Optimal Decolorization Efficiency of Textile Dye via a Nano-TiO_2/Bamboo-Charcoal Photocatalytic Process

Ming-Shien Yen*

Department of Materials Engineering, Kun Shan University, Tainan71003, Taiwan

Abstract — The present work describes the fabrication of a hybrid material made of nanoscale titanium dioxide (TiO_2) and bamboo charcoal (BC) through calcination and the investigation of its decolorization effects on simulated textile wastewater containing the acidic dye C.I. Acid Red 266 solution. The parameters contributing to the photocatalytic decolorization of C.I. Acid Red 266 solution were the concentration of the hybrid-material solution, the proportion of nanoscale TiO_2 and BC in the hybrid material, the change in the pH of the dye solution, and the reaction time under ultraviolet irradiation. The decolorization of C.I. Acid Red 266 by the hybrid material was measured with an ultraviolet spectrometer. The experimental results demonstrated that decolorization was optimal when the pH of the dye solution was 4 and the proportion of the nanoscale $TiO_2$and BC in the hybrid material was 2:8. The TiO_2 in the hybrid material induced a photocatalytic reaction with the dye, adding to the effects attained by the decolorization ability of the BC material.

Keywords — *bamboo charcoal, titanium dioxide, photocatalyst, decolorization, acid dyes*

I. INTRODUCTION

In recent years, the public has paid environmental issues more and more attention. Some of these issues are closely related to daily life, especially in the textile and printing industries. Textile dyes are considered a serious source of environmental pollution, and treatment of coloured wastewater from textile and other industries is a serious problem that has attracted the attention of many researchers during the last few decades. A rich source of textile-dye color is coloured organic compounds. These organic compounds are a growing threat to the environment, as the dye- and textile-manufacturing processes contain large numbers of dyes and produce extremely toxic discharge from the wastewater-intensive plants. The dye wastewater that contains a large portion of organic molecules is not subject to bio-decolorization or degradation [1-4]. In addition, even if the concentration of coloured dye is less than 1 mg/dm^3, there is still a clearly visible impact on water quality. Also, as they reduce light penetration, these dyes largely affect the phenomenon of photosynthesis.

Therefore, the removal of coloured dye from wastewater has become an important environmental issue. Various methods, including coagulation, chemical oxidation [5,6], photocatalysis, and electrochemical and adsorption techniques, have been studied in the related research [7-9]. Of the abovementioned methods, due to its low cost, simple design, and high availability, adsorption is considered to be far superior to the other available technologies [10,11]. Bamboo charcoal has many applications, and the most common involves adsorptions of water constitutes. Bamboo is a low-cost adsorbent for the removal of heavy metals in water as well as organic compounds including dyes. The use of bamboo charcoal to remove both organic and inorganic compounds in water has been very extensive, because of the large surface area of the active charcoal and the porous nature of various chemical substances [12-18]. However, adsorption is nondestructive, because adsorption simply transfers organic compounds from water to another medium, thus causing secondary pollution.

In recent years, advanced oxidation processes (AOPs) have been proposed as alternative methods of dealing with sewage. Indeed, one such highly practical technique is a photocatalytic method for the purification of sewage [19-22]. Heterogeneous photocatalysis is an AOP that can be successfully used to oxidize many organic pollutants present in aqueous systems. Photocatalytic degradation is involved in the degradation of air, water, and wastewater pollutants, which are substances that are particularly difficult to biodegrade. The competitive advantages of photocatalysis include the facts that substances can be completely degraded and that there are no waste disposal problems as well as its low cost and relatively simple operating environment [23-27]. The degradation of organic compounds via titanium-dioxide photocatalysis is an effective method, as titanium dioxide not only has high photocatalytic activity but also has reliable chemical stability in aqueous solutions. Environmentally, photocatalytic titanium dioxide is relatively simple (while using oxygen as a catalyst), as organic compounds can be completely degraded into CO_2 with water. As such, as a photocatalyst, titanium dioxide is low-cost, powerful, and environmentally friendly [28-33].

The present work aims to provide details of hybrid materials (TCs) composed of nanoscale titanium dioxide and bamboo charcoal (BC), fabricated through calcination. The BC adsorption capacity of titanium dioxide, the system of hybrid materials using calcination, and then the decolorization of the solutions of the acid dyes were analyzed. BC can improve the properties of the large surface area of titanium dioxide in respect to its effects on organic pollutants and can increase the sludge filterability. With a reasonable dye concentration and hybrid-material-manufacturing process, we hope to improve the economic efficiency of dye-wastewater treatment.

II.EXPERIMENT

A. Reagents and materials

Everacid Red 3RS (C.I. Acid Red 266) was purchased from Everlight Chemical Industrial Co. (Taiwan). Nanoscale $TiO_2$with an average particle diameter of 30-40 nm was obtained from Ming Yuh Scientific Instruments Co., Ltd. (Tainan, Taiwan). Activated BC (particle size: 60 μm) was obtained from Versicolor Sky Science & Technologies Co., Ltd (Kaohsiung, Taiwan).

B. Instruments and analysis

The instruments used for analysis are a micro-analytical balance (Precisa XS 360M), magnetic stirrer with heater (Globallab glhps-gs/50), UV-visible spectrometer (JASCO V-550), and a UV lamp T5-8W (8W and 60 Hz). X-ray diffraction (XRD) analysis was performed using a RigakuD/MAX 2500V XRD instrument under the following conditions: Cu-Kα radiation, voltage 40 kV, current 80 mA, scanning speed 4°/min, scanning range 20–70°. The composition of the hybrid materials were measured with an energy dispersive spectrometer (EDS) equipped with a field-emission scanning electron microscope (FE-SEM, Philips XL40). The surface area of the hybrid materials were measured using a BET instruments (Micrometrics ASAP 2010). The changes in the spin number of the hybrid material of BC and TiO_2 were observed through electron paramagnetic resonance (EPR) detection using a spectrophotometer (BRUKER EIEXSYS E-580) at a microwave frequency of 9.743 GHz, a center field strength of 3473.9 G, and a scanning width of 100.0 G. From the spectrophotometer observations, it was determined that C.I. Acid Red 266 showed the maximum adsorption wavelength at 524 nm The color removal percentage was calculated by the following equation:

$$R\ \% = [(A_o - A)/A_o] \times 100\ \%$$

where A_o and A are the absorbance values of dye solution before and after treatment.

C. Experimental procedure

Because the discharge color was evident at the mg/dm^3, the concentration of the dye in the textile wastewater was set at 50 mg/dm^3 by mixing 0.0025 g of C.I. Acid Red 266 in 500 cm^3 of water. The TCs were prepared via high-temperature calcination using various proportions of precisely weighed BC and TiO_2 nanoparticles at 300 °C. The hybrid materials CM_1-CM_5 were TCs made using five different doses of BC at 100, 200, 300, 400, and 500 mg/dm^3, respectively; they were mixed with the 50 mg/dm^3 dye solution and had a pH of 4. The hybrid materials TCC_1-TCC_5 had a constant nanoscale TiO_2:BC proportion of 2:8 under ultraviolet (UV) illumination, had different TiO_2 concentrations (100, 200, 300, 400, and 500 mg/dm^3, respectively), were mixed with a 50 mg/dm^3 dye solution, and had a pH of 4. The absorbances of the samples were measured every 5 min. The hybrid materials TCR_1-TCR_5 had a constant concentration of 500 mg/dm^3 under UV illumination and had different nanoscale TiO_2:BC proportions (9:1, 8:2, 7:3, 6:4, 5:5, respectively) they were mixed with a 50 mg/dm^3 dye solution, and had a pH of 4. For all described experimental series, the absorbances of the samples were measured every 5 min. In the case of the 50 mg/dm^3 dye solution mixed with the TCs that had a constant TiO_2:BC proportion (TiO_2:BC = 2:8) and concentration of 500 mg/dm^3under UV illumination, the pH conditions were varied between 2, 4, 6, 8, and 10, and the absorbances were measured every 5 min. A single reaction was carried out for 30 min to obtain an operational parameter, and the absorbance was measured every 5 min for this reaction as well. The temperature of the model dye solutions was maintained at 25 °C during the experiment.

III.RESULTS AND DISCUSSION

A. Analysis of the TC properties

Fig. 1 shows electron-paramagnetic-resonance (EPR) spectrograms of a hybrid material from which the changes in the spin number of BC and the hybrid material can be determined. The fundamental method of producing free radicals from neutral molecules requires photolysis, pyrolysis, and an oxidation-reduction reaction. The BC spin was primarily due to the free radicals formed during the pyrolysis of the raw materials, and the hybrid-material spin was primarily due to the nanoscale TiO_2 under UV irradiation. The electrons (e^-) on the valence band were stimulated to jump to the conduction band. Free radicals (·OHs) were formed by the reactions that occurred between the electron holes (H^+) remaining on the valence band and H_2O in the air and by the reactions between the electrons and the O_2 and H_2O molecules adsorbed on the surface of the BC. Therefore, the spin number of the hybrid material clearly increased, and the combination of circumstances could be analyzed from the results of the EPR spectroscopy.

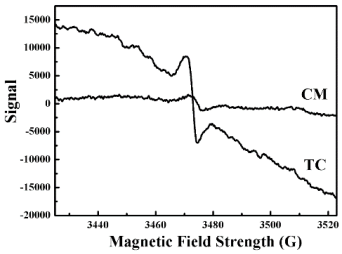

Fig. 1. EPR diagram of the CM and TC materials.

From the results of the XRD analysis, as shown in Fig. 2, the diffraction peak was more distinct between 20° and 30° on the XRD spectrogram of the BC. Fig. 2 depicts the diffraction angles of the titanium-dioxide material at 25°, 37°, and 47°. However, since the CM material does not show the original BC diffraction wave in the hybrid material appearing on titanium dioxide, we inferred that TiO_2 was sintered to the BC in the hybrid material.

The results of the EDS elemental analysis of the hybrid material and the original BC sample are presented in Table 1. According to these results, as the quantity of TiO_2 increased, the content of the elements Ti and O also increased. Table 1 shows the EDS analysis of the TiO_2/BC hybrid materials TCR_1-TCR_5. From the data, when the proportion of TiO_2 and BC in the hybrid material was 5:5, the Ti content in the hybrid material was greater than the C content to the extent that the Ti content was very large for BC to combine entirely with TiO_2.

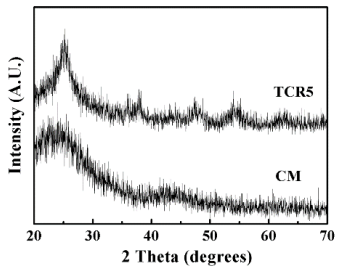

Fig. 2. XRD diagram of the CM and TCR_5 materials.

This observation indicated that the BC holes in the hybrid material might not have been easily filled with more TiO_2 during the sintering process.

Table 1. EDS analysis of the CM and hybrid materials TCR_1-TCR_5.

Compound	Elemental Content (%)		
	C	O	Ti
CM	90.66	7.41	0
TCR_1	72.27	15.09	6.84
TCR_2	64.02	18.81	9.09
TCR_3	61.88	19.74	10.63
TCR_4	61.83	16.54	12.22
TCR_5	52.19	20.69	12.79

The Brunauer–Emmett–Teller (BET)specific-surface-area analysis of the TCs and BC is listed in Table 2. The test results indicated that the specific surface areas, pore volumes, and aperture sizes of the TCs were larger than those of BC. Hence, the adsorption rates of the TCs can be expected to be greater than that of BC.

Table 2. BET analysis of the CM and TC materials.

Compound	BET specific surface area (m^2/g)	Pore specific volume (cm^3/g)	Crystallite size (nm)
CM	526.3885	0.300741	2.28532
TC	780.4949	0.587719	3.01203

B. Influence of different pH values on dye decolorization

For the constant dye concentration of 50 mg/dm^3, the TiO_2:BC proportion in the hybrid materialTCR_2 was fixed at 2:8. The concentration of the hybrid material was 500 mg/dm^3 TiO_2, and the dye pH values were varied between 2, 4, 6, 8, and 10 to observe the effects on the decolorization of C.I. Acid Red 266. Fig. 3 indicates that the decolorization effect on the solution was optimal when the pH was 2. However, because the C.I. Acid Red 266 at a pH of 2 is very costly in terms of the preparation process, an added adjustment liquid was required, and as such, these conditions ceased to detail a cost-effective approach. However, the wastewater discharged by some dye factories has weaker acidity. Therefore, a dye solution with a pH of 4 was chosen to serve as the optimal condition for further experiments in treating dye wastewater. The selection of a pH of 4 as the optimal condition was advisable because the difference in decolorization rates between the pH levels of 2 and 4 was not significant, as shown in Fig. 3.

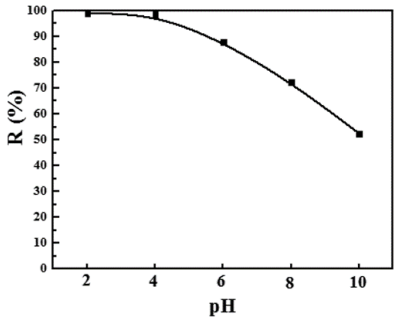

Fig. 3. Effects of the pH value on the color removal. The simulated textile wastewater was 50 mg/dm^3. The hybrid material concentration was 500 mg/dm^3. The reaction time was 30 min. TiO_2:BC = 2:8.

C. Influence of various concentrations of BC on dye decolorization

The dye solution had a fixed concentration of 50 mg/dm^3 and a pH of 4. Hybrid-material samples with

different BC concentrations were used for the decolorization of C.I. Acid Red 266 solution. The variation of the BC concentrations of the hybrid materials CM_1-CM_5 with reaction times within 30 min can be observed in Fig.4. The decolorization rates for CM_1 and CM_5 reached 31% and 72%, respectively. These values confirmed that the adsorption strength increased as the BC content in hybrid material increased. However, the dye solutions after treatment still possessed light coloration. Asample with a very high BC concentration was relatively expensive. Therefore, this study combined TiO_2 with BC, based on the logic that the TiO_2 photocatalytic effect could facilitate an increase in the decolorization effect of the BC. We anticipated that this methodology would increase the ability of the BC to treat dye wastewater while maintaining the cost effectiveness.

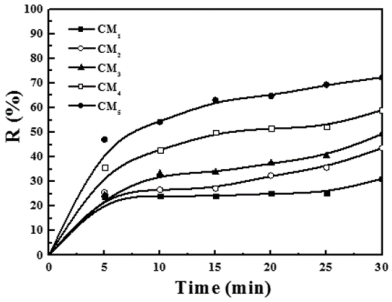

Fig. 4. Effects of the bamboo-charcoal concentration (CM_1-CM_5) on the color removal. The simulated textile wastewater was 50 mg/dm^3. pH = 4.

D. Influence of varying the concentration of the hybrid materials TCC_1-TCC_5 on dye decolorization

The dye solution had a fixed concentration of 50 mg/dm^3 and a pH of 4, and the TiO_2:BC proportion in the hybrid materialsTCC_1-TCC_5 was fixed at 2:8. The decolorization effects of the hybrid materials with different concentrations of TiO_2 (TCC_1-TCC_5) on C.I. Acid Red 266 were evaluated. As shown in Fig. 5, the decolorization rate of TCC_1 (with only 100 mg/dm^3 TiO_2 concentration) only reached 30%, whereas increasing the TiO_2 concentration as in TCC_4(400 mg/dm^3)achieved a rate of 93% and in TCC_5(500 mg/dm^3)achieved a rate of 98%. Moreover, TCC_5effectively decolorized the dye solution to such a degree that the naked eye could barely identify the presence of any remaining color; spectral-analysis instruments were necessary to detect the remnants of the dye in solution. Therefore, the hybrid material with a TiO_2 concentration of 500 mg/dm^3 successfully achieved a decolorization rate of 98% after a treatment time of 30 min.

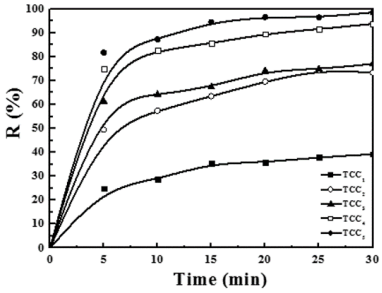

Fig. 5. Effects of various concentrations of the hybrid materials (TCC_1-TCC_5)on the color removal. The simulated textile wastewater was 50 mg/dm^3. TiO_2:BC = 2:8. pH = 4.

E. Comparison between decolorization rates of BC and hybrid materials of different concentrations

The dye solution had a fixed concentration of 50 mg/dm^3 and a pH of 4. The decolorization effects of the BC samples with different concentrations (CM_1-CM_5) and those of the hybrid-material samples with different concentrations of TiO_2 (TCC_1-TCC_5) on C.I. Acid Red 266 solution were observed. Fig. 6 shows that as the concentrations of the BC samples increased fromCM_1 to CM_5 and those of the TCs increase from TCC_1 to TCC_5, the decolorization effects also increased. As shown in Fig. 6, the decolorization effects achieved with the use of TCs were superior to those obtained with the use of the pure-BC material. The decolorization rate of CM_1 after treatment only reached 31%, whereas that of TCC_1 reached 39%. The difference in the decolorization abilities of these two samples was significant. However, the decolorization rate of TCC_5 was as great as 98%, while that of CM_5 (i.e., the BC material at the same concentration of 500 mg/dm^3) only reached 72%. These values indicated that when the concentration increased, the decolorization ability improved; therefore, the hybrid materials had better decolorization efficiencies than did the pure-BC material. Hence, these hybrid materials could be employed to improve the effects of the BC material on dye-wastewater treatment as well as to improve the cost-effectiveness of the treatment process itself.

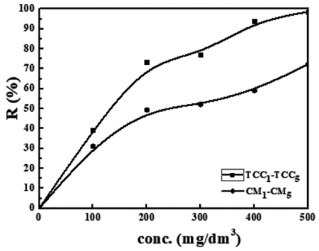

Fig. 6. Effects of various concentrations of the hybrid materials (TCC_1-TCC_5 and CM_1-CM_5)on the color removal. The simulated textile wastewater was 50 mg/dm^3. pH = 4.

F. Influence of hybrid materials with varying proportions of TiO_2 and BC on dye decolorization

The dye solution had a fixed concentration of 50 mg/dm^3 and a pH of 4. The hybrid-material

concentration was fixed at 500 mg/dm^3. The hybrid materials TCR_1-TCR_5 reacted with the dye solution for 30 min. Fig. 7 depicts their UV-absorbance spectra. As shown in Fig. 8, after a 30 min reaction time, the hybrid material TCR_2 (with a TiO_2:BC ratio of 2:8) achieved a 96% decolorization rate after a reaction time of 20 min. However, when the proportion of TiO_2 was increased in the hybrid materials [e.g., TCR_3 (3:7), TCR_4 (4:6), and TCR_5 (5:5), etc.] under the same conditions, the decolorization rates significantly decreased. The hybrid materials TCR_3 and TCR_1 had similar decolorization abilities, but TCR_4 and TCR_5 had decolorization rates worse than that of TCR_1. As such, we deduced that when the TiO_2:BC ratio was too large, the decolorization rate declined, probably due to TiO_2 particles filling the pores of the bamboo charcoal and leading to reduced efficiency. Therefore, percentages of TiO_2 both too high and too low resulted in less capacity for the bleaching effect of TiO_2, and through experiments, we determined that the best TiO_2/BC hybrid material was TCR_2 with its ratio of 2:8.

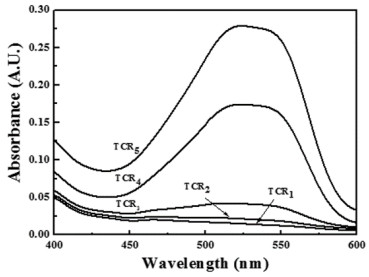

Fig. 7. The UV diagrams of various concentrations of the hybrid materials (TCR_1-TCR_5). The simulated textile wastewater was 50 mg/dm^3. The hybrid material concentration was 500 mg/dm^3. pH = 4.

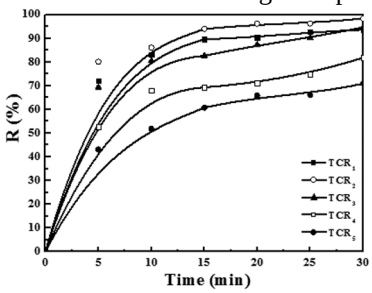

Fig. 8. Effects of various proportions of the hybrid materials (TCR_1-TCR_5)on the color removal. The simulated textile wastewater was 50 mg/dm^3. The hybrid material concentration was 500 mg/dm^3. pH = 4.

G. Comparison between the decolorization rates of CM_5 and the hybrid material TCC_5 over different treatment times

For a dyes with a fixed concentration of 50 mg/dm^3, a pH of 4, a hybrid material with a fixed concentration of 500 mg/dm^3 TiO_2 (TCC_5), and a TiO_2:BC proportion of 2:8, the reaction times were varied to observe the changes in the dye by the hybrid material, and the changes in the reaction times affected the adsorption rate. Fig. 9 shows that at a reaction time of 30 min, the adsorption rate approached 100%, and the decolorization rate reached 99%. In comparison, the effect of the reaction time on the dye-adsorption rate significantly differed in the case of the pure-BC sample. On comparing the decolorization effects of CM_5 and hybrid material TCC_5 on the dye for a reaction time of 30 min, we found that the decolorization rate of CM_5 only reached 71%, whereas that of TCC_5 reached 98%, a difference of approximately 27%. The decolorization ability of the pure-BC material was not significant at the beginning of the reaction but increased with the reaction time, and the decolorization ability of the hybrid material TCC_5 was strong at the beginning of the reaction. These results indicated that the TiO_2 in the hybrid material induced a photocatalytic reaction with the dye, adding to the effects attained by the decolorization ability of the BC material.

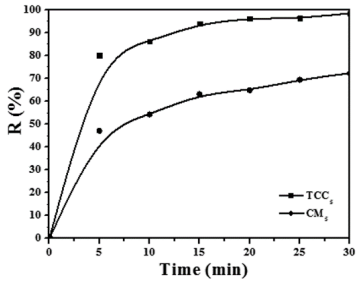

Fig. 9. Effects of the reaction times for the materials CM_5 and TCC_5 on the color removal. The simulated textile wastewater was 50 mg/dm^3. The hybrid material concentration was 500 mg/dm^3. pH = 4.

IV. CONCLUSIONS

When hybrid materials composed of TiO_2 and BC that were sintered together were used to perform a decolorization treatment of the solutions containing acidic dye C.I. Acid Red 266, changes in the hybrid-material concentration, relative proportions of TiO_2 and BC, and reaction time influenced the decolorization. The experimental results showed that for a reaction time of 30 min, BC at a concentration of 500 mg/dm^3 and a pH of 4 had a decolorization rate of only 72% on the acidic dye solution. Under the same conditions, the hybrid material reached a decolorization rate of 98%. The decolorization effects reached 98% when the hybrid material treated the acidic dye solution with a pH of 4. This optimal decolorization effect was attained for hybrid materials with a TiO_2:BC proportion of 2:8. The specific surface area, pore volume, and aperture size of the hybrid material were all greater than those of pure BC. Hence, the decolorization rate of the hybrid material was optimal, and the decolorization rate of the hybrid material was definitely better than that of the pure BC. When the hybrid-material TiO_2

concentration reached 500 mg/dm^3, the decolorization effect reached 98%.

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