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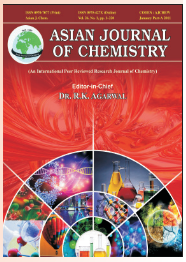

Photocatalytic Degradation of Aniline Using Supported TiO_2/Charcoal Composite†

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TiO_2/bamboo charcoal composites were prepared by sol-gel technique with tetrabutyl titanate as the titanium source and 60-mesh bamboo charcoal as the support. The photocatalytic degradation processes of aniline were studied. The results indicated that the TiO_2/bamboo charcoal composites had quite a good photocatalytic ability. In the UV irradiation, the temperature and pH value had great influence on the effect of degradation. When the pH value was between 1 to 3 and the temperature was 50 ºC, the degradation effects reached more than 93 %. The degradation rate of aniline decreased when the concentration increased but increased with more TiO_2 in it. The degradation achieved balance after 105 min. The photocatalytic degradation of aniline to TiO_2 fitted in with the first reaction kinetic equation.

Keywords: Bamboo charcoal, Aniline, Titania, Photocatalytic degradation.

INTRODUCTION

As the most representative of aromatic amine, aniline an is an aromatic, colourless and oily liquid. With the development of industry, the wastewater containing aniline discharged by the enterprises that yield or use aniline pollute the environment and the air. To the human body, it is the typical formation of methemoglobin, making the cells lose their function of carrying oxygen and causing hemolysis. It is easy to deposition on liver and renal and disorder their functions, causing malnutrition and anemia. So it has been put on the serious pollutant of 14 categories of environmental pollutants in China[1]. The residual of aniline in environment has received great concerns and has been regarded as one of the recurrent items in environment monitoring.

Nanometer semiconductor photocatalytic oxidation technology is a new technology which is to eliminate environmental pollutants, it can oxidize and decompensate the organic pollutants into CO_2 and H_2O or simple inorganic objects[2,3]. It is also a environmental-friendly material that has the function of sterilization, deodorization and fog-anteing and so on. Because of the benefits such as easy operation, no secondary pollution, low consuming and mild reaction conditions, it has become a research focus. Among the nanometer materials, TiO_2 receives extensive attention due to its unique photocatalysis, such as high chemical stability, inexpensive and non-toxic characteristics[4-6]. However, this system discourages practical application, because it is easy to get inactivation and hard to recovery[7-9]. Since TiO_2-supported composite materials have the benefits as easy-separation, easy-recovery, reusing, it has become a new topic of research[10]. Bamboo charcoal is the ideal water-treatment candidate materials which have uniform microporous skeleton structure and stable very rich particular surface area. This research aims to study the preparation and the photocatalytic degradation to aniline of the bamboo charcoal supported TiO_2.

EXPERIMENTAL

Bamboo charcoal, anhydrous ethanol (AR), acetic acid glacial (AR), tetrabutyl titanate (CP), sulfuric acid (AR), sodium hydroxide (AR), nitric acid (AR) and aniline (AR) are analytical grade reagents.

Preparation of TiO_2/bamboo charcoal composite: As reported by Zhou *et al.*[11].

Photocatalytic experiment: 25 mL of aniline solution of a certain concentration was added to a certain amount of composite and the aniline solution was kept under UV irradiation statically until it reached a balance of degradation. The absorbance of the residual aniline was checked in 230 nm after being filtrated. The aniline photocatalytic degradation rate was determined by the following equation.

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$$\text{Photocatalytic degradation rate} = \frac{(c_0 - c)}{c_0} \times 100\ \%$$

where: c_0 and c, for the initial concentration of aniline solution and the residual concentration after photocatalytic degradation, respectively (both mg/L).

RESULTS AND DISCUSSION

Effect of composite amount on the degradation rate of aniline: 0.3000, 0.5000, 0.7000, 0.9000, 1.1000, 1.3000, 1.5000 and 1.7000 g of composites were added, respectively to 25 mL, 50 mg/L of aniline solution. The composites were filtrated after being degraded statically in the ultraviolet irradiation at 25 ºC for 1 h. The concentration of the residual aniline solution from the filtrate was measured and the results were shown in Fig. 1.

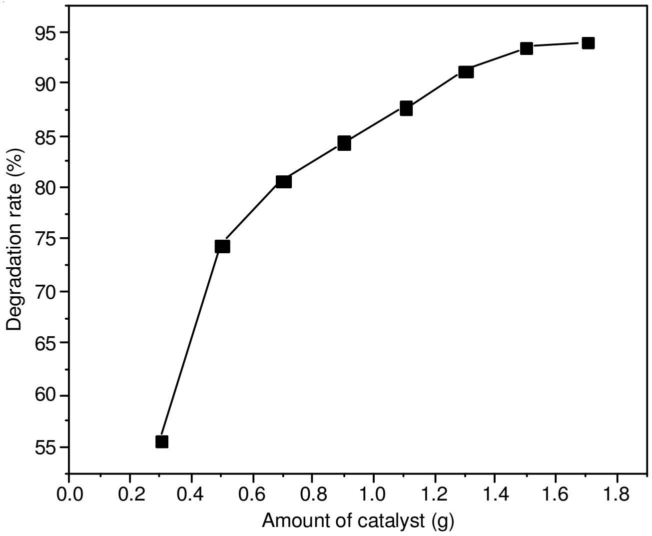

Fig. 1. Effect of composite materials amount on the degradation rate of aniline solution

As can be seen from Fig. 1, the degradation rate of composite materials to aniline solution obviously increased with more composite materials in it. Also, higher amount of TiO_2 composite contributed towards higher suspension turbidity, thus reducing light penetration and inhibiting TiO_2 composite from being efficiently excited by UV irradiation[3,12]. When the amount of composite materials transferred from 0.3 to 1.3 g, the degradation rate increased significantly, while the amount was more than 1.3000 g, the rate gradually slowed down. When the amount of composite materials was 1.5000 g, the degradation rate reached 93.35 %.

Effect of temperature on the degradation rate of aniline: Eight parts of 0.5000 g composites were added to the 25 mL, 50 mg/L of aniline solution. They were filtrated after being degraded statically in the ultraviolet irradiation, respectively at 20, 25, 30, 35, 40, 45, 50 and 55 ºC for 1 h. The concentration of the residual aniline solution from the filtrate was measured and the results were shown in Fig. 2.

As can be seen from Fig. 2, the degradation rate of aniline solution increased with temperature increasing, when the temperature was higher than 50 ºC, the degradation rate dropped slightly. The reason was that aniline dissolved slightly in cold water, with the temperature increasing, the affinity between aniline and water molecules increased, so did the solubility in water. The activity of photocatalyst increased with the temperature and the catalytic effect was high. At the same time photocatalyst itself could easily adsorb hydrophilic substances, the degradation rate of the aniline increased correspondingly. When the temperature was higher than 50 ºC, the adsorption reached saturation point. The activity of the photocatalyst reduced because the intermediates, obtained after degradation, accumulated in the catalyst surface and occupied the active site[13]. The degradation declined, so the best temperature was 50 ºC.

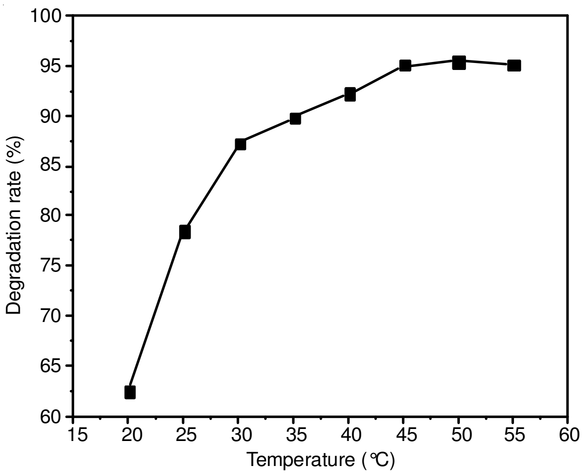

Fig. 2. Effect of solution temperature on the degradation rate of aniline

Effect of solution pH value on the degradation rate of aniline: Twelve parts of 0.5000 g composites were added, respectively to the 25.0 mL, 50 mg/L of aniline solution. Different pH values were measured (adjust the pH value of aniline solution with H_2SO_4 or NaOH) in 1.56, 2.80, 3.64, 4.47, 5.83, 6.70, 7.43, 8.32, 9.96, 11.28, 12.34, 13.19 at 25 ºC in UV irradiation. They were filtrated after being degraded statically for 1 h. The concentration of the residual aniline solution from the filtrate was measured and the results were shown in Fig. 3.

As can be seen from Fig. 3, the effect of pH on the degradation rate of aniline was high under acidic conditions than under alkaline conditions. Under acidic conditions, the degradation rate was lower when the pH value was increasing, under alkaline conditions, the effect of pH on the degradation rate of aniline was lower.

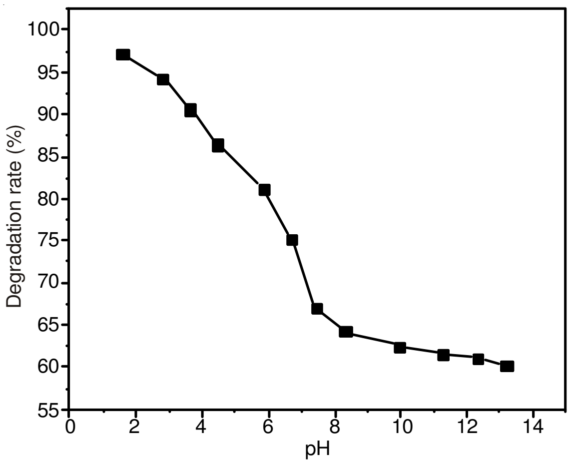

Fig. 3. Effect of pH on the the degradation rate of aniline

The aniline showed the nature of weak ion when under specific conditions and the ionization's degree was not the same along with different pH. It had the ionic and the non-ionic shapes in the peroxide solution. The change of the pH value would alter the electric charge nature of the median surface in solutions, then influenced the degeneration behaviour on the surface. The surface charge nature of composite influenced the surface adsorption of composite materials to the pollutants in reacting system. Under acidic conditions, the composite surface had a positive charge, the adsorption was mainly water. The water and the composite had the following function: $h^+ + H_2O = {}^{\bullet}OH + H^+$, which would be good for migration of the photoproduction electron to the catalyst surface, then responded with the oxygen adsorbed on the surface. The compounding of the electronic hole was suppressed, the response of the photoproduction electron with the oxygen was the source of ${}^{\bullet}OH$. Under alkaline conditions, the surface of the composite had the negative charge because of OH, fastening the leaving of photoproduction electron, which was not good for e- to arrive at the surface as well as the degradation of the pollutants because h^+ would be simultaneously caught[14]. Therefore, the acidic condition was favorable to the aniline degeneration. In this experiment, the photocatalytic degeneration effect of aniline was best when the pH value was 1 to 3.

Effect of time on the degradation rate of aniline: Eight parts of 0.5000 g composites were added, respectively to 25 mL, 50 mg/L of aniline solution. The effect of different times, 15, 30, 45, 60, 75, 90, 105 and 120 min, were measured in the UV irradiation at 25 ºC. The concentration of the residual aniline solution from the filtrate were measured after being filtrated and the results were shown in Fig. 4. Thus the rate of degradation gradually increased with the degradation time growing, the degradation rate tended to slow when the time was greater than 1 h; when the time was more than 105 min it had a degradation balance. As the charcoal itself had a good adsorption ability, so before 1 h, the adsorption and degradation happened at the same time; after 1 h, the adsorption reached a balance, the main reaction was degradation. As the input of catalyst reached a set amount and the light intensity to a certainty, the activity of the catalyst reduced in a set of time. Therefore, when the degradation time was more than 105 min, it reached balance.

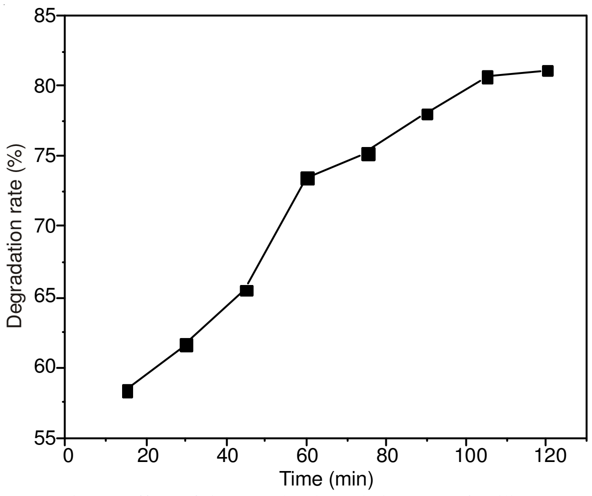

Fig. 4. Effect of time on the degradation rate of aniline

Effect of the initial concentration aniline solution on degradation rate of aniline: Six parts of 0.5000 g composites were added, respectively to 25.0 mL of aniline solution with the original solution of 50, 100, 150, 200, 250, 300 mg/L. They were filtrated after being degraded statically in the UV irradiation at 25 ºC for 1 h, the results were shown in Fig. 5.

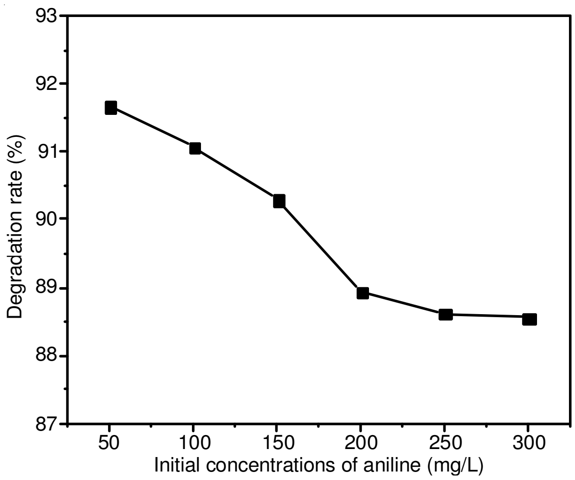

Fig. 5. Effect of the original concentration aniline solution on degradation rate of aniline

As can be seen from Fig. 5, the composite degradation rate to aniline gradually reduced with the increasing of the aniline original concentration. For heterogeneous phocatalysis reaction of TiO_2, the reaction rate was determined by the concentration of the strong oxidizing free radicals, including ${}^{\bullet}OH$, ${}^{\bullet}O_2$, ${}^{\bullet}HO_2$, *etc.*[14]. These radicals were originated when oxygen or water molecular excited by TiO_2 under UV irradiation condition and engendered by combination of light-generated electron and the hole on the surface of catalyst. When the concentration of the reactant was higher, reactant molecules could reach an adsorption saturation on the catalyst surface, so the TiO_2 surface defects reduced and eventually led to the decline in the concentration of oxidizing free radicals, then the system reaction rate slowed down. When the reactant concentration was lower, the reactant molecules would be adsorbed on the active site first and the photolysis rate was increased[15].

Photocatalytic kinetics study of aniline degradation: The data of the photocatalytic oxidation of aniline solution with the initial concentration of 50 mg/L by integration was showed in Fig. 6. It can be seen from the graph that ln c was linear with time and the correlation coefficient R was 0.98749, indicating that the photocatalytic degradation of aniline to TiO_2 fitted in with the pseudo-first-order kinetic equation[10].

Conclusion

The TiO_2/bamboo charcoal composites prepared by sol-gel technique have quite a good photocatalytic ability and a stronger degradation to aniline. The temperature and pH value have great influence on the degradation. When the pH value is 1 to 3 and the temperature is 50 ºC, the degradation is better. The degradation rate of aniline decreases when the concentration increases but increases with more TiO_2 in it. The degradation reaches balance when the degradation time is more than 105 min. The photocatalytic degradation of aniline to TiO_2 fits in with the pseudo-first-order kinetic equation.

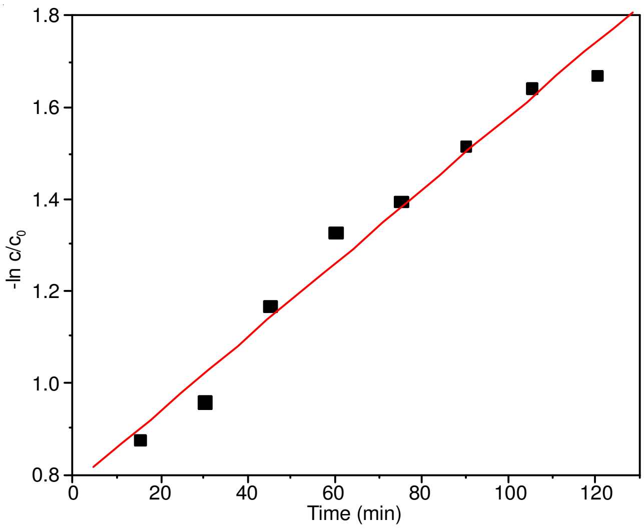

Fig. 6. Relationship of –ln c/c$_0$ and time

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