



Degradation of *p*-Toluene Sulfonic Acid Wastewater by Combined Photocatalysis and Ozonization

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The degradation of low concentration of *p*-toluene sulphonic acid (*p*-TSA) in aqueous solution by three photochemical methods (O_3 , TiO_2/UV , $TiO_2/UV/O_3$) were compared and the effects of initial pH, *p*-TSA concentration and ozone dosage on the *p*-TSA degradation by $TiO_2/UV/O_3$ were studied. The results show that the degradation of *p*-TSA in three processes- O_3 , TiO_2/UV , $TiO_2/UV/O_3$, follow the apparent first-order reaction kinetics. The rate constant of $TiO_2/UV/O_3$ is larger than sum of those of TiO_2/UV and O_3 , which indicates a synergistic effect of photocatalysis and ozonization. The effect of pH on *p*-TSA degradation by $TiO_2/UV/O_3$ can be ignored. The rate constant decreases with the increase of initial concentration of *p*-TSA, while the absolute removal amount of *p*-TSA increase of its initial concentration. The rate constant decreases with the increase of ozone dosage. Small organic molecules are identified as the main intermediate product during *p*-TSA degradation; and the ultimate products were H_2O , CO_2 , indicating that $TiO_2/UV/O_3$ is a safe and effective method to remove *p*-toluene sulphonic acid.

Key Words: Ozone oxidation, TiO_2/UV , Degradation, Wastewater of *p*-toluene sulfonic acid.

INTRODUCTION

As an important chemical raw material, *p*-toluene sulphonic acid (*p*-TSA) exists widely in the waste water of many fields as petrochemical industry, plastic, pharmaceuticals industry *etc.* *p*-TSA is a biological toxic substance¹ with poor biodegradability², high water-solubility and strong polarity, making the wastewater riching in such substance can not be efficiently treated by conventional methods³. At present, the industrial treatment of such wastewater still remains many difficulties.

Ozonization and photocatalysis, called as the green technology and environment-friendly technology have drawn researchers' much attention⁴⁻⁶. Based on the earlier research on degradation *p*-TSA by photocatalysis⁷, our group combined photocatalysis with ozonation to degrade *p*-TSA. Then the degradation effects by O_3 , TiO_2/UV , $TiO_2/UV/O_3$ were compared and the influencing factors of $TiO_2/UV/O_3$ on the degradation *p*-TSA were examined. Also the intermediates and mineralization of *p*-TSA degradation were analyzed and detected and mechanism of *p*-TSA degradation by $TiO_2/UV/O_3$ was discussed, providing a reference for practical application.

EXPERIMENTAL

p-Toluene sulphonic acid (*p*-TSA) (AR, Shanghai Miura Chemical Company), TiO_2 (Hongsheng Materials Technology Co. Ltd., Zhejiang, particle size of 5-10 nm with surface area of $(210 \pm 10)m^2g^{-1}$, crystal form of anatase, purity > 99 %), potassium iodide (AR), sodium thiosulfate (AR), sodium hydroxide (AR), sulfuric acid (AR), deionized water.

Ozone generator-DHX-SS-03B (Harbin Jiujiu Electrochemical Engineering Co. Ltd.), multi-photochemical reaction instrument SGY-I (Nanjing Sitongke Electric Equipment Co. Ltd.), high performance liquid chromatograph (Shimadzu, Japan), ultraviolet spectrophotometer UV-2000 (Beijing Lab Tech. Instrument Co. Ltd.), UV radiation meter UV-B (Optical Instrument Factory of Beijing Normal University), electronic analytical balance (Beijing Sartorius Instrument Systems, Inc.), HI 98128 acidometer (Italy Hana), microwave digestion COD tachometer WMX-1 (Shantou Huanhai Engineering Corporation), ozone concentration analyzer (UK BEHRINGER), total organic carbon analysis meter liqui TOC II (German Elementar Company), infrared spectrometer AVATAR 360 (American Nicolet Company).

Measurement processes and experimental methods: As Fig. 1 showed the $TiO_2/UV/O_3$ experimental facility mainly

included four parts: source of oxygen, ozone generators, ozone oxidation-photocatalytic reactor and exhaust gas treatment. Reactor was made of quartz glass, a cylinder with a length of 300 mm and diameter of 60 mm. About 60 mm above the centre-line of the reactor was the light source, 300 W ultraviolet lamp with a wavelength of 365 nm and light intensity $450 \mu\text{W}/\text{cm}^2$. It was turned on after TiO_2 and *p*-TSA solution were mixed under the reaction conditions in the dark for 30 min. Then ozone entered the reactor from porous sand core distribution board at the bottom of the reactor and flowed up to get in touch with the mixture above and reacted. Redundant ozone was absorbed by KI and then discharged to the air. The target product was measured by sampling with Na_2SO_3 at specific interval.

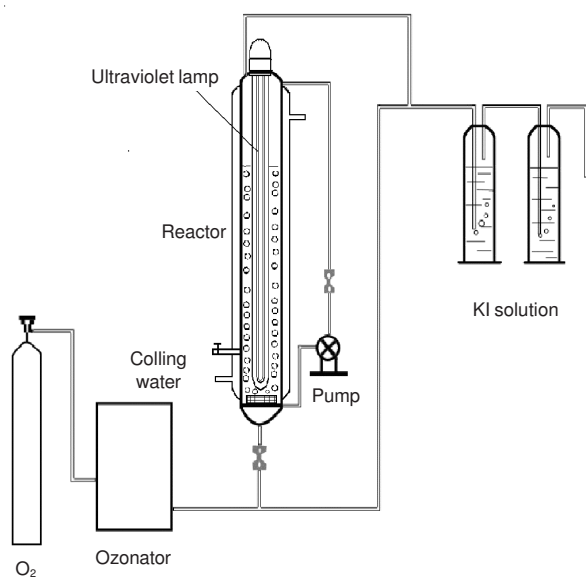


Fig. 1. Schematic diagram of the experimental apparatus

Gas chromatographic conditions: OV-1701 column ($30 \text{ m} \times 0.32 \text{ mm} \times 0.5 \mu\text{m}$), column temperature 210°C , sample injector and detector temperature 300°C , pre-column pressure 0.06 MPa , split ratio 30:1, hydrogen flow $30 \text{ mL}/\text{min}$, air flow $300 \text{ mL}/\text{min}$.

Analytical methods: Concentration of *p*-TSA was analyzed by HPLC, with the chromatographic column ODS C_{18} column ($250 \text{ mm} \times 5 \text{ mm} \times 5 \mu\text{m}$), made in Agilent, USA. Volume ratio of acetonitrile and secondary water was 1:1 (50:50 %, v/v) with column temperature 30°C , flow rate $0.4 \text{ mL}/\text{min}$, injection volume $40 \mu\text{L}$ and detection wavelength of 220 nm . pH value was determined by glass electrode. Chemical oxygen demands COD was measured by potassium dichromate method using sealed microwave digestion tachymeter. Ozone concentration in gas was obtained by iodometry and ozone analyzer and indigo method in liquid⁸. Total organic carbon (TOC) was determined by liquid TOC II analysis meter and the concentration of SO_4^{2-} by barium chromate spectrophotometry.

RESULTS AND DISCUSSION

Degradation effects of *p*-TSA by photochemical methods:

The degradation of *p*-TSA experiment was carried in the same

reactor with three different methods and the results were shown in Fig. 2. It indicated that at the time of 30 min, degradation rate by O_3 was only 28.1 % and 43.4 % by TiO_2/UV , while the rate by $\text{TiO}_2/\text{UV}/\text{O}_3$ reached 73.6 %, larger than sum of those of TiO_2/UV and O_3 , which indicated a synergistic effect of photocatalysis and ozonization, increasing the degradation rate of *p*-TSA.

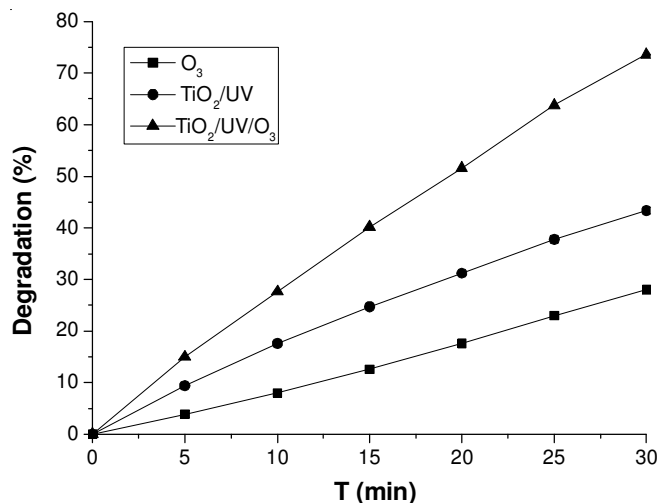


Fig. 2. Comparison of three methods for *p*-TSA degradation; Reaction condition: Initial concentration of *p*-TSA, 100 mg L^{-1} , pH 7.0, 25°C , TiO_2 dosage 100 mg L^{-1} , Ozone dosage 10.8 mg L^{-1}

Degradation of *p*-TSA in aqueous solution could be described by Langmuir-Hinshelwood (L-H) reaction kinetics model:

$$r = -\text{d}C/\text{d}t = \text{K}bC/(1 + bC) \quad (1)$$

where, *r*-reaction rate; *C*- concentration of reactants at the time of *t*; *K*- reaction rate constant of solids surface; *b*-constant relative to solid adsorption heat and temperature.

When concentration of organics was very low, $bC \ll 1$, format (1) could be rewritten as:

$$r = -\text{d}C/\text{d}t = \text{K}bC = kC \quad (2)$$

where, it was boiled down to first order reaction and $k = \text{K}b$. Then, taking the integral of (2), linear relation was obtained between C_0/C and *t* and the slope *k* was the rate constant of the first-order reaction.

The first-order kinetics fitting of *p*-TSA degradation was shown in Fig. 3. It could be seen that C_0/C and *t* had a good linear correlation in the process of *p*-TSA degradation by O_3 , TiO_2/UV and $\text{TiO}_2/\text{UV}/\text{O}_3$ and the related coefficients *R* were 0.9947, 0.9999, 0.9902, respectively. All of the three processes followed the apparent first-order reaction kinetics, with the rate constant of $0.0103 \text{ mg (L}^{-1} \text{ min}^{-1})$, $0.0191 \text{ mg (L}^{-1} \text{ min}^{-1})$, $0.0403 \text{ mg (L}^{-1} \text{ min}^{-1})$ separately by O_3 , TiO_2/UV and $\text{TiO}_2/\text{UV}/\text{O}_3$. Obviously, the rate constant of $\text{TiO}_2/\text{UV}/\text{O}_3$ was larger than sum of those of TiO_2/UV and O_3 , which indicated that in the $\text{TiO}_2/\text{UV}/\text{O}_3$ process, not the photocatalysis or ozonization existed, but also ozone, as electron capture agent⁹, greatly increased the efficiency.

Effect of initial pH on *p*-TSA degradation by $\text{TiO}_2/\text{UV}/\text{O}_3$: In the process of organics degradation by $\text{TiO}_2/\text{UV}/\text{O}_3$, pH had an induced effect on $\cdot\text{OH}$ radical chain reaction, affecting the substance change¹⁰. Therefore, the effect of initial pH

on *p*-TSA degradation by $\text{TiO}_2/\text{UV}/\text{O}_3$ was investigated and results could be drawn from Fig. 4 that different pH had little different influence on *p*-TSA degradation. As for the photocatalytic degradation, HCO_3^- or CO_3^{2-} produced by organic mineralization in alkaline circumstance could neutralize $\cdot\text{OH}$ promptly. But under acidic conditions, HCO_3^- and CO_3^{2-} would escape in the form of CO_2 , no inhibitory action on $\cdot\text{OH}$. In alkaline solution HO_2^- from ozone self decomposition could catalyze and induce active $\cdot\text{OH}$. Ozone had higher electrode potential and electron affinity than other common strong oxidants and could react with organics in waste water rapidly in any conditions¹¹, also the speed of ozonolysis to $\cdot\text{OH}$ accelerated as pH rose. However, the effect of initial pH on *p*-TSA degradation by $\text{TiO}_2/\text{UV}/\text{O}_3$ was less remarkable compared with that by O_3 and TiO_2/UV , which illustrated *p*-TSA degradation by $\text{TiO}_2/\text{UV}/\text{O}_3$ had a more extensive pH adaptation, offering commendable reference for project application.

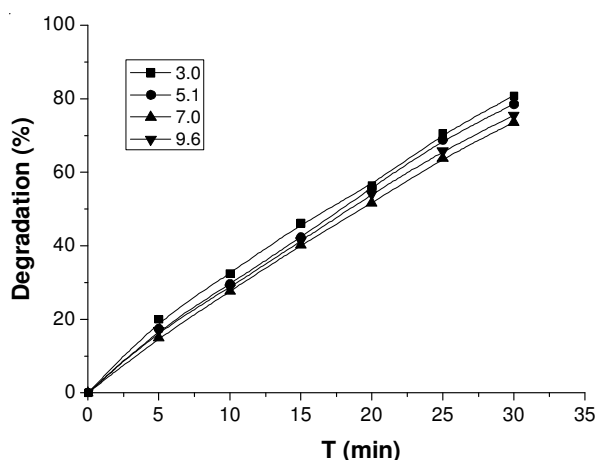


Fig. 3. First-order kinetics fitting of *p*-TSA degradation; Reaction condition: Initial concentration of *p*-TSA, 100 mg L⁻¹, pH 7.0, 25 °C, TiO_2 dosage 100 mg L⁻¹, ozone dosage 10.8 mg L⁻¹

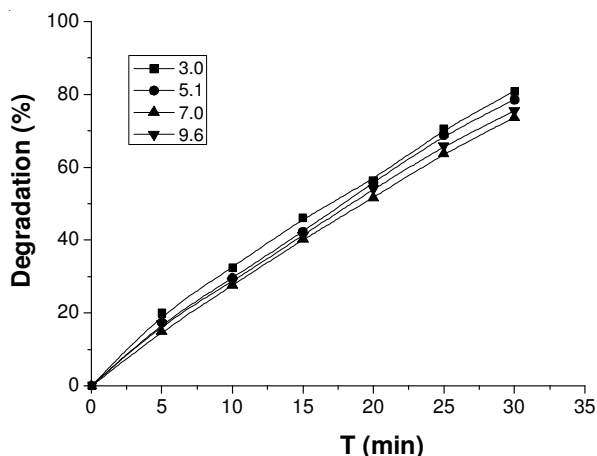


Fig. 4. Effect of initial pH on *p*-TSA degradation; Reaction condition: initial concentration of *p*-TSA, 100 mg L⁻¹, 25 °C, TiO_2 dosage 100 mg L⁻¹, ozone dosage 10.8 mg L⁻¹

Effect of initial mass concentration on degradation ratio of *p*-TSA: Influence of initial concentration on degradation ratio of *p*-TSA was presented in Fig. 5. It could be known from the graphic that the initial concentration had a great impact on *p*-TSA degradation rate. As initial concentration increased,

degradation rate by $\text{TiO}_2/\text{UV}/\text{O}_3$ descended. When initial concentration of *p*-TSA was 10 mg L⁻¹, limit of detection could be achieved 20 min later, but when it was 30, 50, 80 and 100 mg L⁻¹, degradation rate was respectively 99.6, 92.2, 81.3 and 73.6 % after 30 min. Also the apparent first-order rate constant reduced with the increase of *p*-TSA concentration and was 0.3148, 0.1826, 0.0859, 0.0539 and 0.0403 mg (L⁻¹ min⁻¹) separately. It frequently emerged in homogeneous and heterogeneous photochemistry degradation reaction^{12,13} because it was a complex reaction, not elementary reaction simply. Intermediate product would generate and participate in competitive reactions. The higher initial concentration was, the more intermediate product generated and the greater effect on the reaction had. Though the apparent first-order rate constant reduced as initial concentration elevated, absolute degradation ratio of *p*-TSA in unit interval was still remarkably aggrandized, not a constant.

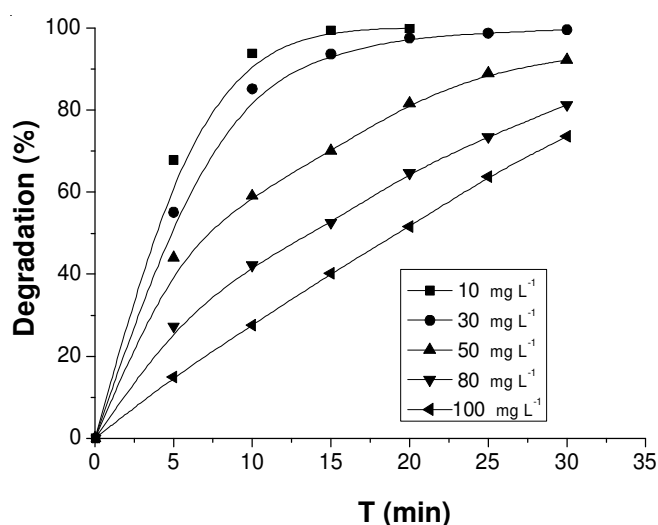


Fig. 5. Effect of initial concentration on degradation ratio of *p*-TSA Reaction condition: pH 7.0, 25 °C, TiO_2 dosage 100 mg L⁻¹, Ozone dosage 10.8 mg L⁻¹

Effect of ozone dosage on *p*-TSA degradation: Ozone was the external dynamic of *p*-TSA degradation and its effect was plotted in Fig. 6. With the increase of ozone dosage, degradation rate rose, indicating that larger ozone dosage was in favour of degradation, though the increase trend was not linear. But the increase trend of degradation rate with ozone dosage was no longer obviously when ozone dosage reached 22 mg L⁻¹. It could be explained that ozone could not only promote the generation of $\cdot\text{OH}$, but capture $\cdot\text{OH}$ and the latter was more notable when ozone dosage was large. Therefore, it was diseconomy for enhancing degradation rate by blindly adding ozone dosage in practical application. Instead, ozone dosage should be estimated in accordance with expenses and efficiency.

Product analysis of *p*-TSA degradation

Degradation rate of *p*-TSA, COD, TOC and concentration change of SO_4^{2-} : Degradation rate of *p*-TSA, COD, TOC at different time, under the initial conditions of 100 mg L⁻¹ *p*-TSA, 160 mg L⁻¹ COD and 88 mg L⁻¹ TOC, was given in Fig. 7. It can be seen from the figure that the degradation rate

of *p*-TSA was so fast that limit of detection had achieved at time of 60 min, when that of COD and TOC was only 78.6 % and 52.2 %, illustrating degradation rate of COD lagged behind that of *p*-TSA and pulled ahead of TOC. What's more, TOC had a slight trend of decline, further demonstrating that *p*-TSA was not totally mineralized, but generated certain intermediate product and the ultimate product was CO₂ and H₂O. At the same time, SO₄²⁻ concentration also increased.

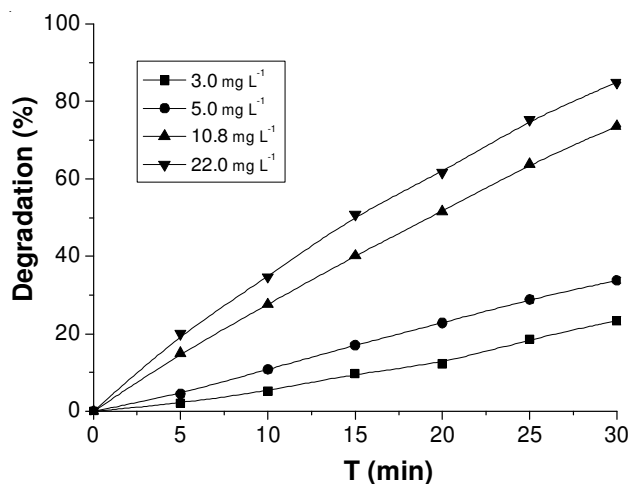


Fig. 6. Effect of ozone dosage on *p*-TSA degradation; Reaction condition: initial concentration of *p*-TSA, 100 mg L⁻¹, 25 °C, pH 7.0, TiO₂ dosage 100 mg L⁻¹

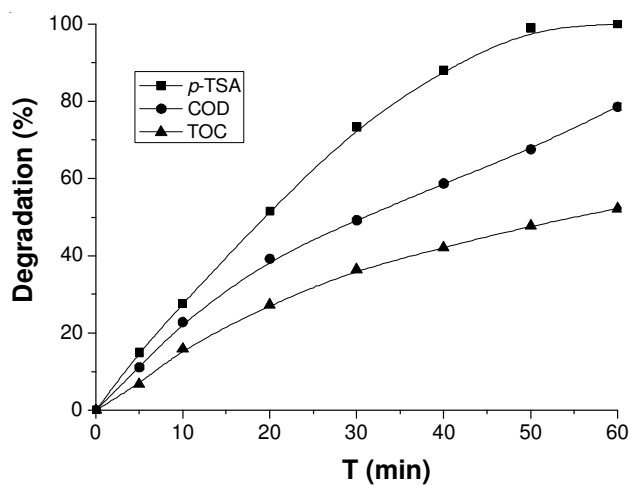


Fig. 7. Effect of initial concentration on degradation ratio of *p*-TSA Reaction condition: pH 7.0, 25 °C, TiO₂ dosage 100 mg L⁻¹, ozone dosage 10.8 mg L⁻¹

Intermediate product analysis of *p*-TSA degradation:

Intermediate product analysis of *p*-TSA degradation was carried on comparing retention time of experimental chromatographic peak with that of criterion peak under experimental conditions, followed by qualitative analysis. Retention time of the standard solution was measured as 1.747, 1.998, 3.085 and 3.522 min respectively, averaging on six sample intro-

duction of acetic acid, maleic acid, fumaric acid and phenol, which could also be all detected in the solution of *p*-TSA degradation, the chromatogram of degradation was taken at 60 min. But formic acid and oxalic acid were not detected by GC, probably on account of pyrolysis.

After degradation for 60 min, pH was also measured in the system and it was changed from the initial pH of 3.0, 5.1, 7.0, 9.6 to 3.4, 3.4, 3.6, 4.0, separately, which declared acid organics generated and accumulated in the process of *p*-TSA degradation. In addition, BOD/COD ascended to 0.35, achieving biochemistry scope, in accordance with the reference¹⁴.

Conclusion

The three photochemical methods (O₃, TiO₂/UV, TiO₂/UV/O₃) were all effective on *p*-TSA degradation, following the apparent first-order reaction kinetics and there was a synergistic effect of photocatalysis and ozonation. The effect of pH on *p*-TSA degradation by TiO₂/UV/O₃ can be ignored. The rate constant decreased with the increase of initial concentration of *p*-TSA, while the absolute removal amount of *p*-TSA increase of its initial concentration. The rate constant decreased with the increase of ozone dosage. Small organic molecules were identified as the main intermediate product during *p*-TSA degradation, with an increase of biochemistry property. And the ultimate products of *p*-TSA mineralization were H₂O and CO₂.

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