PREPARATION OF TiO_2 FILMS ON COMMERCIAL ACTIVATED CARBON FOR APPLICATION ON DECOLORIZATION OF BASIC DYES

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ABSTRACT

Development of photocatalysis in conjunction adsorption by titanium dioxide (TiO_2) coated on commercial activated carbon (AC-TiO_2) for decolonization of basic dyes from textile industry wastewater was investigated. TiO_2 were prepared by the sol–gel technique from titanium tetraisopropoxide and iso-propanal of 1:20 (V/V) and adjusted to pH = 2 by nitric acid. TiO_2 solution was coated on commercial activated carbon by dip coating of 1 and 5 cycles. After coating, AC-TiO_2 samples were treated at annealed temperature and annealed time of 500 °C and 1 hour, respectively. The crystalline structures and morphology of the samples were characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM). SEM images showed that TiO_2 films were coated on surface and hole of porous commercial activated carbon. Photocatalytic activity was tested on decolorization of basic dyes under UVA irradiation time of 40 min. Basic dye solution had concentration of 50 mg/L. UVA was irradiated at peak wavelength ≈ 365 nm and intensity of 0.88 mW/cm^2. Ratio of AC-TiO_2 or AC per basic dyes solution was 1g/100 ml. For the first test, decolorization efficiencies were 89.43, 96.44 and 97.23 percents and when the experiment was repeated 4 times the decolorization efficiencies were decreased 33.19, 88.53 and 93.10 percents for AC, AC-TiO_2 of 1 cycle and AC-TiO_2 of 5 cycles; respectively.

KEYWORDS: TiO_2, activated carbon, photocatalytic activity, decolorization, basic dye

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INTRODUCTION

Dye pollutants produced from the textile industries are becoming a major source of environmental contamination. Traditional methods such as flocculation, carbon adsorption, reverse osmosis and activated sludge process have difficulties in the complete destruction of dye pollutants for the treatment of dye-containing wastewater [1]. Titanium dioxide (TiO_2) has been studied for environmental purification applications, due to it good characteristic of powerful oxidation strength, chemicals ability, nontoxicity and in expensive ness. This work, TiO_2 was coated on activated carbon (AC-TiO_2) to observe photo-catalytic activity that TiO_2 was used as the photocatalyst while, activated carbon was used to adsorb basic dye. Thus, this combination was used for decolorization of basic dyes from textile industrial wastewater.

MATERIALS AND METHODS

1. Sol-gel technique

The reagents were used in the preparation steps for the sol–gel-derived TiO_2 composite, 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.

After that, the solution was stirred of 2 hr and then kept in the dark of 24 hr. TiO_2 sol-gel was coated on commercial activated carbon by dip coating of 1 and 5 cycles. The obtained sample was centrifuged and rinsed by water for five times before it was dried at 100 °C in the oven. Finally, the sample was annealed at 500 °C for 1 hr.

2. Characterization

The structure was determined by X-ray diffractometer (XRD) (Bruker AXS Model D8 Discover) that used graphite monochromatic copper radiation Cu-Kα radiation (λ= 0.154 nm.) at 30 kV and 15 mA. 2-Theta was recorded from 10-80 degree, scan step of 0.02 degree/step. Surface morphologies were characterized with a scanning electron microscopy (SEM) (FE-SEM MODEL: HITACHI – S4700).

3. Photocatalytic activity tests

The commercial activated carbon were coated by TiO_2 of 1 and 5 cycles (AC-TiO_2) and pure AC immersed in basic red dyes solution that had concentration 50 mg/L. Photocatalytic activity test occurred under UVA irradiation time of 40 min. UVA was irradiated at peak wavelength ≈ 365 nm and intensity of 0.88 mW/cm^2. Ratio of AC-TiO_2 or AC per basic dyes solution was 1g/100 ml. After that, per basic dyes solution were measured the absorbance by using UV Spectrophotometer to observe decplorization. (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.

RESULTS AND DISCUSSION

1. Crystallinity TiO_2 coated on AC

Crystallinity of pure AC and AC-TiO_2 were observed by X-rays diffraction technique (Bruker AXS Model D8 Discover). XRD pattern showed in Fig. 1. From the pattern, it did not clearly see to compare difference between AC and AC-TiO_2. However, for the little amount of TiO_2 when we compare with amount of AC, it not easy to observe signal of TiO_2 crystal. Because, may be signal of TiO_2 crystal was smaller than back-ground signal. XRD pattern showed 2 broaden peaks of AC that appeared in the range 2-theta of 20-30 and 40-48 degree. That result showed forming slightly periodic pattern of AC.

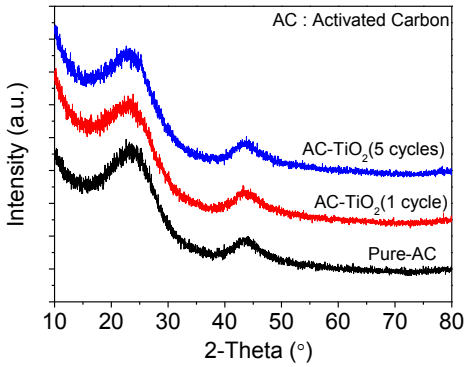
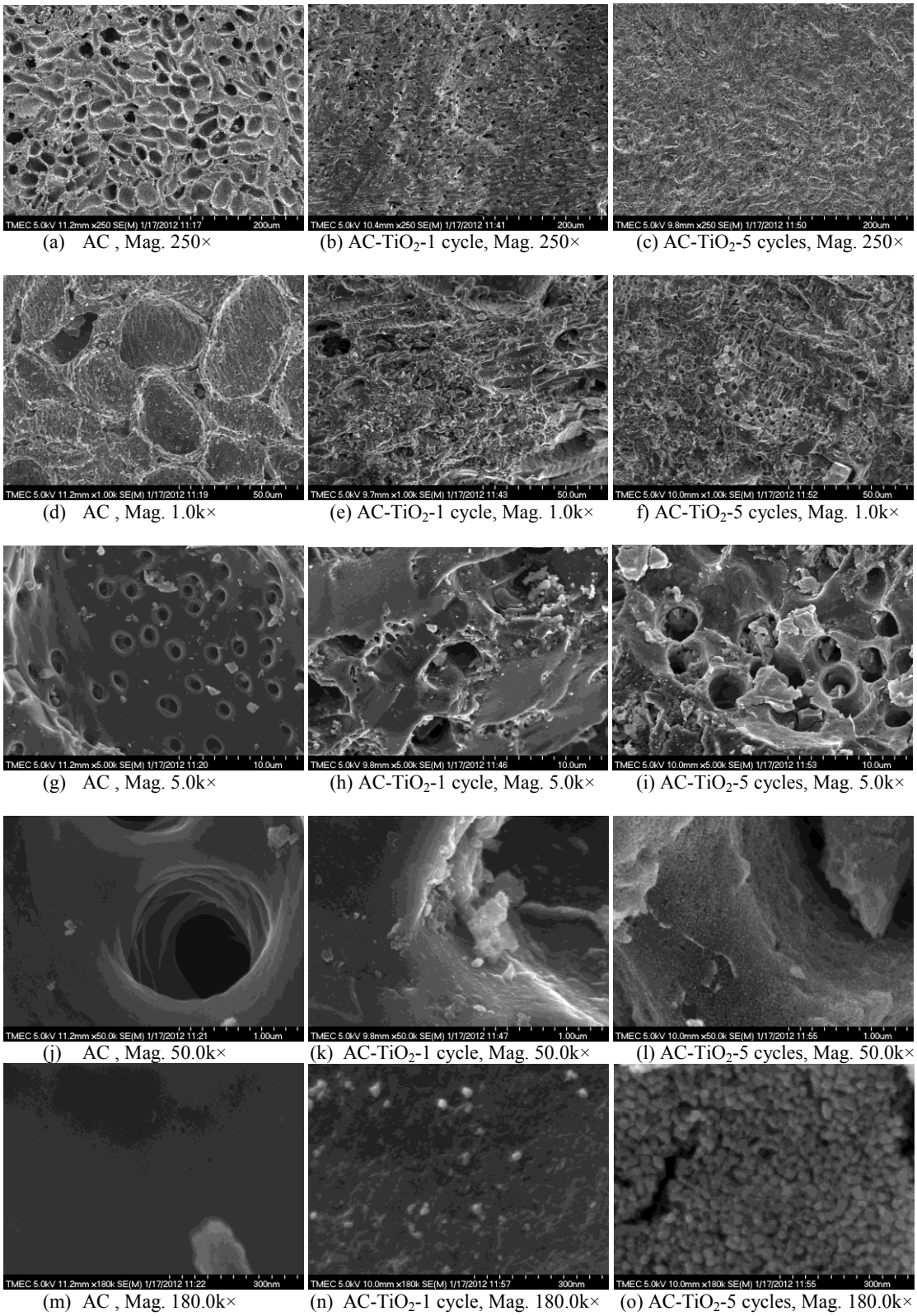


Fig. 1. Show XRD pattern of pure activated carbon: AC and TiO_2 film coated on activated carbon: AC-TiO_2 for number of coating cycle of 1 and 5 times

2. Surface Morphology

Surface morphology of AC and AC-TiO_2 was observed by scanning electron microscope (SEM). SEM images of AC and AC-TiO_2 are shown in Fig. 2, Fig. 2 (a), (b) and (c) showed the images for AC, AC-TiO_2 of 1 cycle and 5 cycles; respectively at magnification of 250×. Fig. 2 (a) was exposed inhomogeneous void that distributed all over of AC piece. The voids shape look like semi-egg shell. The long axle had in the range of 10-60 µm. Enlargement of AC images were shown in the Fig. 2 (d), (g), (j) and (m) of 1000×, 5000×, 50000×, and 180000×; respectively. Enlarged void of AC sample showed a lot of holes in the voids (Fig. 2 (d) and (g)). The voids of AC formed pattern like the tree with the branch. Diameter of the branch- holes were showed in the range of 1-3 µm (Fig. 2 (g) and (j)). On the surface of AC appeared the very small holes, the diameter had less than 20 nm (Fig. 2 (m)). In general the voids of porous AC open more surface area to increase adsorbed activity. When we compare between AC and AC-TiO_2, Fig. 2 (b) and (c) showed TiO_2 films were coated on AC voids.



(a) AC , Mag. 250× (b) AC-TiO_2-1 cycle, Mag. 250× (c) AC-TiO_2-5 cycles, Mag. 250×

(d) AC , Mag. 1.0k× (e) AC-TiO_2-1 cycle, Mag. 1.0k× f) AC-TiO_2-5 cycles, Mag. 1.0k×

(g) AC , Mag. 5.0k× (h) AC-TiO_2-1 cycle, Mag. 5.0k× (i) AC-TiO_2-5 cycles, Mag. 5.0k×

(j) AC , Mag. 50.0k× (k) AC-TiO_2-1 cycle, Mag. 50.0k× (l) AC-TiO_2-5 cycles, Mag. 50.0k×

(m) AC , Mag. 180.0k× (n) AC-TiO_2-1 cycle, Mag. 180.0k× (o) AC-TiO_2-5 cycles, Mag. 180.0k×

Fig. 2. SEM images of AC and AC-TiO_2 for coating cycle of 1 and 5 at various magnification

For AC-TiO_2 of 1 cycle, TiO_2 films could not distribute over all. Some areas still remain naked voids. While, AC-TiO_2 of 5 cycles, TiO_2 films were coated almost over all surface area (Fig 2 (c)). However, when we look at the branch holes (Fig. 2 (e), (f), (h), (i), (k) and (l)), we could see TiO_2 powders were fill in the hole that clearly seen for AC-TiO_2 of 5 cycles. However, we could observe TiO_2 powder that non-uniform distribution over AC surface. The highest enlargement of magnification of 180,000× exposed the grain granular shape of TiO_2 films on porous AC surface. For AC-TiO_2 of 1 cycle (Fig. 2 (n)), TiO_2 particles slightly appeared on AC surface, because TiO_2 film was ultrathin. While, granular shape of TiO_2 particles for AC-TiO_2 of 5 cycles were around 20 nm (Fig. 2 (o)).

3. Photocatalytic activity

The decolorization efficiencies of experiment 1 time were 96.44, 97.23 and 89.43 percents. When the experiment was repeated 4 time, the decolorization efficiency were decreased 88.53, 93.10 and 33.19 percents, respectively. (Fig. 3 and Fig. 4) The results showed that repeat times with the decolorization efficiencies decrease of AC. The pore of AC was inserted by dye pollutants into until the pore of AC was decreased and full. Compare with AC-TiO_2 a high-efficiences of the decolorization. Because dye pollutants into the pore of AC/TiO_2 was decomposed to CO_2 H_2O and other gases by the photocatalytic. [3-5] (Fig. 5) As a result, the decolorization efficiency of the photocatalysis time that is longer than the adsorption.

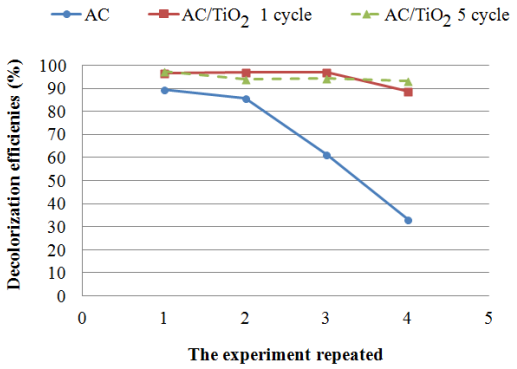
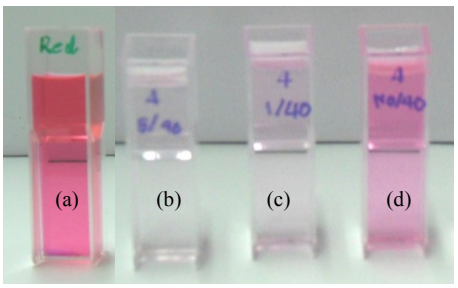


Fig. 3. Show the decolorization efficiency of experiment repeated 4 times by the commercial activated carbon coated TiO_2 1 and 5 cycle (AC-TiO_2) and uncoated TiO_2 (AC) irradiated time 40 min to decolorize basic red dyes solution had concentration 50 mg/L



(a) Start (b),(c) AC-TiO_2 5 and 1 cycle (d) AC

Fig. 4. Comparison of basic red dyes solution images of AC-TiO_2 5 and 1 cycle and AC after UV irradiation time of 40 min

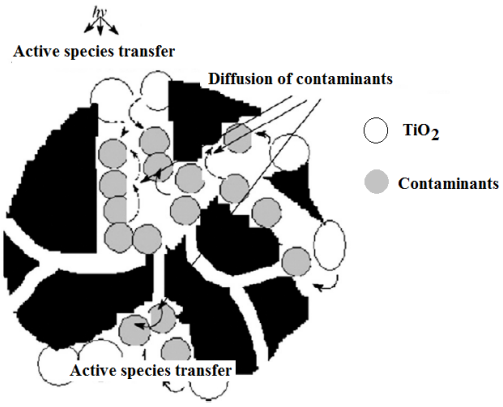


Fig. 5. The role of activated carbon in enhancing the concentration of contaminant molecules [2]

The photocatalytic reaction by UV light, the decoclorization of basic red dyes should go through the interaction with the electron hole pair (e^-_{cb}, h^+_{vb}) as usual. The recently proposed basic red dyes degradation mechanism for the irradiated AC/TiO_2 system as follows (2) - (10) [3-5]

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

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

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

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

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

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

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

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

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

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. Even though XRD pattern did not clearly seen TiO_2 crystal, but the samples were still working and showed high efficiency on decolorization. Moreover, from the forth test, if we want efficiency was higher than 90% for decolorization, AC sample had to spend the UV irradiation time around 120 min., while UV irradiation time for AC-TiO_2 were around 40 min.

CONCLUSION

From this work, AC samples which were coated by TiO_2 can enhance efficiency on decolorization of textile industrial wastewater. Moreover, it can improve working treatment period.

ACKNOWLEDGMENT

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