency due to the reduction of the number of cavitational bubbles. In addition, the ultrasonic intensity in a large reactor decreased, resulting in the poor distribution of cavitational activity.

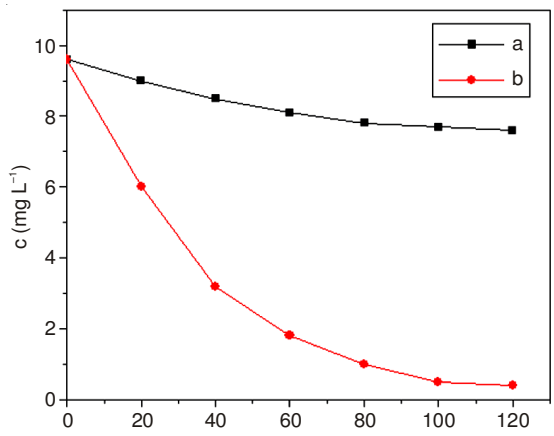

Fig. 6. Radial sonophotocatalytic degradation of methylene blue with different reactor (a) 100L; (b) 10L; c_o = 9.0 mg L^{-1}; ultrasound power 200 W

Conclusion

A new type of radial sonophotocatalytic reactor was designed in this paper. The reactor was applied to degrade methylene blue using TiO_2 as photocatalyst assisted with radial ultrasound. The results showed that methylene blue was removed efficiently by a considerable synergetic effect between the radial sonolysis and photocatalysis, which was closely related with the sonophotocatalytic parameters, such as US power, UV power, the amount of TiO_2 and reactor volume. By contrast to the conventional ultrasonic technique, the radial sonolysis could maintain uniform distribution of cavitational activity in large-scale reactor. The radial sonophotocatalytic reactor could be a better alternative for high concentration POPs wastewater treatment.

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