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## Kinetics of Photodegradation of Alizarin Green in an Acoustic Fluidized Bed Using TiO<sub>2</sub> Catalyst<sup>1</sup>

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**Abstract**—The kinetics of photodegradation of alizarin green (AG) in an acoustic fluidized bed was investigated using Degussa P25 catalyst and N-doped TiO<sub>2</sub> catalyst, respectively. The effects of initial concentration of AG, catalyst amount, initial pH value and liquid flow rate on the photodegradation rates were the main goal of present study. The degradation rate increased with increasing amount of photocatalyst, pH value and liquid flow rate, reached a maximum and then decreased. The degradation rate decreased with increasing initial concentration. According to the Langmuir–Hinshelwood model, the disappearance of the AG followed pseudo-first-order kinetics. Experimental results showed that AG can be degraded effectively by Degussa P25 catalyst and N-doped TiO<sub>2</sub> catalyst in an acoustic fluidized bed reactor. N-doped TiO<sub>2</sub> catalyst has high and significant photocatalytic activity and in comparison with Degussa P25 catalyst was photocatalyst.

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**Keywords:** TiO<sub>2</sub> catalyst, photodegradation, fluidized bed, acoustic.

### INTRODUCTION

Advanced oxidation processes (AOP) are recognized as a high and significant alternative to transform and decontaminate the dye-containing waste water [1]. These processes named AOP all rely on the generation of highly reactive ·OH radical as the main oxidative species for the potential destruction and conversion of organic pollutants into harmless substances [2, 3]. Photocatalysis is one typical example of AOP for the degradation of dye-containing and other organic pollutants in water [4, 5].

The utilization of titanium dioxide (TiO<sub>2</sub>) to the removal of organic pollutants in a fluidized bed reactor (FB) has been widely investigated [6–8]. Roberto et al. [8] studied a comprehensive kinetic model for the photo oxidation of oxalic acid (C<sub>2</sub>O<sub>4</sub>H<sub>4</sub>) in a fluidized bed. Wang et al. [9] reported photocatalytic oxidation of acid dye under visible light irradiation in a recycle fluidized bed reactor and found the photocatalytic degradation follows the pseudo-first-order reaction kinetics with respect to the concentration of acid dye. Dong et al. [10] investigated five oxidation processes for phenol degradation in fluidized bed and found the photocatalytic ozonation was the highest phenol conversion in the liquid phase. It was confirmed that the fluidized bed with sound assistance could achieve the smooth and steady fluidization of nanoparticles in the bed thus improve good contacting between reactants and photocatalysts [11, 12]. In our previous study, photocatalytic degradation of formaldehyde in AFBR was investigated using Degussa P25 and N-doped TiO<sub>2</sub> catalysts particles as the fluidized media [13]. As a typical anthraquinone dye, Xiong et al. [14] studied the photocatalytic degradation of alizarin green (AG) in aqueous TiO<sub>2</sub> suspensions under UV-Vis irradiation by a microwave discharged electrodeless lamp.

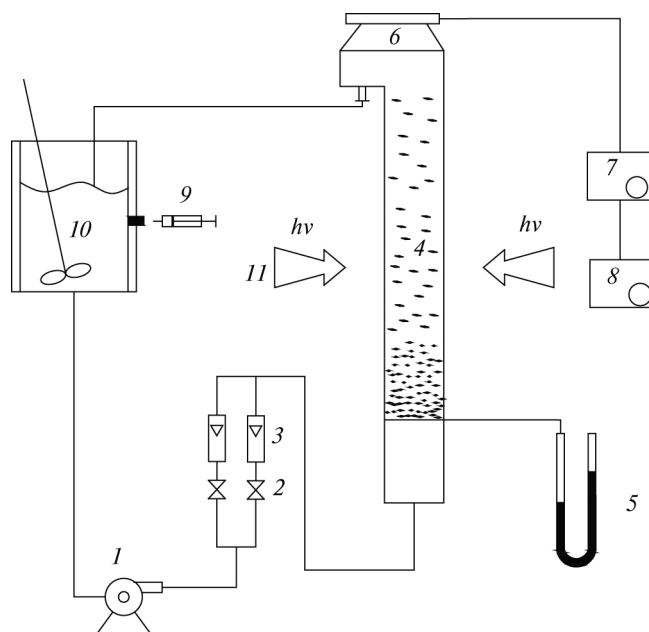
In this study, a novel designed acoustic fluidized bed reactor using Degussa P25 catalyst and N-doped TiO<sub>2</sub> catalyst as the fluidizing media is developed to continuously photodegrade AG. The effects of initial concentration of AG, catalyst amount, initial pH value and liquid flow rate on the degradation rate were investigated in an acoustic fluidized bed.

<sup>1</sup> The text was submitted by the authors in English.

## EXPERIMENTAL

*The Reactor*

The schematic diagram of the experimental set-up is shown in Fig. 1. The experimental equipment consists of a fluidized bed reactor, a sound field supply system, a light wave supply system, a circulation pump, a reservoir tank and some sampling instruments. The cross-section area of the fluidized bed is  $60 \times 20$  mm with a height of 600 mm. Two sides of the fluidized bed, two 125 W high-pressure mercury lamps as the UV-light source was installed in the internal cylinder made of quartz tube. An electric pulse with various waveforms was produced by a signal generator (WY32003, China). A loudspeaker is placed on the top of 2D bed. A precision sound pressure level meter (Center Type 320, China) was used to measure the sound pressure level. The pH of the solution was controlled by adding NaOH or H<sub>2</sub>SO<sub>4</sub> and was measured by means of a pH meter (PHS-2C, China), while the temperature of the solution was measured by thermometer. Experiment was operated at ambient conditions.



**Fig. 1.** Schematic diagram of experimental apparatus: 1—pump; 2—valve; 3—flow meter; 4—fluidized bed; 5—manometer; 6—loudspeaker; 7—sound amplifier; 8—signal generator; 9—sampling outlet; 10—recycling tank; 11—UV lamp.

*Materials and Reagents*

Degussa P25 catalyst and N-doped TiO<sub>2</sub> catalyst were employed as the photocatalyst. The particle size of Degussa P25 catalyst was about 21 nm and its BET surface area was  $50 \text{ m}^2 \cdot \text{g}^{-1}$ . The N-doped TiO<sub>2</sub> was prepared by hydrothermal method according to the previous study and employed in this experiment (pH 8, temperature at 500°C for 3 h) [13]. AG, a toxic anthraquinone dye, was used as the target pollutant in this series of experiments.

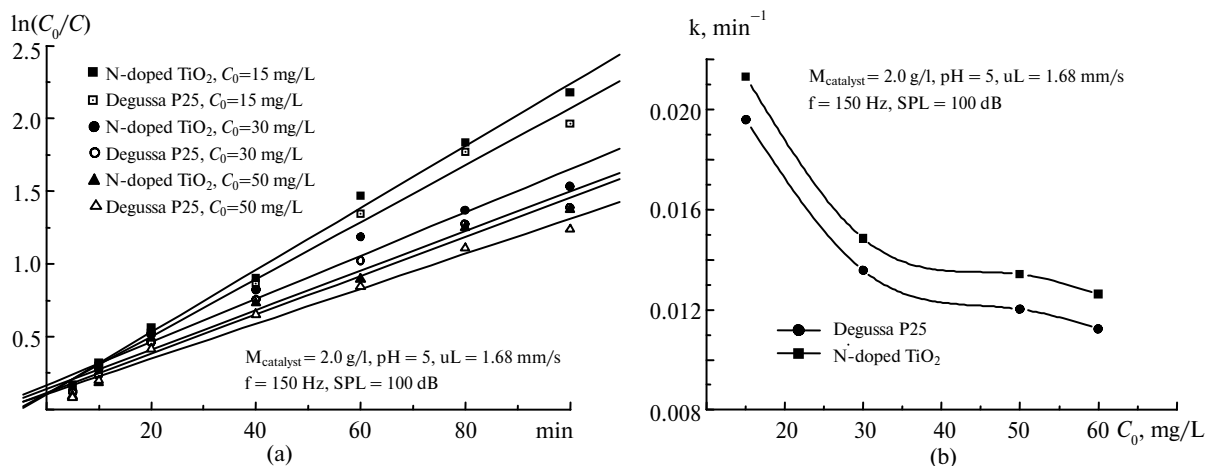
*Photocatalytic Procedures*

The absorption spectrum of AG with the maximum adsorption wavelength is 415 nm. Initially, a certain amount of wastewater containing AG was introduced to the storage tank and then passed through the fluidized bed reactor. There was no obvious concentration change during this process and the adsorption is very low. Afterwards, the lamp was turned on and sound waves were initiated. The flow rate of liquid was regulated by a flow meter and introduced into the bottom of the fluidized bed reactor. During the process, samples of the reaction solution were taken at time intervals of 10 min for concentration analysis. AG concentration was determined by means of a UV Vis-NIR spectrometry (Varian Cary 50, USA) and the maximum absorbance of the surfactant occurred at a wavelength of 415 nm. Analytical results were calibrated using a series of standard solutions corresponding to a range of concentrations used in the experiments.

## RESULTS AND DISCUSSIONS

*Effect of Initial Concentration*

The photodegradation kinetics of the AG with illumination time for various initial concentrations using Degussa P25 catalyst and N-doped TiO<sub>2</sub> catalysts was showed in Fig. 2, respectively.



**Fig. 2.** Effect of initial concentration on degradation rate of AG: a—effect of initial concentration on irradiation time; b—effect of initial concentration on the rate constants using Degussa P25 and N-doped TiO<sub>2</sub> catalysts.

$M_{\text{catalyst}} = 2.0 \text{ g/L}$ ,  $\text{pH} = 5$ ,  $uL = 1.68 \text{ mm/s}$ ;  $f = 150 \text{ Hz}$ , Sound pressure level (SPL) = 100 dB. The initial concentration of AG increased the degradation rates decreased. It was showed that the increased concentration affects light penetration into the AG solution. Therefore, at higher initial concentration, the light pathway to the surface of TiO<sub>2</sub> was reduced and the fewer photons from the light source reached the catalyst surface. The degradation kinetics fit the Langmuir–Hinshelwood model [15]:

$$r_0 = -\frac{dc}{dt} = \frac{kKC_0}{1 + KC_0}, \quad (1)$$

where  $r_0$  is the degradation rate of the reactant,  $k$  is the reaction rate constant and  $K$  and  $C_0$  are the adsorption equilibrium constant and concentration for the reactant, respectively. When the concentration is very low (i.e.  $KC \ll 1$ ), Eq. (1) simplifies to a pseudo-first-order kinetic law:

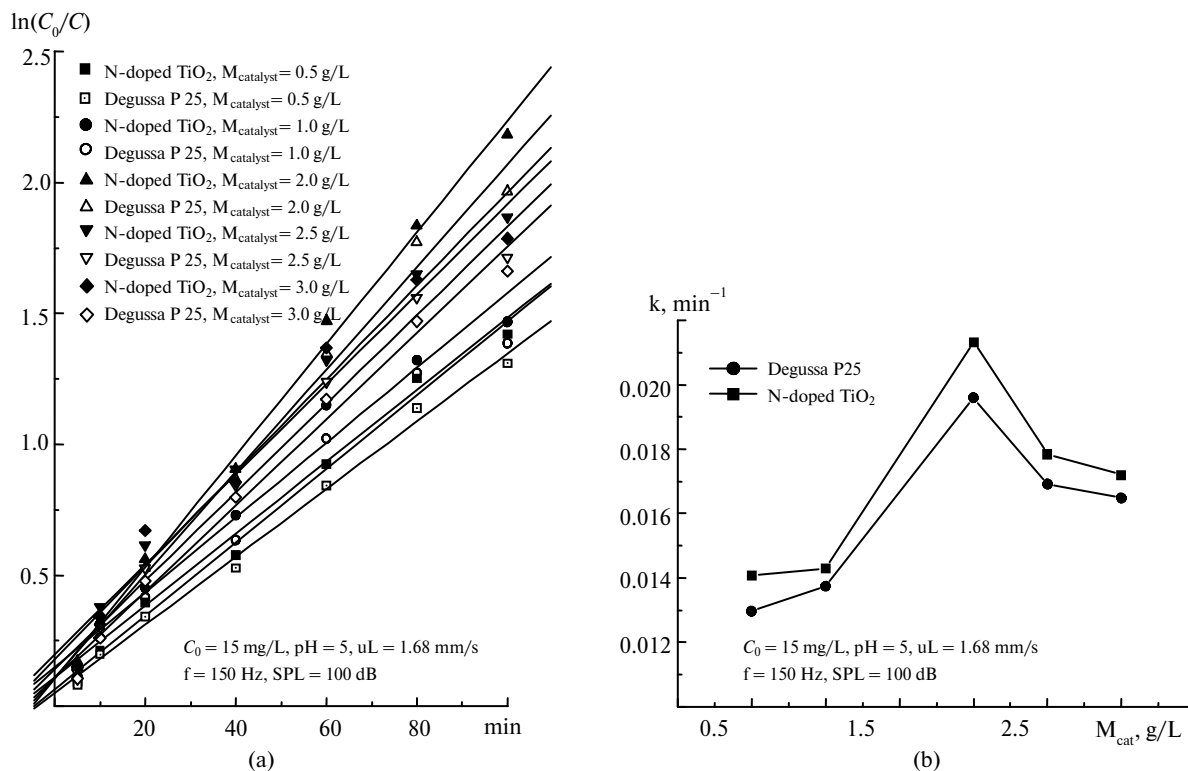
$$r_0 = \frac{dc}{dt} = k'C_0, \quad (2)$$

where  $k'$  is the pseudo-first-order rate constant. The rate constants were calculated as  $0.0196$  and  $0.0213 \text{ min}^{-1}$  at initial concentration value  $15 \text{ mg/L}$  using Degussa P25 catalyst and N-doped TiO<sub>2</sub> catalyst, respectively, shown in Fig. 2b. So it can be observed that the degradation rate using N-doped TiO<sub>2</sub> catalyst was better than that using Degussa P25 catalyst in the experimental range of the surfactant concentration. The possible reason for this might be that the implantation of nitrogen modifies the electronic structure by introducing localized states in the band gap, thereby improving the degradation rate of AG [13].

*Effect of Catalyst Amount*

The linear fit between the  $\ln(C_0/C)$  and irradiation time with different amounts of catalyst was showed in Fig. 3a. It is observed that the degradation rate increased with increasing amount of photocatalyst, reached a maximum and then decreased. The number of photons absorbed and the number of dye molecules adsorbed are increased with the increase in catalyst concentration thereby enhancing the rate of degradation. At a higher catalyst amounts will leads to lower photon transmission due to the higher solid particle concentration. Hence further addition of catalyst does not lead to the enhancement of the degradation rate. The degradation rate also decreases due to the aggregation of TiO<sub>2</sub> particles at higher concentrations causing decrease in the number of surface active sites and also due to the increase in opacity and light scattering of TiO<sub>2</sub> particles at high concentration through the sample.

Effect of catalyst amounts on the rate constants using Degussa P25 catalyst and N-doped TiO<sub>2</sub> catalyst was showed in Fig. 3b. The optimum catalyst concentration for the degradation of AG is 2.0 g/L. According to Fig. 3b, the rate constants were calculated as 0.0169 and 0.0178 min<sup>-1</sup> at catalyst amount value 2.5 g/L using Degussa P25 catalyst and N-doped TiO<sub>2</sub> catalyst, respectively. Sound waves with a high sound pressure level have relative greater force which disrupted effectively the inter-particles force [12]. Thereby, the sound waves can decrease the agglomerate size of TiO<sub>2</sub> nanoparticles and improve the degradation rate of AG in an acoustic fluidized bed.



**Fig. 3.** Effect of amount of catalyst on degradation rate of AG: a—effect of catalyst amounts on irradiation time; b—effect of catalyst amounts on the rate constants using Degussa P25 and N-doped TiO<sub>2</sub> catalysts.

#### Effect of pH

The effect of the initial pH value on the photocatalytic degradation rate was studied by adjusting the initial pH value of the reaction solution, with dilute solution of NaOH. Fig. 4 showed the degradation rate of AG in the range of pH 3–9 using Degussa P25 catalyst and N-doped TiO<sub>2</sub> catalyst in an acoustic fluidized bed, respectively. According to Fig. 4b, the degradation rate constant was higher at pH value 5 and decreased with the increase in pH. Ti is in the OH<sub>2</sub><sup>+</sup> ionic state in weak acidic solution. Hence, anionic surfactants are easily adsorbed on the surface of the photocatalyst, and this causes the degradation rate to increase, because the chances of the Ti ions encountering ·OH radicals become higher [6]. Conversely, at alkaline pH, Ti is present in the O<sup>-</sup> ionic state, so that anionic surfactants are repulsed from the photocatalyst surface, thus lowering its efficiency [6].

According to Fig. 4b, the rate constants were calculated as 0.0165 and 0.0173 min<sup>-1</sup> at pH value 3 using Degussa P25 catalyst and N-doped TiO<sub>2</sub> catalyst, respectively. It was also found that the AG degradation rate was obvious lower using Degussa P25 catalyst than N-doped TiO<sub>2</sub> catalyst.

#### Effect of Liquid Flow Rate

The liquid flow rate significantly influences the residence time of liquid and the mass transfer in the reactor, which in turn affects the photocatalysis degradation performance. The AG degradation rate was showed Fig. 5 under four different liquid flow rates where the behaviors of TiO<sub>2</sub> catalyst are typical (e.g. fixed bed, fluidized

bed).  $\text{TiO}_2$  catalyst was almost fixed at flow rate of  $0.37 \text{ mm}\cdot\text{s}^{-1}$ . Lower liquid flow rate leads to lower transfer of momentum and mass.  $\text{TiO}_2$  catalyst started to fluidize when the flow rate was increased to  $1.31 \text{ mm}\cdot\text{s}^{-1}$ . The improvement on the AG degradation rate by fluidized bed reactor was remarkable. Higher flow rate results in shorter residence time of liquid in the reactor and shorter contacts between organic pollutant and particle photocatalyst.

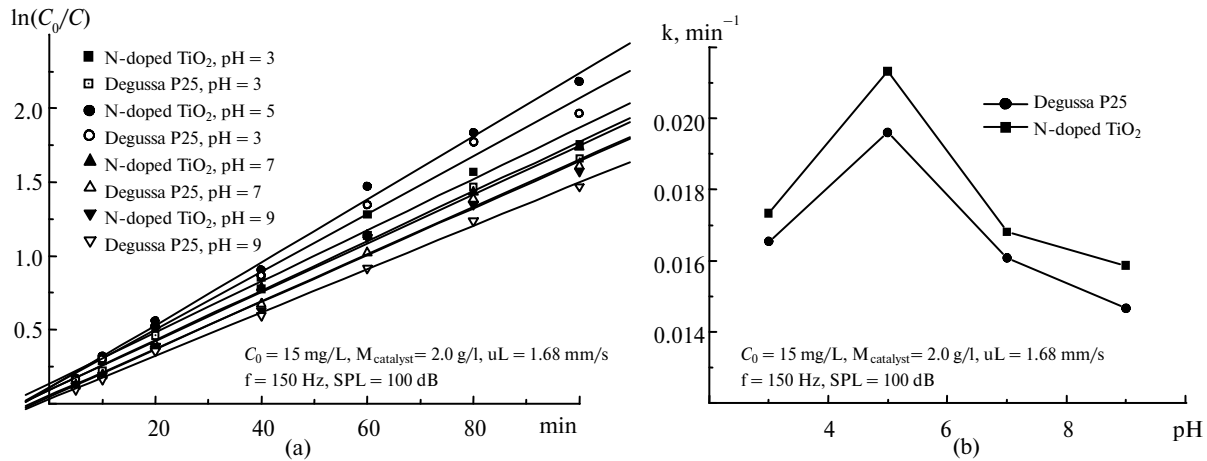


Fig. 4. Effect of pH values on degradation rate of AG: a—effect of pH value on irradiation time; b—effect of pH value on rate constants using Degussa P25 and N-doped  $\text{TiO}_2$  catalysts.

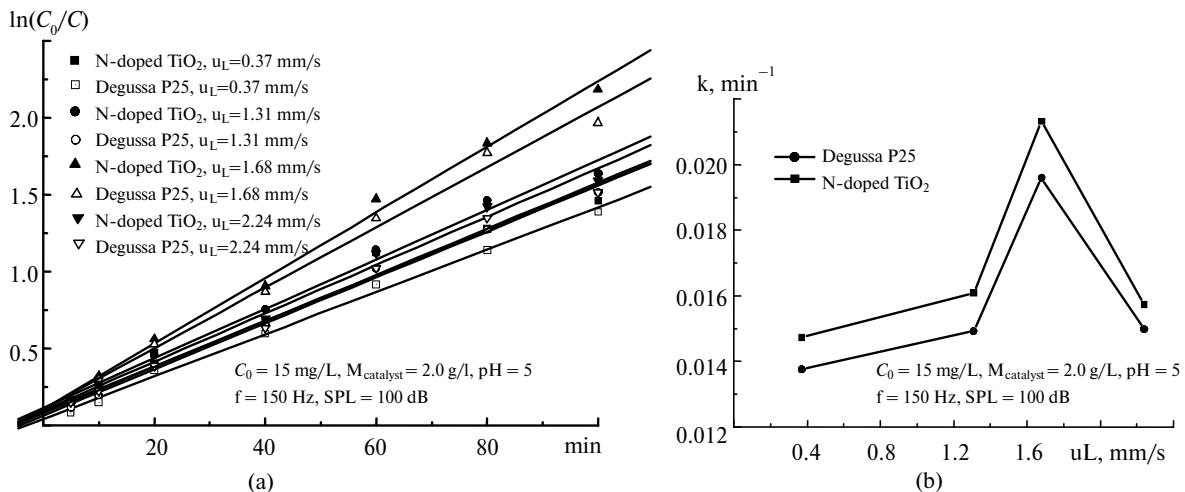


Fig. 5. Effect of liquid flow rate on degradation rate of AG: a—effect of liquid flow rate on irradiation time; b—effect of liquid flow rate on the rate constants using Degussa P25 and N-doped  $\text{TiO}_2$  catalysts.

When the flow rate increases, two antagonistic effects are brought into play: the decrease in the residence time in the photocatalytic reactor and the increase in the mass transfer rate [16]. Therefore, when liquid flow rate increased to  $1.68 \text{ mm}\cdot\text{s}^{-1}$ , such enhancement became insignificant. This fact indicated that the AG degradation rate was no longer mass-transfer controlled when the liquid flow rate was higher than  $1.68 \text{ mm}\cdot\text{s}^{-1}$ . The same results were also observed in a novel labyrinth flow bubble photoreactor for degradation of organic pollutant from water [17]. In the present experiment, the rate constants were calculated as  $0.0150$  and  $0.0157 \text{ min}^{-1}$  at liquid flow rate  $2.24 \text{ mm}\cdot\text{s}^{-1}$  using Degussa P25 catalyst and N-doped  $\text{TiO}_2$  catalyst in an acoustic fluidized bed, respectively.

## CONCLUSIONS

The AG solution was successfully degraded by the photocatalytic reaction in two different  $\text{TiO}_2$  catalysts in an acoustic fluidized bed. Compared with Degussa P25, the degradation efficiency of AG was preferable using the N-doped  $\text{TiO}_2$  catalyst. The higher initial concentration decreased the light penetration thus decreased the

degradation rate of photocatalytic reaction. It was observed that there was an optimum amount of catalyst. It was also found that pH is another important parameter in determining the reaction rate and the acidic condition was favorable for the AG and TiO<sub>2</sub> system. The liquid flow rate had an optimum value and played an important role by increasing the mass transfer and by decreasing the residence time. According to the Langmuir–Hinshelwood model, the photocatalytic decomposition reaction followed a pseudo-first-order kinetic law.

#### ACKNOWLEDGMENTS

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