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The Photocatalytic Degradation of Basic Dyes by Application of Titanium Dioxide (TiO_2) Films Coated on Coconut Shell-Charcoal

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Abstract

In this experiment the degradation of basic dyes was studied in photocatalysis process. Titanium dioxide (TiO_2) films coated on coconut shell-charcoal were used as photocatalysts and photocatalysis process occurred under UV irradiation. TiO_2 were prepared by the sol–gel technique from titanium tetraisopropoxide and iso-propanal of 1:20 (V/V). TiO_2 films were coated on coconut shell-charcoal by dip coating of 5 and 20 cycles. After coating, TiO_2 films were treated at annealed temperature and annealed time of 500 ◦C and 1 hour, respectively. The crystalline structures and morphologies of the samples were characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM). TiO_2 films showed crystalline phase of anatase phase and the highest intensity plane was (101). SEM images showed that TiO_2 film were coated on coconut shell-charcoal surface and it could coat to inside of the hole of coconut shell-charcoal. However, distribution of TiO_2 films was non-uniform on charcoal. Photocatalytic activities were tested under UV-A at middle wavelength of 365 nm, intensity of 0.88 mW/cm^2 and irradiation time of 6 hours. Basic dyes that had concentration 20-50 mg/L were used as wastewater from textile dyes to test photocatalytic activity. The reduction of color removal were 20-50% and about 90% for rate of TiO_2 film coated on coconut shell-charcoal: the solution basic dyes (1:100) and (1:10), respectively. These results showed that the reduction of color was treated from photocatalytic activity of TiO_2 and adsorption of coconut shell-charcoal.

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Keywords: TiO_2; Film; Coconut shell- charcoal; Photocatalytic activity; Decolorization; Textile Dye

1. Introduction

Textile industry wastewater is heavily charged with unconsumed dyes, surfactants and sometimes traces of metals. These effluents cause a lot of damage to the environment. In most countries researchers are looking for

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appropriate treatments in order to remove pollutants, impurities and to obtain the decolorization of dyehouse effluents. Various chemical are currently used, which work by direct precipitation and separation of pollutants [1], or elimination by adsorption on activated carbon or similar materials. In this case, the photocatalysis with absorption process of coconut shell-charcoal by dip coating TiO_2 5 and 20 cycles in decolorization was used.

Nomenclature

A_0	initial absorbance	V/V	volume/volume
A	absorbance after irradiated UV	UV	ultraviolet
e^-_{cb}	electron in the conduction band	hν	incident photon energy
h^+_{vb}	holes in the valence band	λ_{max}	maximum wavelength

2. Experimental

2.1 Sol-gel technique

The preparation steps for the sol–gel-derived TiO_2 composite are shown in Figure 1. The reagents were used in condition such as Isopropanal (C_3H_7OH) (Merck) was used as the solvent to prevent fast hydrolysis of Titanium tetraisoproproxide (TTiP,$Ti(OC_3H_7)_4$) (Merck) and Nitric acid (HNO_3) (Merck) for adjust the pH 2 and The solution was Stirred 2 hr. and kept in the dark for 24 hrs. The coconut shell-charcoal was then dipped into a solution of 5 and 20 with TiO_2. The obtained sample was centrifuged and washed by water for five times before it was dried at 100 ˚C under oven. Finally, the sample was calcined at 500 ˚C for 1 hr.

2.2 Characterization

The structure properties were determined by Rigaku Japan X-ray diffractometer (XRD) using graphite monochromatic copper radiation Cu-Kα radiation (λ=1.54056 Angstrom) at 30 kV and 15 mA. The morphologies were characterized with a scanning electron microscopy (SEM) (FE-SEM MODEL: HITACHI – S4700).

2.3 Photocatalytic activity tests

The coconut shell-charcoal coated TiO_2 and uncoated TiO_2 immersed in concentration of Basic blue dyes 20-50 mg/L . Then, irradiated with UV-A at middle wavelength of 365 nm over 6 hr to decolorize Basic blue dyes solution. Measured the absorbance every 1 hr by using UV Spectrophotometer (UV – 1100 Spectrophotomerter : Techcomp)

The percentage of decolorization was calculated by using the equation given below:

$$Decolorization\,(\%) = \frac{A_0 - A}{A_0} \times 100 \qquad (1)$$

In which A_0 is the initial dye concentration and A is the dye concentration after irradiated UV.

3. Results and discussion

3.1 Crystallinity and Surface Morphology of coconut shell-charcoal coated TiO_2

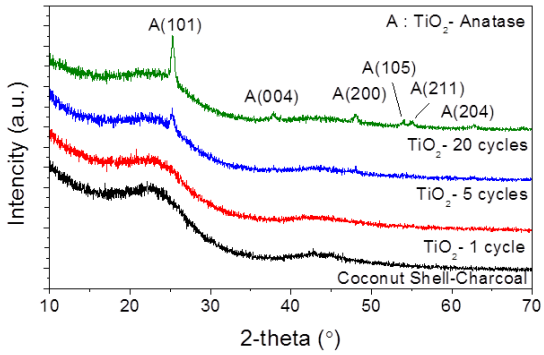
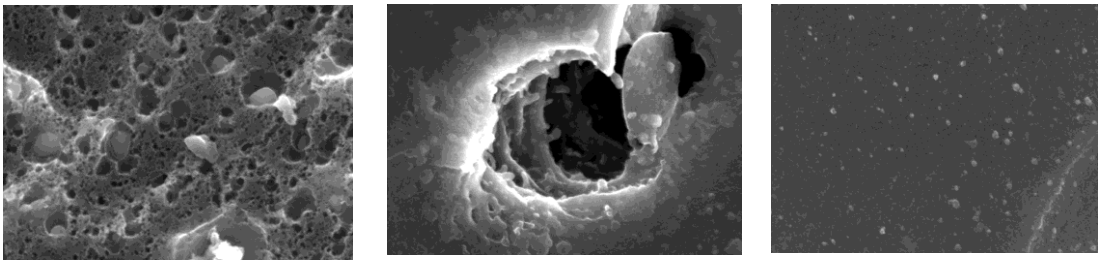
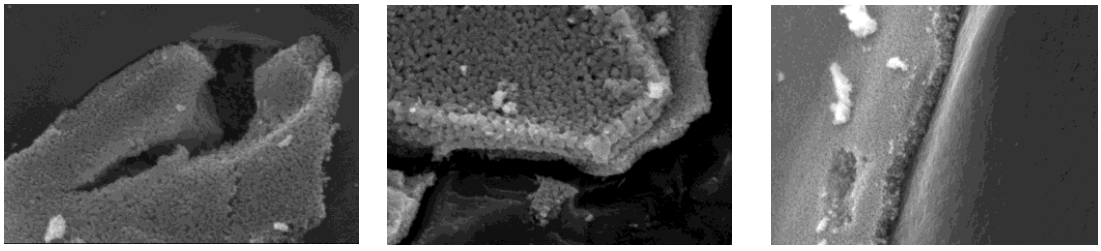


Fig. 1. XRD Pattern of coconut shell- charcoal coconut shell- charcoal with coated TiO_2 for dip coating cycles of 1 5 and 20 cycles

Crystallinity of the samples was observed by x-ray diffraction technique. Fig. 1 showed XRD pattern of the samples, the result showed that coconut shell-charcoal was amorphous structure. In the same way, diffracted peak disappeared for TiO_2 1 cycles. However, in the case that the sample had very small crystal structure under the large amorphous structure, crystal structure could not prominent signal. Because, the background signal was higher than crystal signal. For TiO_2 5 cycles, diffracted pattern showed crystal structure in anatase phase that appeared the only main crystal plane of A(101). In the same way, TiO_2 20 cycles showed anatase but showed intensity of crystal plane higher than TiO_2 5 cycles. Because the film's thickness of TiO_2 20 cycles was higher than TiO_2 5 cycles that could observe higher amount of crystal. Besides, for TiO_2 20 cycles could observe another plane of anatase phase that consisted of A(004), A(200), A(105), A(211) and A(204). [1] These result showed that amount of crystal increased as dip coating cycles increased.



(a) S1: mag. x50,000 (b) S2: mag. x50,000 at void position (c) S2: mag. x50,000



(d) S3: mag. x50,000 at void position (e) S3: mag. x50,000 at surface position (f) S4: mag. x50,000 at surface position

Fig. 2. SEM images of various samples from different source and preparation

Comparison of surface morphology of various samples was observed by scanning electron microscope: SEM. Substrates were used for coating consisting of coconut shell-charcoal: S2 and Iodine Number 600- Activated carbon: S1. Fig. 2. (a) showed surface morphology of S1, cross section of S1 was full of the void. The big voids were in the range of 1.5-2.5 μm. While, Fig. 2. (b) and (c) showed void of S2 and surface of S2, respectively. From the figure showed S1 had amount of the void higher than S2. At, magnification of 50,000, surface of S2 rather had a smooth surface but could see some part of the surface. While, S1 brunched out from big void to small void that it look like a tree. The small voids of S1 were less than 100 nm. The coconut shell-charcoal was used as substrate for coating TiO_2 films. S3 and S4 were coated- TiO_2 on coconut shell-charcoal of 5 and 20 cycles, respectively. The film had higher thickness and higher distribution on the surface as coating cycles increased. Films were distributed on the surface and filled in the void of charcoal. Grain sizes of the films were in the range of 20-60 nm. and high porosity between the grains. The small grain size and high porosity of the film brought to high surface area and high photocatalytic activity.

3.2 Efficiency decolorization of Photocatalysis and Absorption

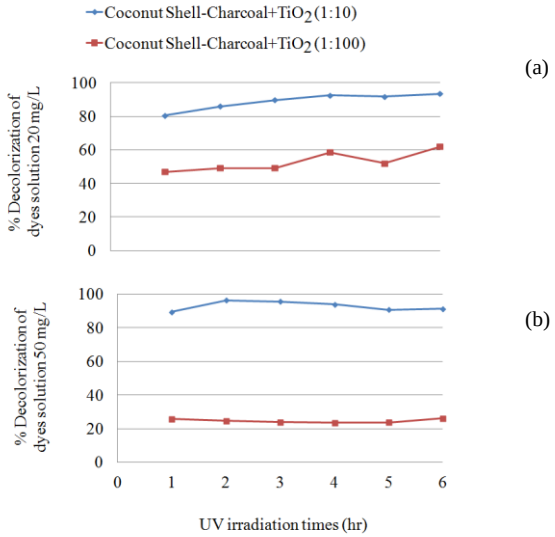


Fig. 3. The decolorization efficiency of the coconut shell-charcoal coated TiO_2 20 cycles at 1:10 and 1:100 ratio with 20 mg/L. and 50 mg/L. basic blue dyes solution

As shown in Fig. 3. (a), the decolorization efficiency of the coconut shell-charcoal coated TiO_2 20 cycles with 20 mg/L basic blue dyes solution at 1:10 and 1:100 ration and Fig. 3. (b) shown the decolorization efficiency of 50 mg/L. basic blue dyes solution. It was found that the efficiency of 1:100 ratio was 40-50% in 20 mg/L. solution and the efficiency was decreased to 20% when increased the concentration of dyes solution to 50 mg/L. But the 1:10 ratio had a constant efficiency at 80-90% both of 20 mg/L. and 50 mg/L. solution because there were appropriate amount of the catalyst to do reaction.

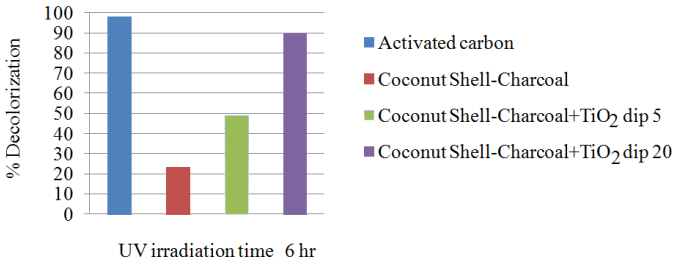


Fig. 4. Comparison of decolorization efficiency of the coconut shell-charcoal coated TiO_2 5 , 20 cycles and Activated carbon

The comparison of decolorization efficiency between the coconut shell-charcoal coated TiO_2 5 and 20 cycles at 6 hr irradiation time were 48% and 90%, respectively. Fig.4 showed the adsorption efficiency of commercial activated carbon equal 98% according to Fig.2 the surface morphology of commercial activated carbon have a high porosity when compared with the coconut shell-charcoal, however, the activated carbon were just only adsorption but did not degrade the basic blue dyes. Oppositely, the coconut shell-charcoal that can do both of the adsorption and decolorization in the same time.

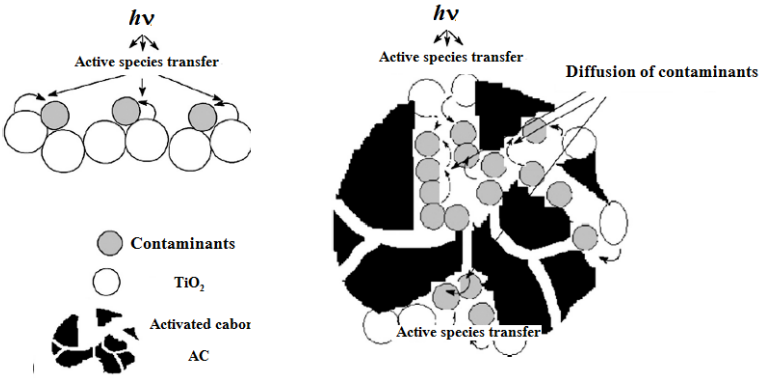


Fig. 5. The role of activated carbon in enhancing the concentration of contaminant molecules [2]

Fig. 5. The preventing pollution by the photo decomposition reactions. Nonetheless, the porosity (macro and micropores) hybrid catalyst could limit the pore plugging or pore blocking of the accessible sites, thus provided an easy filtering option for recovery and a new route increasing its repeating circles and widening its applications. [2] The photocatalytic reaction by UV light, the decoclorization of basic blue dyes should go through the interaction with the electron hole pair (e^-_{cb}, h^+_{vb}) as usual. The recently proposed basic blue dyes degradation mechanism for the irradiated TiO_2 system as follows (2) – (10) [3-5]

$$TiO_2 + h\upsilon \rightarrow TiO_2(e^-_{cb}, h^+_{vb}) \quad (2)$$

$$TiO_2(h^+_{vb}) + H_2O \rightarrow TiO_2 + H^+ + OH^\bullet \quad (3)$$

$$(H_2O \leftrightarrow H^+ + OH^-)_{(ads)} + h^+_{vb} \rightarrow H^+ + OH^\bullet \quad (4)$$

$$O_2^\bullet + H^+ \rightarrow HO_2^\bullet \quad (5)$$

$$2HO_2^\bullet \rightarrow H_2O_2 + O_2 \quad (6)$$

$$H_2O_2 + e^- \rightarrow OH^\bullet + OH \quad (7)$$

$$Dye + OH^\bullet \rightarrow degradation\ products \quad (8)$$

$$Dye + h^+_{vb} \rightarrow oxidation\ products \quad (9)$$

$$Dye + e^-_{cb} \rightarrow reduction\ products \quad (10)$$

The trapped holes may be regarded as surface-bound hydroxyl radicals. The bound radicals can also diffuse away from the surface toward the solution bulk and exist transiently as free $OH^{\bullet}$. This mechanism suggests that hydroxyl radicals and photogenerated holes (h^{+}_{vb}) are the primary oxidizing species for the adsorbed or free dye molecules, while photogenerated electrons (e^{-}_{cb}) are the reducing species,[5-7] in photocatalytic reaction by UV light.

4. Conclusion

Application of photocatalysis with absorption process of coconut shell-charcoal by dip coating TiO_2 5 and 20 cycles under weakly-UVA of photocatalytic system has successfully improved the color degradation of Basic dyes that had concentration 20-50 mg/L capability. The result showed that coconut shell-charcoal by dip coating TiO_2 5 and 20 cycles were tested under UV-A at middle wavelength of 365 nm, intensity of 0.88 mW/cm^2 and irradiation time of 6 hours. Basic dyes that had concentration 20-50 mg/L were used as wastewater from textile dyes to test photocatalytic activity. The reduction of color removal were 20-50% and about 90% for rate of TiO_2 film coated on coconut shell- charcoal : the solution basic dyes (1:100) and (1:10), respectively. These results showed that, reduction of color were treated from photocatalytic activity of TiO_2 and adsorption of coconut shell- charcoal.

Acknowledgements

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