

The Degradation of Reactive Black Wastewater by Fe/Cu Co-doped TiO₂

Junrui Liu (Corresponding author), Zhewei Zhang, Li Yang, Yanzong Zhang & Shihuai Deng
Sichuan Agricultural University, Yaan 625014, China
E-mail: liujunrui163@163.com

Received: February 22, 2011 Accepted: March 7, 2011 doi:10.5539/ijc.v3n3p87

Abstract

The organic contaminant, REACTIVE Black 5 (RB5) was degraded by Fe/Cu co-doped TiO₂ nano-particles under mercury lamp. In the present study, the combined effects of Fe/Cu doping amount, calcination temperature and calcination time on catalyst activity were investigated, and through quadratic regression general rotation design, the optimal condition for preparing the catalyst was obtained as follows: calcination time, 3.55h; calcination temperature, 453 °C; Cu doping amount, 1.89%; Fe doping amount, 1.62%.

Keywords: Cu doping amount, Fe doping amount, Calcination temperature, Calcination time, RB5

Printing and dyeing wastewater with complex composition, high concentration and large color, could not only contribute to water staining, but also bring toxicity to water. It has been the major source of environmental pollution, and serious threat to the security of water resources and human health (Muruganandham, 2006, pp.133-142). Since reactive dyes possessed simple dyeing process and high stability, it has been applied extensively and intensively in dyeing and printing industry. However, due to its complex molecular structure, decolorization and degradation using the traditional biological treatment methods was not very effective, and physical or chemical treatment methods had their own limitations (Amrit, 2006, pp.53-60; Patricia, 2004, pp.3807-3820). In recent years, degrading organic wastewater by nono-TiO₂ photocatalyst has attracted many researchers' attention all over the world, and also has been applied extensively and intensively in the treatment of organic pollution (Tanaka, 1997, pp.67-74; Zahraa, 1999, pp.167-173) and dyeing wastewater (Poulios, 1999, pp.479-487; So, 2002, pp.905-912). However, due to its large band gap, it could only be excited by UV, and failed to make good use of sunlight. In order to expand the optical properties of TiO₂ absorption, people tried numerous approaches, such as surface sensitization (Moon, 2003, pp.77-86; Lliev, 2003, pp.281-287; Konstantinou, 2004, pp.12-14), metal doping (Iwasaki, 2000, pp.202-204; Yamashita, 2003, pp.191-196; Wang, 2004, pp.151-154), non-metal doping (Asahi, 2001, pp.269-271; Umebayashi, 2003, pp.310-311) and so on. Ion doping is a more effective way to improve the photocatalytic effect, and metal ions doping, non-metal nitrogen, carbon, sulfur, boron doping, semiconductor composite or sensitization by photo-sensitive dyes, could all extend the light response range of TiO₂, reduce photo-holes and electron recombination, enhance the efficiency of sunlight absorption and ameliorate the photocatalytic properties. In the reports on single metal ions doping, Fe or rare earth metal ions doping brought better effects. Synergic effects among different ions could ameliorate the photocatalytic activity of TiO₂ further.

Accordingly, in the present paper, we used Fe/Cu co-doping, in combination with quadratic regression general rotation design, taking account of calcination temperature, calcination time and other factors to degrade RB5. The degradation conformed to first order kinetics $c = c_0 e^{-kt}$, and quaternary quadratic equation was obtained according to the k value. The most value of the equation was obtained by planning, and the optimal condition of each factor was verified.

1. Experimental

1.1 Test design (Table 1)

1.2 Material preparation

17 mL TiO₂ was added to 50 mL ethanol solution, and 10 mL acetic acid solution followed, which we called as A; Different amount of ferric sulfate and copper sulfate was added to 10 mL water and mixed, which we called as B. B was slowly added to A along with magnetic stirring, agitating after addition, and then the resultant solution was dried at 80 °C oven. The obtained powder was grinded to pieces, and calcined in muffle furnace, and Fe/Cu

co-doped TiO₂ was obtained.

1.3 Photocatalytic degradation of RB5

After preparing 10 mg/L RB5 solution, the absorbance of the solution with different concentration was measured by 721B spectrophotometer at the wavelength of 600 nm, and working curve was depicted. The prepared TiO₂ was added to RB5 solution, and photocatalytic degradation experiments were undertaken under the condition of UV irradiation and magnetic stirring. The absorbance of the solution was measured every 5 min, and the concentration curve along with time variation was depicted.

2. Results and discussions

2.1 Initial tests on the experimental condition

2.1.1 Effects of catalyst addition on the decolorization rate

Experimental conditions were as follows: light source, a 150W ultraviolet light; initial concentration of RB5, 30 mg/L, pH, 10.67; calcination temperature, 450 °C; calcination time, 3h; TiO₂, not doped.

As seen from Figure 1, decolorization effects of RB5 were quite low without the addition of catalyst. When catalyst concentration reached to 2 g/L, the degradation rate attained the maximum level which was higher than that when catalyst concentration reached to 1 g/L or 3 g/L. When the concentration was 1 g/L, less amount of catalyst couldn't make full use of ultraviolet rays generated by UV light; when the concentration was 3g/L, the collisions among small particles in too much amount of catalyst increased, and the generated energy could not be well used. Therefore, we selected 2 g/L in the following experiments.

2.1.2 Effects of pH value on the decolorization rate

Experimental conditions were as follows: light source, a 30 W ultraviolet light; the initial concentration of RB5, 30 mg/L; calcination temperature, 450 °C; calcination time, 3h; not doped TiO₂, 2 g/L.

As seen from Figure 2, acidic conditions (PH = 3.26) resulted in the worst treatment effects, neutral conditions (PH = 7.08) followed, while alkaline conditions brought in the best results. Under alkaline conditions, a large amount of -OH existed in the solutions, •OH was more conducive to produce, and the removal of RB5 primarily depended on the large amount of •OH generated in the solution; the reason might be related to the properties of the solution itself when acidity and alkalinity reduced. We select pH 10.67 in the following experiments.

2.2 Experimental design result and verification test

2.2.1 Experimental design result

Based on the preliminary exploration, we continued the following tests. We used $c = c_0 e^{-kt}$ to fit with the variation curve of concentration against time, and found that c_0 in each treatment was the same, namely initial concentration of the solution. Consequently, we used k value to represent the effects of each treatment. Results were listed in Table 2 in detail.

After calculation, regression equation was obtained as follows:

$$k = 2.07 - 0.333x_1^2 - 0.177x_2^2 - 0.128x_3^2 - 0.139x_4^2 + 0.169x_1 + 0.310x_2 - 0.291x_3 + 0.088x_4 - 0.233x_1x_2 - 0.117x_1x_3 + 0.055x_1x_4 - 0.049x_2x_3 + 0.004x_2x_4 + 0.128x_3x_4$$

After the obtained equation was substituted into treatment conditions, it was found that serial number 18, 20, 21 and 24 varied greatly from the equation. Therefore, we discarded these treatments. After variance analysis, the lack of fit was not significant, and regression relationship was greatly significant, which showed that the quadratic regression equation fitted very well.

For discarding those 4 treatments, the equation was undertaken programming solution within $-1 \leq x_1 \leq 2$, $-1 \leq x_2 \leq 2$, $-2 \leq x_3 \leq 1$, $-1 \leq x_4 \leq 2$, and when $x_1 = 0.55$, $x_2 = -1.47$, $x_3 = -1.78$, $x_4 = 1.23$, $k_{\max} = 2.66$. Results indicated that the optimum experimental parameters were calcination time, calcination temperature, Cu doped amount and Fe doped amount as 3.55h, 453 °C, doped copper, 1.89% and 1.62%, respectively. At the right moment, treatment rate after 1h was $1 - \exp(-2.66) = 93\%$.

2.2.2 Verification tests

We applied the above-mentioned optimal experimental conditions to prepare the catalyst, and added 2 g/L catalyst into RB5 with the pH value of 10.67 to react. Reaction results were depicted in Figure 3.

After fitting, $c = 29.45e^{-2.70t}$ was obtained (where the unit of t was h), and closer to the obtained k_{\max} , which simultaneously showed that the quadratic regression equation fitted very well.

2.3 Result analysis

2.3.1 Effects of Cu and Fe doped amount on the catalyst

Compared to pure TiO₂, co-doped metal ions resulted in better effects than single doped metal ions. When Cu and Fe doped amount reached to 1.89% and 1.62%, mineralization effects were the best. Proper amount of Cu and Fe co-doping could enhance the catalytic activity of TiO₂, which was determined by the natural properties of TiO₂ and doped ions. When TiO₂ semiconductor was lighted by photons higher than or equal to the forbidden gap energy, it would be excited to generate electron (e⁻) hole (h⁺) pairs. e⁻ and h⁺ was capable of oxidizing and reducing the substances absorbed on the surface. e⁻ and h⁺ pairs had a very short life span, and if there was no suitable e⁻ or h⁺ trapping agent, the energy would be consumed by recombination within a few microseconds (Asahi, 2001, 269-271). Proper amount of Cu²⁺ and Fe³⁺ could generate e⁻ capture traps; when co-doped Cu and Fe exceed certain level, the average distance among traps decreased, the recombination rate of e⁻ and h⁺ increased, which reduced the quantum efficiency of photons on one hand, resulted in the reduction of the carrier number that migrated to the surface of TiO₂ on the other hand, and thus declined the photocatalytic activity of catalyst.

2.3.2 Effects of calcination temperature on catalyst

When calcination temperature was 453 °C, the catalytic activity attained the maximum level. Because when temperature was lower than 450 °C, TiO₂ crystallization failed to complete, samples still contained more amorphous TiO₂, not beneficial to the producing of the above-mentioned e⁻ and h⁺, and therefore the catalytic activity decreased. With the increasing of temperature, the transformation from amorphous to anatase increased while anatase TiO₂ had higher photocatalytic activity, and therefore photocatalytic activity increased gradually. When activation temperature was above 450 °C, TiO₂ would change from anatase to rutile, particle size would increase with the increasing of temperature. Its internal porosity and specific surface reduced, recombination rate between e⁻ and h⁺ increased, and therefore the catalytic activity reduced.

2.3.3 Effects of calcination time on catalyst

With the increasing of calcination time, the catalytic activity also increased gradually. When calcination time was 3.55 h, the catalytic activity attained the maximum level. With the continuous increasing of time, the catalytic activity began to decline. When calcination time was too short, dry gel failed to discard the water and alcohol absorbed in the surface completely, co-doped TiO₂ was not able to transform into the required crystal form, and therefore the catalytic activity was not high. However, when calcination time was too long, the particles of co-doped TiO₂ agglomerated, made the average particle size and specific surface of photocatalyst increase and reduce, respectively, which led to the reduction of catalytic activity.

3. Conclusions

1 The degradation process of RB5 by TiO₂ catalysis and UV conformed to the first-order kinetic equation.

2 Preparing Cu/Fe co-doped TiO₂ photocatalyst by sol-gel method, the degradation of RB5 was investigated, and the impact of each factor on the first-order kinetics, viz. k value was obtained. The optimum preparation condition was obtained as follows: calcination time, 3.55 h; calcination temperature, 453 °C; Cu doping amount, 1.89%; Fe doping amount, 1.62%.

References

- Amrit, P.T., Anoop, V., Jotshi C.K., et al. (2006). Photocatalytic degradation of Direct Yellow 12 dye using UV/TiO₂ in a shallow pond slurry reactor. *Dyes and Pigments*, (68):53-60.
- Asahi, R., Morikawa, T., & Ohwaki T, et al. (2001). Visible-light photocatalysis in nitrogen doped titanium oxides. *Science*, 293 (5528):269-271.
- Iwasaki, M., Hara, M., Kawada, H., et al. (2000). Cobalt Ion doped TiO₂ photocatalyst response to visible light. *Journal of Colloid and Interface Sci*, 224 (1):202-204.
- Konstantinou, I.K., Albanis, T.A. (2004). TiO₂ assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations. *Applied Catalysis B: Environmental*, 49(1):12-14.
- Lliev, V., Tomova, D., Bilyarska, L., et al. (2003). Phthalocyanine Modified TiO₂ or WO₃-catalysts for photooxidation of sulfide and thiosulfate ions upon irradiation with visible light. *J Photochem Photobiol C*, 159 (3):281-287.
- Moon, J., Yun, C.Y., Chung, K., et al. (2003). Photocatalytic activation of TiO₂ under visible light using Acid Red 44. *Catal Today*, 87(1/4):77-86.
- Muruganandham. M., & Swaminathan, M. (2006). Photo catalytic decolourisation and degradation of Reactive

Orange 4 by TiO₂-UV process. *Dyes and Pigments*, (68):133-142.

Patricia, A.C., Marly, E.O., Jeosadaque, J.S., et al. (2004). Evaluation of color removal and degradation of a reactive textile azo dye on nanoporous TiO₂ thin-film electrodes. *Electrochimica Acta*, (49): 3807-3820.

Poulios, I., & Aetopoulou, I. (1999). Photocatalytic degradation of the textile dye reactive orange 16 in the presence of TiO₂ suspensions. *Environ Technol*, (20):479-487.

So, C.M., Cheng, M.Y., Yu, J.C., et al. (2002). Degradation of azo dye procion Red MX 2 5B by photocatalytic oxidation. *Chemosphere*, (46):905-912.

Tanaka, K., Luesai, W.W., & Hisanaga, T. (1997). Decolourization of reactive photocatalytic degradation of mono, di and tri nitro-phenolin aqueous TiO₂ suspension. *Mol Catal*, (122): 67-74.

Umebayashi, T., Yamaki, T., & Tanaka, et al. (2003). Visible light 2 induced degradation of methylene blue on S 2 doped TiO₂. *Chem Lett*, 32(4):310-311.

Wang, J., Uma, S., & Klabunde, K.J. (2004). Visible light photocatalysis in transition metal incorporated titania silica aerogels. *Applied Catalysis B: Environmental*, 48(2):151-154.

Yamashita, H., Harada, M., Misaka, J., et al. (2003). Photocatalytic degradation of organic compounds diluted in water using visible light-responsive metal-ion-implanted TiO₂ catalysts: Fe ion-implanted TiO₂. *Catal Today*, 84 (3/4):191-196.

Zahraa, O., Chen, H.Y., & Bouchy, M. (1999). Photocatalytic degradation of 1, 2-dichloroethane on supported TiO₂. *Adv Oxid Technol*, (4):167-173.

Table 1. Factor level coding

Serial number	Calcination time	Calcination temperature	Fe doping amount	Cu doping amount
2	5	800	2%	2%
1	4	700	1.5%	1.5%
0	3	600	1%	1%
-1	2	500	0.5%	0.5%
-2	1	400	0	0
∠	1	100	0.5%	0.5%

Table 2. Four-factor quadratic regression general rotation design results

Serial number	X ₁	X ₂	X ₃	X ₄	k
1	1	1	1	1	1.364
2	1	1	1	-1	0.816
3	1	1	-1	1	0.831
4	1	1	-1	-1	0.782
5	1	-1	1	1	2.517
6	1	-1	1	-1	1.983
7	1	-1	-1	1	1.796
8	1	-1	-1	-1	1.783
9	-1	1	1	1	1.615
10	-1	1	1	-1	1.257
11	-1	1	-1	1	0.609
12	-1	1	-1	-1	0.814
13	-1	-1	1	1	1.823
14	-1	-1	1	-1	1.609
15	-1	-1	-1	1	0.687
16	-1	-1	-1	-1	0.853
17	2	0	0	0	0.427
18	-2	0	0	0	0.768
19	0	2	0	0	2.012
20	0	-2	0	0	2.417
21	0	0	2	0	2.234
22	0	0	-2	0	0.968
23	0	0	0	2	1.986
24	0	0	0	-2	1.388
25	0	0	0	0	2.058
26	0	0	0	0	2.077
27	0	0	0	0	2.063
28	0	0	0	0	2.086
29	0	0	0	0	2.105
30	0	0	0	0	2.007
31	0	0	0	0	2.057

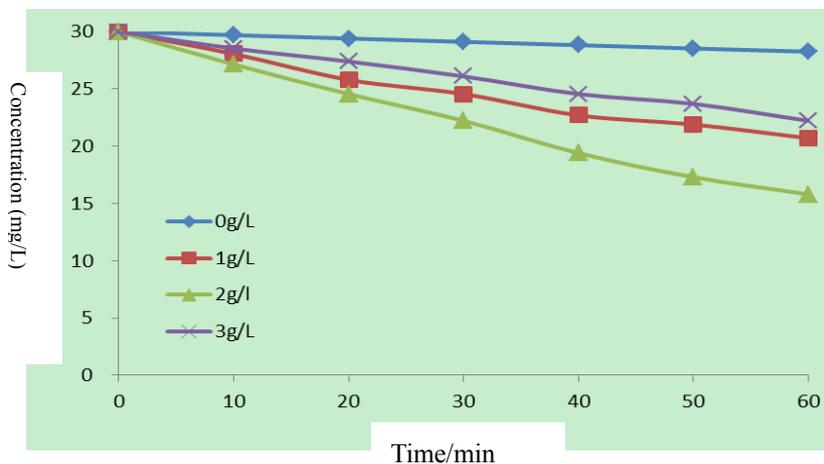


Figure 1. Effects of catalyst level on the decolorization of dye wastewater

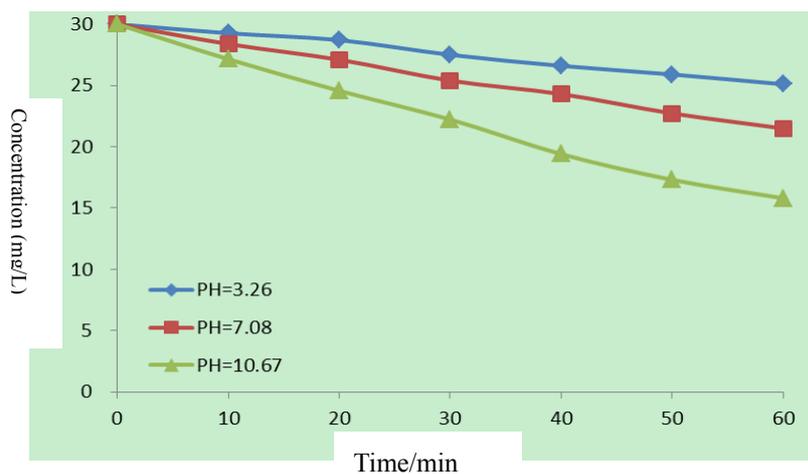


Figure 2. Effects of pH on the decolorization of dye wastewater

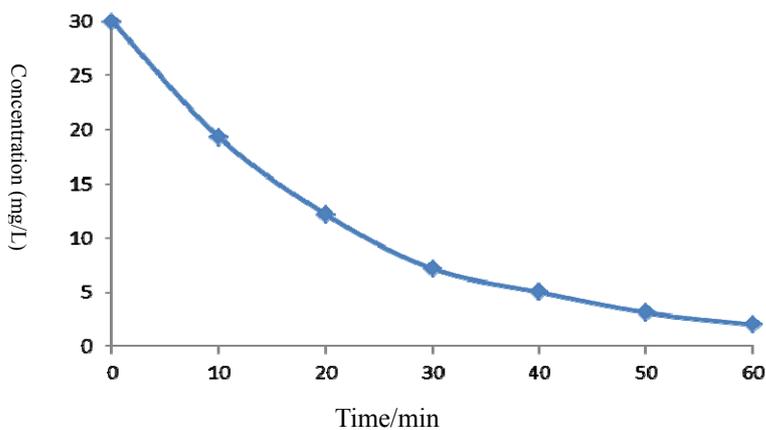


Figure 3. Verification tests