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Process intensification of heterogeneous photocatalysis with static mixer: Enhanced mass transfer of reactive species

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ABSTRACT

The process intensification (PI) of heterogeneous photocatalysis using the Kenics static mixer was investigated and its mechanism was proposed. Three model compounds (phenol, Cr(VI), and acid orange 7 (AO7)) with different photocatalytic reaction mechanisms were selected. The use of the Kenics static mixer increased the degradation rate of phenol from 20% to 150%, but appeared to have no effect on the photodegradation of Cr(VI) and AO7. However, with the addition of formic acid and NaF to the Cr(VI) and AO7 systems, respectively, the reaction mechanism shifted from a surface-mediated reaction to a radical-mediated reaction, and the photoreduction of Cr(VI) and photo-oxidation of AO7 using the Kenics static mixer exhibited higher reaction rates. In addition, the results of experiments with the terephthalic acid (TA) fluorescence probe indicated that the Kenics static mixer increased the yield of hydroxyl radicals. Based on the reaction mechanisms, we propose that the Kenics static mixer played a role in heterogeneous photocatalysis by creating intense mixing and increasing the interfacial mass transfer, which resulted in the enhanced mobility of reactive radicals from the catalyst surface or boundary layer to the solution. This approach intensified the heterogeneous photocatalysis process by enhancing the mass transfer of the reactive species rather than the reactant substrate, provided an alternative to the PI of heterogeneous photocatalysis, and allowed for easier engineering applications.

1. Introduction

Photocatalysis has been attractive to the energy and environment fields since the discovery of photocatalytic splitting of water on TiO_2 electrodes by Fujishima and Honda in 1972 [1]. However, almost four decades have passed but the industrial applications of photocatalysis still remain limited [2–4]. The low photocatalytic process efficiency and the lack of knowledge about efficient photoreactor design and process intensification (PI) may be the main reasons [5].

In general, there are two approaches to improve the overall efficiency of a photocatalytic process: the first involves the fabrication of novel photocatalysts with high activity and visible light response; the second resorts to PI. The first approach has obtained significant achievements recently by biomimetics [6–8], whereas the PI of heterogeneous photocatalysis has developed slowly. PI is considered as one of the most important progress areas for modern chemical engineering [9]; it concerns engineering methods and equipment [10]. Currently, the PI of heterogeneous photocatalysis includes the coupling of physical or chemical operations such as adsorption, ultrasonic irradiation, ozonation, electrochemical treatment [11], and the elimination of photon transfer limitations or mass transfer limitations [5]. Correspondingly, photoreactors have been designed, such as the TiO_2-coated fiber-optic cable reactor [12], the ultraviolet (UV) light-emitting diode photocatalytic reactor [13], the rotating disk photocatalytic reactor [14], the fountain photocatalytic reactor [15], the monolith photoreactor [16], and the microreactor [17]. However, due to the coupling of photons in the reaction, the PI of heterogeneous photocatalysis is more challenging than that of conventional thermal catalysis, especially in terms of mass transfer characteristics and engineering scale-up issues [18,19]. Therefore, a simple method of PI of heterogeneous photocatalysis, which allows for easier engineering applications, is needed.

Heterogeneous photocatalysis involves two kinds of reactions, classified according to mechanism: one is the direct photo-generated electron reduction and photo-generated hole oxidation; the other is the radical-mediated reaction, which involves reactive species such as hydroxyl ($^\bullet OH$) radicals, superoxide ($O_2^{\bullet-}$) radicals, and α-hydroxyalkyl radicals generated in the reactions [20]. The former mechanism occurs only at the surface of photocatalysts and is, therefore, a heterogeneous reaction; the latter can occur near the boundary layer or in the bulk solution [21], and thus can be a homogeneous reaction. Since a heterogeneous reaction is a multi-

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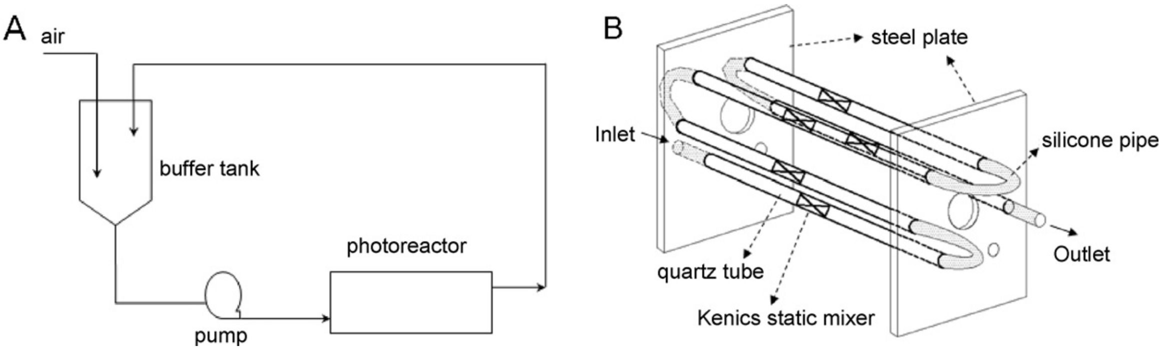

Fig. 1. Schematic diagram of (A) experimental set-up and (B) photoreactor.

step process, it is more complex than a homogeneous reaction. And mass transfer is usually the rate-limiting step in the heterogeneous photocatalysis, although some strategies to enhance it have been applied [22]. Meanwhile, a homogeneous radical reaction in liquid is fast, with rate constants usually in the order of 10^6–10^9 M^{-1} s^{-1} [23,24]. On the other hand, the generated radicals originate from the catalyst surface. Once the surface-bound radicals leave the catalyst surface, more radicals can subsequently be generated under UV irradiation and can be produced constantly; this increases the process efficiency. Therefore, an alternative way of intensifying heterogeneous photocatalysis by enhancing the homogeneous radical reaction may be effective. In other words, the photocatalytic reaction rate can be increased if the reactive species transfer from the catalyst surface to the solution bulk instead of making reactant diffuses from the solution to the catalyst surface.

Static mixers are motionless devices installed inside reactors to improve radial mixing, and thus increase mass transfer, local shear rates, and interfacial mass transfer. They can be used as interface generators in multiphase flows [25]. Static mixers have been widely used in process industries such as biochemical [26], pharmaceutical [27], and chemical manufacturing [28]. However, no PI of photocatalysis using a static mixer has been proposed. The objective of the present study was to analyze and determine the role of static mixers in the PI of heterogeneous photocatalysis. For this, the Kenics static mixer, which is one of the simplest and most common industrial mixers, was used, and three model reactants (phenol, Cr(VI), and acid orange 7 (AO7)) with different photocatalytic reaction mechanisms were selected.

2. Experimental

2.1. Materials

Phenol, potassium dichromate, acid orange (AO7), terephthalic acid (TA), and other chemicals were of AR grade and procured from Sinopharm Chemical Reagent Co., Ltd. (China). Deionized water (resistivity > 18 MΩ cm) was used to prepare the solutions. A Degussa P25 catalyst provided by the Degussa Company (Germany) was used without further modification throughout this work. Its main physical parameters are as follows: Brunauer–Emmett–Teller surface area, 55 ± 15 m^2 g^{-1}; average primary particle size, around 30 nm; purity, >97%; anatase/rutile content (w/w), 80:20.

2.2. Experimental setup

The experimental setup is shown in Fig. 1A. It consisted of a photoreactor, a buffer tank, a water pump, an air pump, and connecting pipes. The photoreactor was composed of a tubular UV lamp (40 W, maximum emission at 254 nm) surrounded by five quartz tubes (ID = 9 mm, L = 30 cm), with each quartz tube passed through two steel plates and connected with silicone pipes (Fig. 1B). The distance between the UV lamp and each quartz tube was kept the same. Five Kenics static mixer units, each consisting of two elements, were placed individually in the center of each quartz tube.

2.3. Experimental procedure and analysis

To investigate the effects of the static mixers on photocatalytic redox reactions, experiments were performed with and without static mixers. A required amount of the stock solution of the model reactant was added to deionized water to obtain the desired initial concentration of the reactant. A 400 mL reactant solution and the required amount of catalyst were then added to the buffer tank and circulated for 30 min before the reaction. At the same time, oxygen or nitrogen was introduced into the buffer tank continuously to keep the concentration of oxygen constant and to produce a homogeneous suspension of the catalyst in the solution. For analysis, samples were taken out at specified time intervals and filtered through a 0.22 μm syringe filter for further analysis. The phenol concentration was analyzed through a standard colorimetric method [29], using a UV–vis spectrophotometer (UNICO UV-2802S). The Cr(VI) concentration was determined at 540 nm by the diphenyl carbazide colorimetric method [29]. The degradation of AO7 was monitored by UV–vis spectrophotometry by measuring the absorbance at 485 nm as a function of irradiation time. The intensity of the fluorescence peak at 426 nm with 312 nm excitation, which is attributed to 2-hydroxyterephthalic acid (TAOH), was measured in fluorescence spectrophotometer (VARIAN Cary Eclipse). The reaction rate was expressed as the average rate at the initial 10 min of the reaction. The reproducibility was within ±10%.

3. Results and discussion

3.1. Photocatalytic oxidation of phenol

The reaction rate of phenol degradation with and without the Kenics static mixer is shown in Fig. 2. With the Kenics static mixer, a 20–150% increase in the photodegradation rate of phenol compared with the value obtained without static mixers was observed at different catalyst concentrations and flow rates. Furthermore, the largest increase was obtained at both low catalyst and initial phenol concentrations. On the other hand, the rate of phenol degradation increased with the recirculation flow rate from 0.8 L min^{-1} (Re = 1876) to 2.2 L min^{-1} (Re = 5135); this indicates the existence of a mass transfer limitation. The rate of phenol degradation was independent of the recirculation flow rate when the Kenics static mixer was used. This means that the addition of the Kenics static mixer could increase mass transfer and thus eliminate mass transfer limitations from the system. The photocatalytic oxidation of phenol has been extensively investigated; its degradation proceeds