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

Dong Li, Kui Xiong, Zhuhong Yang, Chang Liu, Xin Feng, Xiaohua Lu*

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, 5# Xinmofan Road, Nanjing 210009, Jiangsu, China

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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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* Corresponding author. Tel.: +86 25 83588063; fax: +86 25 83588063.
E-mail address: xhlu@njut.edu.cn (X. Lu).

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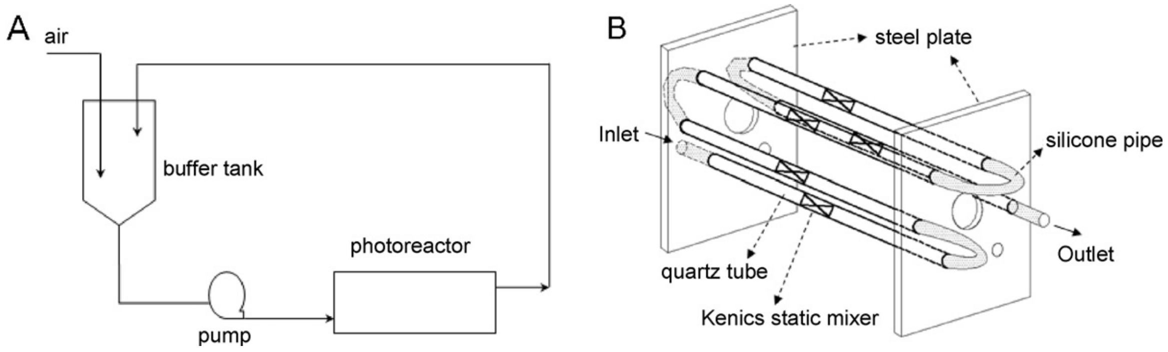


Fig. 1. Schematic diagram of (A) experimental set-up and (B) photoreactor.

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

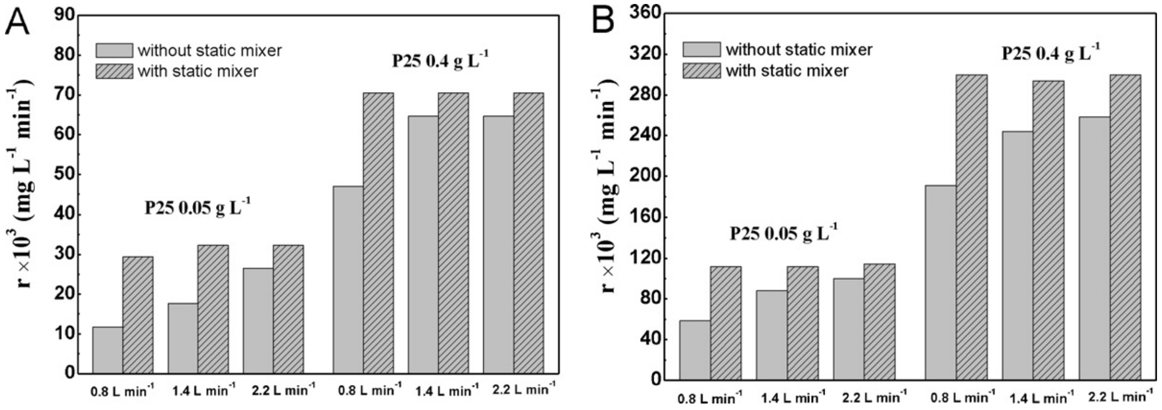


Fig. 2. The photodegradation rate of phenol with and without Kenics static mixer (A: 1 mg L^{-1} phenol; B: 8 mg L^{-1} phenol).

predominately via •OH [30–33]. The above results indicate that the Kenics static mixer could enhance the •OH radical-mediated photocatalytic process.

3.2. Photocatalytic reduction of Cr(VI)

No apparent difference in the photoreduction rate with or without the Kenics static mixer was observed (Fig. 3A). The photocatalytic reduction of Cr(VI) also appeared to be independent of the recirculation flow rate, which increased from 0.8 to 2.2 L min^{-1}. As can be seen in Fig. 3B, the addition of 10 mM formic acid significantly accelerated the photocatalytic reduction of Cr(VI) from ∼200 to ∼450 mg L^{-1} min^{-1} (Fig. 3B). In the Cr(VI)/formic acid system, one distinct phenomenon, which was different from Cr(VI) alone, was that the photoreduction rate of Cr(VI) intensified in the Kenics static mixer, and the rate increased from 9% to 18% compared with the reaction without the Kenics static mixer at the same flow rate.

The photoreduction of Cr(VI) is a typical reduction by electrons from the conduction band, and occurs on the surface of the catalyst rather than in the bulk solution [34]. However, in the presence of organic species, the photoreduction of metal ions can occur via two pathways: one is direct, where metal ions are reduced by reaction with the conduction band electrons on the TiO_2 surface; another is indirect, where the metal ions are reduced by aqueous radical species [35–37]. In the Cr(VI)/formic acid system, the organic radicals HCOO•, which are produced by the oxidation of photogenerated holes, are highly reducing and are negative enough to reduce Cr(VI) [38,39]. On the other hand, the organic species can be oxidized by photogenerated holes; this consequently suppresses electron–hole recombination on the catalyst, and accelerates the reduction of Cr(VI) by photogenerated electrons [40]. Therefore, the addition of formic acid not only increased the photoreduction rate of Cr(VI) but also partially converted the surface reduction to a homogeneous radical reduction. Furthermore, the Kenics static mixer clearly enhanced the rate of homogeneous radical reduction.

3.3. Photocatalytic oxidation of AO7

The photodegradation rate of AO7 with and without the Kenics static mixer is shown in Fig. 4A. Apparently, the Kenics static mixer had no effect on the degradation of AO7 in all studied catalyst concentrations and flow rates. The degradation of AO7 also seemed to be independent of the recirculation flow rate, which increased from 0.8 to 2.2 L min^{-1}. While in the AO7/NaF system, the degradation of AO7 performed with the Kenics static mixer showed a higher reaction rate than the one without the mixer (Fig. 4B). Compared with the absence of the Kenics static mixer, the reaction rates at flow rates of 0.8 L and 1.4 L min^{-1} increased by 17% and 11%, respectively. Meanwhile, the degradation rate of AO7 increased with increasing recirculation flow rate. This indicates that the mass transfer limitation occurred in the AO7/NaF system. The photocatalytic oxidation of AO7 has been extensively investigated; studies have suggested that holes play a major role in its degradation [33,41]. However, with the addition of 10 mM NaF, the mechanism via direct oxidation by valence band holes could be shifted to a mechanism via •OH, and even the reaction sites could shift from the catalyst surface to the solution [41,42]. Therefore, the Kenics static mixer appeared to enhance partially the homogeneous radical oxidation.

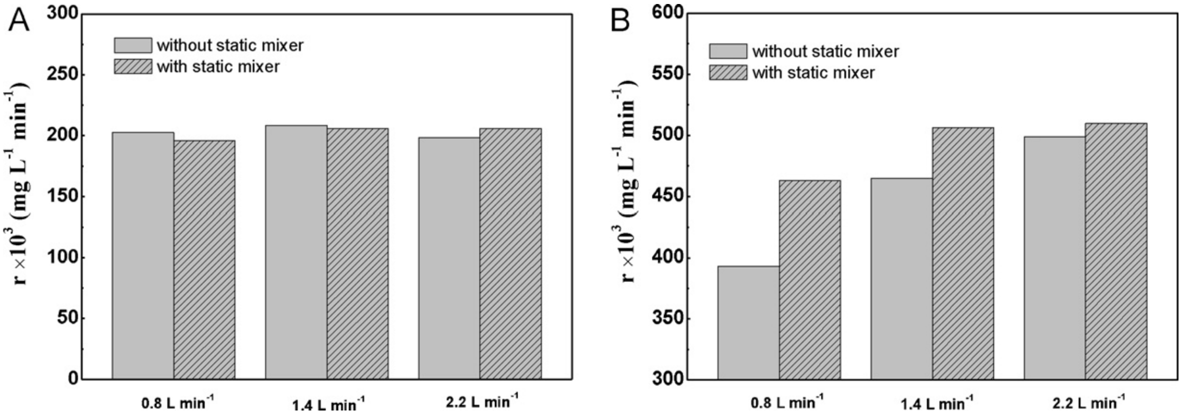


Fig. 3. The photoreduction rate of Cr(VI) with and without Kenics static mixer (A: 8 mg L^{-1} Cr(VI); B: 8 mg L^{-1} Cr(VI) + 10 mM formic acid).

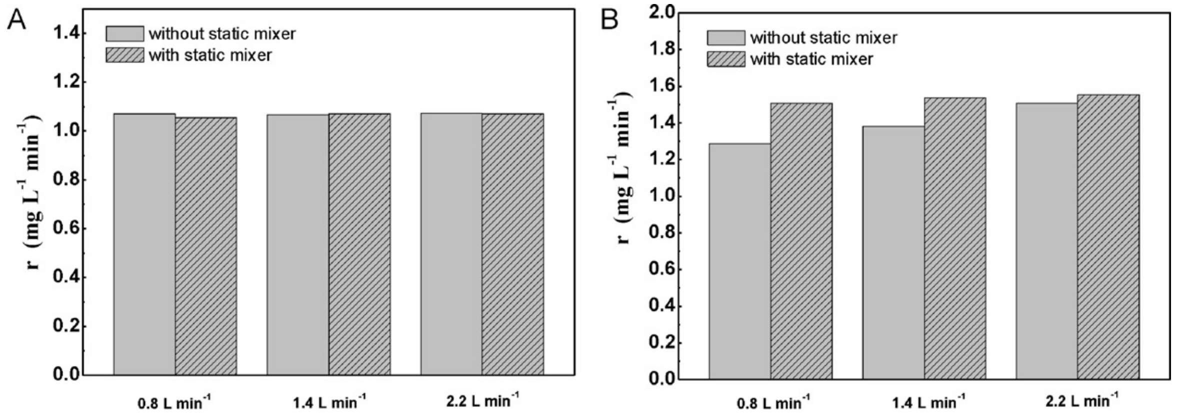


Fig. 4. The photodegradation rate of AO7 with and without Kenics static mixer (A: 40 mg L^{-1} AO7; B: 40 mg L^{-1} AO7 + 10 mM NaF).

3.4. TA fluorescence probe

Recently, the TA fluorescence probe method has been widely used for the detection of $^{\bullet}$OH [43,44]. The mechanism of this method involves the reaction between $^{\bullet}$OH and TA and generation of TAOH, which fluoresces at around 426 nm on excitation at the 312 nm absorption band. Furthermore, the TA fluorescence method only detects the free $^{\bullet}$OH radicals in bulk solution [45]. The fluorescence intensity is therefore linear with the yield of free $^{\bullet}$OH. The effect of the Kenics static mixer in the production of free $^{\bullet}$OH is shown in Fig. 5. With the static mixer in the reactor tube, the yield of free $^{\bullet}$OH noticeably increased compared with the yield without the static mixer. As shown in Fig. 5, the yield of free $^{\bullet}$OH with the Kenics static mixer at 20 min was 40% higher than in the absence of the mixer. A notable observation is that the rate of formation of free $^{\bullet}$OH appeared to be constant when the Kenics static mixer was used, whereas the rate gradually decreased with reaction time in the absence of the static mixer. The rate of $^{\bullet}$OH formation has been reported to be constant when the concentration of TA is beyond a critical concentration [44]. In this study, this critical concentration was found to be 4 mM, which was used for TA in the TA fluorescence probe method. This suggests that the formation of free $^{\bullet}$OH radicals was inhibited by the reduction of free $^{\bullet}$OH generated in solution, and not by the reduction of TA. On the other hand, the experiments carried out by purging air and nitrogen indicate that the dissolved oxygen had little effect on $^{\bullet}$OH production. This suggests that the production of $^{\bullet}$OH was mainly from the oxidation of chemisorbed OH$^-$ or H_2O by photogenerated holes and not from the reduction of oxygen by photogenerated electrons [46].

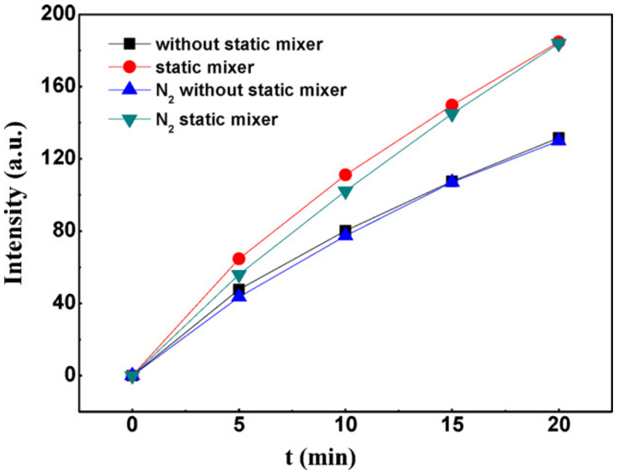
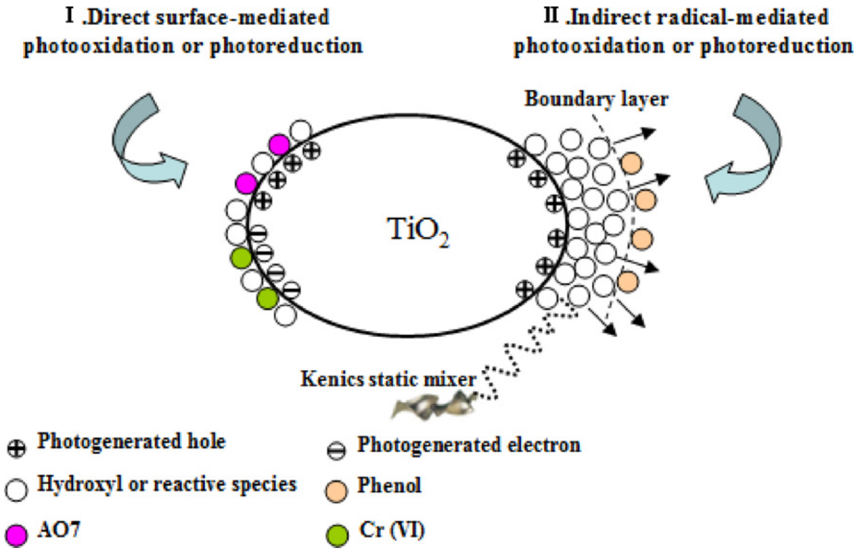


Fig. 5. The TA–fluorescence probe with and without Kenics static mixer.

3.5. Proposed mechanism of the static mixer in heterogeneous photocatalysis

The role of the static mixer in heterogeneous photocatalysis is of interest. As shown in Figs. 2–4, the photocatalytic degradation of phenol, Cr(VI) in Cr(VI)/formic acid system and AO7 in AO7/NaF system could be intensified with the Kenics static mixer, whereas the Kenics static mixer seemed to have little effect on the photocatalytic degradation of Cr(VI) and AO7. Despite the argument of active species in the reaction mechanism, the heterogeneous photocatalysis involves two reaction approaches: the direct surface-mediated redox reaction of the reactant with photogenerated holes or electrons; the indirect radical-mediated reaction. For a typical reaction, determining which approach plays the main role in the reaction is relevant to the nature of the catalyst and the reactant. In general, for strongly adsorbed reactants, the direct surface-mediated redox reaction plays a significant role, and for weakly adsorbed substrates, the indirect radical-mediated reaction plays a greater role [47]. In the present investigation, both Cr(VI) and AO7 were specifically adsorbed on the TiO_2 surface [33,48–50]; thus the photoreduction of Cr(VI) and photo-oxidation of AO7 were mainly through direct surface-mediated photogenerated electrons and direct surface-mediated photogenerated holes, respectively [34,41]. Phenol is weakly adsorbed on TiO_2 in aqueous solution [51,52] and its photodegradation proceeds mainly through the indirect radical-mediated reaction [53]. However, in the Cr(VI)/formic acid system, the formation of HCOO$^{\bullet}$ radicals, which are highly reducing and are negative enough to reduce Cr(VI), could progressively shift the initial process from direct surface-mediated photoreduction to indirect radical-mediated reaction. Similarly, in the AO7/NaF system, the $^{\bullet}$OH radical-mediated oxidation pathways were enhanced, and the initial process could shift progressively from direct surface-mediated photo-oxidation to indirect radical-mediated reaction. Therefore, for heterogeneous photocatalysis, the static mixer can partially intensify the radical-mediated reaction and have little effect on the surface-mediated reaction.

According to the results of the TA fluorescence probe reaction (Fig. 5), the static mixer increased the yield of $^{\bullet}$OH radicals. The active radicals involved in the reactions were generated mainly on the catalyst surface and then diffused to the boundary layer (surface-adsorbed $^{\bullet}$OH or surface-bound $^{\bullet}$OH) and even to the bulk solution (free $^{\bullet}$OH) [45,53]. The static mixer can create intense mixing and increase interfacial mass transfer [54], and thus enhance the mobility of photogenerated $^{\bullet}$OH radicals which bond with the catalyst surface or are limited in the boundary layer. This facili-



Scheme 1. Schematic illustration of the roles of static mixer in intensification of heterogeneous photocatalysis.

tates the movement of the •OH radicals from the catalyst surface or the boundary layer to the solution. This means that the static mixer helped the surface-adsorbed •OH or surface-bound •OH to move into the solution to form free •OH. In other words, to some extent, the static mixer facilitated the shift from a heterogeneous reaction to a homogeneous reaction. The possible reasons for the intensification of heterogeneous photocatalysis when the Kenics static mixers were used are as follows: first, the higher oxidation potential of free •OH than the potential of the surface-adsorbed or surface-bound •OH has been reported [45,55]. Second, once the reaction sites transfer from the catalyst surface to the solution, the heterogeneous reaction changes into a homogeneous reaction, which eliminates the mass transfer limitation for the heterogeneous photocatalytic process and increases the reaction rate. Third, once the surface-adsorbed •OH or surface-bound •OH leave the catalyst surface, more radicals can be generated under UV irradiation and can be produced constantly in solution. Fourth, if the surface-adsorbed or surface-bound •OH cannot be eliminated in time, it would become the combination center of photogenerated charges and could even reduce the light intensity on the catalyst surface.

In general, in a radical-mediated heterogeneous photocatalytic reaction, the static mixer could help the surface-adsorbed radicals or surface-bound radicals move into the solution to form free radicals, and thus intensify the whole heterogeneous photocatalysis (Scheme 1).

4. Conclusions

The PI of heterogeneous photocatalysis with the Kenics static mixer was investigated, and a possible mechanism was proposed. The main conclusions are as follows:

(1) The degradation rate of phenol increased from 20% to 150% with the installation of the Kenics static mixer at different catalyst concentrations and initial phenol concentrations.
(2) The Kenics static mixer did not appear to have an effect on the photodegradation of Cr(VI) and AO7. However, with the addition of formic acid (FA) and NaF to the Cr(VI) and AO7 systems, respectively, the photoreduction of Cr(VI) and photo-oxidation of AO7 showed higher reaction rates with the Kenics static mixer than without it.
(3) The results of the experiments with the TA fluorescence probe indicate that the Kenics static mixer increased the yield of •OH.
(4) The static mixer could help the surface-adsorbed radicals or surface-bound radicals to move into the solution to form free radicals, and thus intensify the heterogeneous photocatalytic process.

Acknowledgments

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