



Reaction kinetics of photocatalytic degradation of sulfosalicylic acid using TiO₂ microspheres

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ABSTRACT

The photocatalytic (PC) degradation kinetics of sulfosalicylic acid (SSA) at different pH using TiO₂ microspheres were elucidated by modeling. The resultant model had special consideration of adsorption and pH. The adsorption isotherms showed that the LC/MS²-identified intermediates were weakly adsorbed on the TiO₂ microspheres, thus their adsorption was neglected in the modeling. By contrast, the SSA was significantly adsorbed, thus its adsorption retained as an item in the model. Consequently, a non-first-order model was obtained. Through the modeling, it was elucidated that the reaction rate increased non-linearly with the SSA adsorption equilibrium constant. Meanwhile, it was elucidated that a pH increase favored the hydroxyl radical production to accelerate the SSA degradation, while impeded the SSA adsorption to slower it, hence a neutral pH caused the fastest SSA degradation.

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1. Introduction

Photocatalytic (PC) reaction using TiO₂ to degrade biorefractory organic contaminants has a promising prospect in water treatment, and has been widely investigated in recent decades [1–6]. During this process, the highly active hydroxyl radicals ($\cdot\text{OH}$) non-selectively attack the organic substrates to yield desired inorganic minerals.

For a best performance of the PC reaction, a variety of means including using modified TiO₂ [7–10], preparing novel TiO₂-based photocatalysts [11,12], and designing alternative reaction configurations [13–15] have been reported.

A photocatalyst different from the TiO₂ powders named TiO₂ microspheres has also been fabricated [16] for a best performance of the PC reaction. It has been established that the PC system with the microspheres ensures an efficient degradation of sulfosalicylic acid (SSA) and salicylic acid (SA). Moreover, the microspheres can be advantageously dispersed by air bubbling for efficient illumination, and can settle down to the reactor bottom quickly through gravity for a rapid separation from the aqueous phase once the air bubbling stops. It is claimed that the sufficiently robust microspheres not only take care of the illumination losses encountered in the

immobilized PC system but also overcome the main drawback of TiO₂ separation faced by the suspended PC system [16].

Along with the performance evaluation, the kinetics of the substrate degradation are of profound interest for optimizing the PC system. Although the pseudo-first-order reaction model has been frequently employed to describe the degradation kinetics of PC reaction [17,18], it is not capable of fitting the degradation data of SSA and SA adequately in the TiO₂ microsphere PC system. Instead, a different reaction kinetic equation well fits the degradation data [16]. Such equation includes the item of adsorption, thus is more informative than the pseudo-first-order one that is oversimplified without any inclusion of the influencing factors. Obviously, the inclusion of vital factors in the kinetic model is of importance, because the factors such as adsorption influence the PC kinetics significantly [11,19–21], and understanding them helps one to evaluate the process efficiency and optimize the operating parameters.

More recently, a study continues to disclose the relationship between the adsorption and the degradation kinetics of SA at different pH [22], since the pH is another vital factor influencing the PC reaction significantly [2]. However, the kinetics, particularly the effects of adsorption and pH, have not been elucidated by modeling.

Accordingly, herein we extend the previous study by conducting the SSA degradation using the TiO₂ microspheres at different pH values, then focusing on elucidating the reaction kinetics through modeling on the basis of the generally accepted PC mechanism. The

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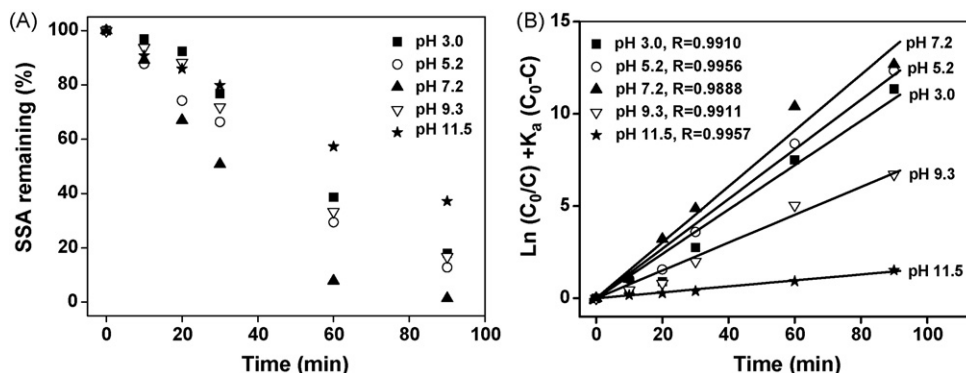


Fig. 1. SSA degradation at different pH (A) and the fitting results of the SSA degradation data by Eq. (1).

resultant model includes various factors, yet of them the adsorption and the pH are addressed.

2. Experimental methodology

2.1. Chemicals and instruments

The acetonitrile used for the present study was of HPLC grade and all the other chemicals were of analytical grade. Moreover doubly distilled water was used throughout the experiment. TiO₂ microspheres were prepared in accordance with a previously described method [16]. A Coulter (DELSA 440SX) Doppler electrophoretic light scattering analyzer was employed for the measurement of zeta potential. HPLC (Waters 486) equipped with a reverse phase column (Waters, XTerra™ MS C-18, 5 μm) and a UV detector was employed for the quantification of SSA concentrations. The composition of the mobile phase was acetonitrile and water, 40:60% for SSA, *p*-phenolsulfonic acid and benzenesulfonic acid, and 20:80% for phenol. The detection wavelength was 296 nm for SSA, 269 nm for phenol, 264 nm for *p*-phenolsulfonic acid, and 229 nm for benzenesulfonic acid. A liquid chromatography–Mass/Mass (LC/MS²) system was employed for the identification of the intermediates of SSA degradation. The LC part consists of a gradient pump (Spectra System P4000), an autosampler (Spectra System Tem AS3000) with a 20 μL injection loop, a Thermo Ques Hypersil ODS column (C18, 5 μm, 250 mm × 4.6 mm ID) and a photodiode array UV detector (Spectra SYSTEM UV6000LP). The intermediates were determined by an ion trap mass spectrometer (Finnigan Duo LCQ MS/MS system) with either electrospray ionization probe or atmospheric pressure chemical ionization probe. Nitrogen gas was generated by a generator (NITROX) and used as both sheath and auxiliary gases.

2.2. Experimental procedure

Adsorption experiments of SSA and its degradation intermediates were performed in the dark by shaking 10.0 mL adsorbate with a known concentration and 0.20 g TiO₂ microspheres in a container at 130 r min⁻¹ for 24 h at 25 °C. The zeta potential of TiO₂ microspheres was measured. Prior to measurement, the TiO₂ microspheres were suspended by an ultrasonic for 60 min in 0.01 M KNO₃ solution. The PC degradation of SSA was conducted in a cylindrical quartz reactor with an effective volume of 165 mL as described previously [16]. Briefly, in the reactor, 3.5 g L⁻¹ TiO₂ microspheres were fully fluidized through air bubbling. A 6 W near UV lamp with a main emission at 365 nm illuminated the reactor. The illumination intensity was 2.0 mW cm⁻² measured by a black-ray ultraviolet meter (Model No. J221, USA).

3. Results and discussion

3.1. PC degradation of SSA

Fig. 1 illustrates the PC degradation results of SSA using the TiO₂ microspheres at different pH values. Clearly, the PC degradation rate increased from pH 3.0 to 7.2, then decreased from pH 7.2 to 11.5, and the fastest degradation occurred at pH 7.2 while the slowest at pH 11.5. In the previous study [16], the pseudo-first-order reaction model was inadequate to fit the SSA degradation at pH 7.2, whereas, a different model was adequate to describe the SSA degradation at pH 7.2:

$$\ln\left(\frac{C_0}{C}\right) + K_a(C_0 - C) = K_{app}t \quad (1)$$

where K_a and K_{app} are adsorption equilibrium constant of SSA and apparent rate constant, respectively. In this work, the similar inadequacy was also encountered to fit the data in Fig. 1A by using the pseudo-first-order reaction model, whereas Eq. (1) fitted the SSA degradation data quite well (Fig. 1B).

3.2. Model development

As generally accepted, the PC reaction begins with a generation of electrons and holes (e–h pairs) upon irradiation by energy higher than the TiO₂ band gap [1]. The holes move to the TiO₂ surface and react with the water molecule to produce •OH radicals [23]. Also, the substrate adsorption on the TiO₂ microspheres should be considered since the microspheres are featured with a relatively large pore volume of 0.388 cm³ g⁻¹ and surface area of 1208 m² g⁻¹ [16]. The adsorption/desorption equilibrium of the organic substrate on the TiO₂ microspheres can be expressed as:



where Or is the organic substrate and $[\text{Or} - \text{TiO}_2]_{\text{adsorb}}$ is its adsorbed species, and the generation of e–h pairs can be expressed as:



Then, the production of •OH radicals can be written as follows:



where k_{+1} , k_{+2} and k_{+3} are rate constants of forward reactions, and k_{-1} , k_{-2} and k_{-3} of backward reactions. The •OH radicals attack the

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