

# Efficiency Comparison of TiO<sub>2</sub>-Coated Pine Wood, Bamboo and Coconut Shell Charcoals in Real Textile Wastewater Decolorization

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## ABSTRACT

The photocatalytic decolorization of real textile wastewater using pine wood (PW), bamboo (BB) and coconut shell (CS) charcoals TiO<sub>2</sub>-coated under UV irradiation were investigated. Biomass charcoals TiO<sub>2</sub>-coated were synthesized by the sol-gel and dip-coating technique. The structure features of biomass charcoals TiO<sub>2</sub>-coated were investigated by X-ray diffractometer (XRD) and scanning electron microscopy (SEM). Our finding indicated that XRD data characteristic anatase phase reflections and SEM showed that TiO<sub>2</sub> thin films distributed in the pores and cover on biomass charcoals. BB-TiO<sub>2</sub> and CS-TiO<sub>2</sub> showed high covering films of TiO<sub>2</sub> on surface and filled full in the small pores but PW-TiO<sub>2</sub> still had many large pores. Decolorization of real textile wastewater using photocatalytic process was measured by Space Unit Method; S. U. with UV-VIS spectrophotometer. The photocatalytic tests indicated that decolorization of biomass-TiO<sub>2</sub> were CS-TiO<sub>2</sub>, BB-TiO<sub>2</sub> and PW-TiO<sub>2</sub>, respectively. Details of the synthesis of biomass charcoals TiO<sub>2</sub>-coated and results of the characterization and decolorization studies are presented in this paper.

**Keywords:** Pine wood; Bamboo; Coconut shell; TiO<sub>2</sub>; Photocatalysis; Decolorization

## 1. Introduction

Textile industry is a vital and quickly emerging industrial segment in Thailand. Processing operation such as scouring, bleaching, mercerizing, dyeing, printing and

finishing stages are included in wet fabric processing industry. [1] The textile industry is a main creator of effluent wastewater due to a more consumption of water for its

different wet processing operations. These effluent wastewater contains chemicals like acids, alkalis, dyes, hydrogen peroxide, starch, surfactants dispersing agents and soaps of metals [2]. Therefore, many research groups have paid increasing attention to the degradation of these colored wastewaters in recent years [1-15].

Several techniques such as activated carbon (charcoal) [3-10], membrane filtration [11,12], adsorption and coagulation [13,14] have been used to solve the problems caused by the toxic substance contained in these colored wastewaters. Many studies on development of activated carbon with far superior adsorption capacity. The chemical activation methods has the most promising techniques for preparing activated carbon. The chemical was typically an acid, strong base, or a salt (phosphoric acid, potassium hydroxide, sodium hydroxide, calcium chloride, and zinc chloride 25%) which is produced toxic waste in the process.

Biosorption, a biological method of environmental control can be an alternative to conventional waste treatment facilities. Biomass materials (coconut shell, pine wood, bamboo, sawdust, rice husk, nut shell, etc.) that are available in large quantities or certain waste from agricultural operations may have potential to be used as low cost adsorbents, because they represent unused resources that are widely available and environmentally friendly. Some investigators have reported processing of pine wood [5], bamboo [6] and coconut shells [7] wastes into charcoals for the treatment of industrial and municipal wastewaters.

Recently, the photocatalytic application has been received much attention to solve the environmental problems.  $\text{TiO}_2$  has been known as the leading photocatalyst due to its good photoactivity, high chemical stability, low cost, and nontoxicity [3,15]. To produce  $\text{TiO}_2$  to be a good photocatalyst under low cost,  $\text{TiO}_2$  is prepared as the films for two dimensional contacts [16, 17] on the substrates such as glass, stainless steel and

activated carbons [18]. However, these materials are complicated in productive process and expensive.

Therefore, the object of this work was to develop the biomass charcoals  $\text{TiO}_2$ -coated. The effects of biomass charcoals (pine wood, bamboo and coconut shell) that were coated by  $\text{TiO}_2$  on decolorization of dyes in textile were also investigated.

## 2. Materials and Methods

### 2.1 Preparation of biomass charcoals

Biomass charcoals were passed through a screen before use, and particle size was controlled in the range of 0.5-2.0 mm, washed with water to remove dusts and dried 1 h at  $105^\circ\text{C}$ . The porosity of biomass charcoals and active carbon (AC) were analyzed by Iodine number [19], methylene blue test [20] and scanning electron microscopy (SEM).

### 2.2 Synthesis of biomass charcoals- $\text{TiO}_2$

The reagents used in this work steps for the sol-gel derived  $\text{TiO}_2$  composite were isopropanol ( $\text{C}_3\text{H}_7\text{OH}$ ) (Merck) as the solvent to prevent fast hydrolysis of titanium tetra isopropoxide ( $\text{Ti}(\text{OC}_3\text{H}_7)_4$ ) (Merck), and nitric acid ( $\text{HNO}_3$ ) (Merck) for adjust the pH2. After that, the solution was stirred of 2 h and then kept in the dark of 24 h  $\text{TiO}_2$  sol-gel was coated on biomass charcoals by dip coating with immersed time 10 min. The obtained sample was centrifuged and rinsed by water for five times before drying at  $100^\circ\text{C}$  in the oven.  $\text{TiO}_2$  films were coated on charcoals 5 cycles. Finally, the sample was annealed at  $500^\circ\text{C}$  for 1 h.

### 2.3 Characterization

The structure was determined by X-ray diffractometer (XRD) (Bruker AXS Model D8 Discover) that used graphite monochromatic copper radiation  $\text{Cu K}\alpha$  radiation ( $\lambda=0.154\text{ nm}$ ) of 30 kV and 15 mA. 2-Theta was recorded from 10-80 degree, scan step of 0.02 degree/step. The porous

texture of sample was observed by using a scanning electron microscopy (SEM) (FE-SEM MODEL: HITACHI-S4700).

#### 2.4 Decolorization tests of dyes in real textile industry wastewater

The photocatalytic system included: (A) the photocatalytic reactor ( $35 \times 35 \times 20$  cm<sup>3</sup>: L×W×H) was divided to be four channels. Each box was filled real textile industry wastewater of 5 liters; (B) UV A lamp of 400 W (Osram made in Japan) middle wavelength of 365 nm, intensity of 1.64 mW/cm<sup>2</sup>. The distance between UV lamp and real textile industry wastewater was 45 cm; (C) propeller with the speed of 200 rpm; (D) photocatalytic reactants that were biomass charcoals- TiO<sub>2</sub> (pine wood: (PW-TiO<sub>2</sub>), bamboo (BB-TiO<sub>2</sub>), coconut shell (CS- TiO<sub>2</sub>) and AC ( the reference)) (Fig. 1). Ratio of biomass charcoals -TiO<sub>2</sub> to real textile industry wastewater of 1/20 mL. After that, sample was irradiated by UV A. Wastewater of each samples were kept every 30 min over 120 min to measure the absorbance by UV- VIS spectrophotometer (UV-1100 Spectrophotometer: Techcomp) for observation of decolorization. Then, repeated experiments in dark condition.

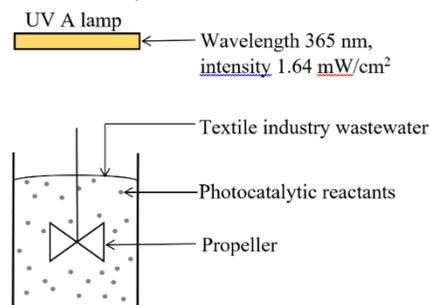
Decolorization for real textile industry waste- water was measured by Space Unit Method; S.U. [21]. After irradiation with UV for a fixed time, the solution was filtered and the concentration of respective dyes was measured at the wavelengths of 400, 500, 600 and 700nm. The data were plotted into graph between absorbance and the wavelength. The area under graph was colored as intensity of the S.U. Unit. In the photocatalytic experiments, the extent of decolorization of dye in terms of the percentage has been calculated using the following relationship.

$$\text{Decolorizaion (\%)} = \frac{A_0 - A_t}{A_0} \times 100$$

Where  $A_0$  and  $A_t$  are the initial and final areas under graph of dye (S.U.) in real textile industry wastewater, respectively. All the experiments were three replications to

ensure accuracy, reliability and reproducibility of the collected data. The experimental results were reported as mean values  $\pm$  standard deviation of percentages of decolorization of wastewater from textile dye.

Fig. 1. Photocatalytic reactor used in this study.



### 3. Results and Discussion

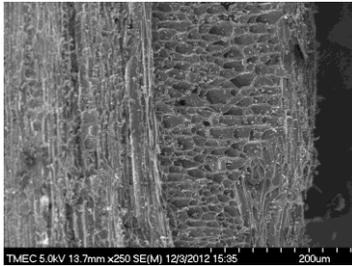
#### 3.1 The porosity of biomass charcoals

Volume absorption of iodine and methylene blue are used to indicate amount of porous of biomass charcoals. Iodine was used as an indicator for adsorption of the small molecule pollutants that has the molecular mass less than of 253.8 g/mol, and methylene blue was used as the bigger molecule for adsorption of pollutants with molecular mass of 525.3 g/mol. The results of volume absorption iodine number and methylene blue (Table. 1) showed that volume absorption of iodine for pine wood charcoal (PW), coconut shell-charcoal (CS) and bamboo-charcoal (BB) were 175, 182 and 222 mg/g, respectively. While, volume absorption of methylene blue were 43, 45 and 55 mg/g, respectively. The results were consistent with surface morphology of adsorbents in SEM images (Fig. 2).

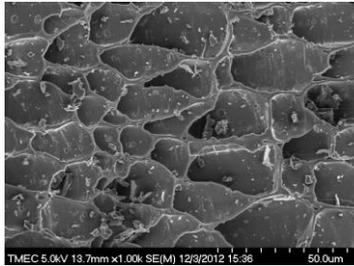
Table 1. Volume absorption of adsorbents (mg/g).

Adsorbents	Iodine	Methylene blue
pine wood	175	43
coconut shell	182	45
bamboo	222	55
activated carbon	693	141

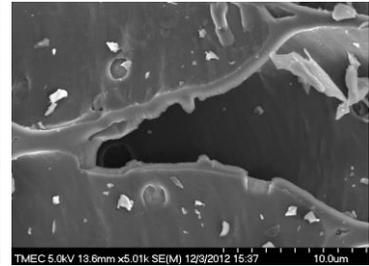
(a) Pine wood charcoal (PW)



Mag.  $\times 250$

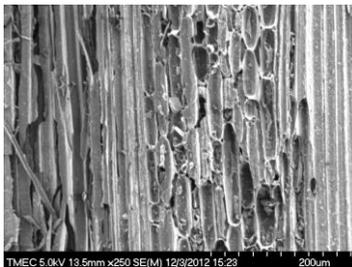


Mag.  $\times 1000$

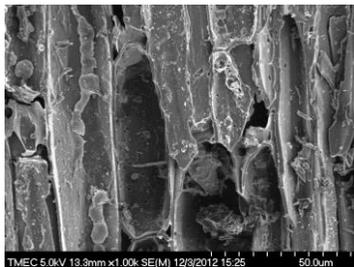


Mag.  $\times 5000$

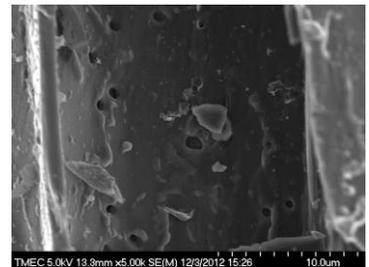
(b) Bamboo charcoal (BB)



Mag.  $\times 250$

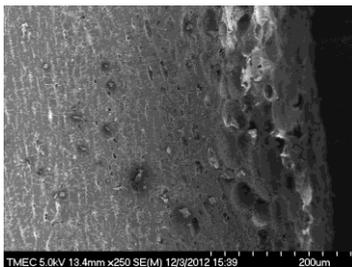


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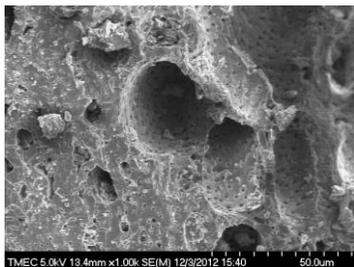


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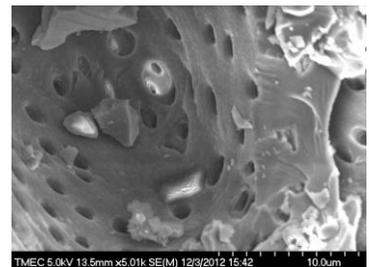
(c) Coconut shell charcoal (CS)



Mag.  $\times 250$

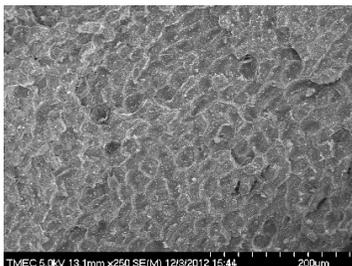


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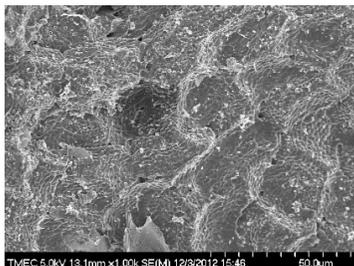


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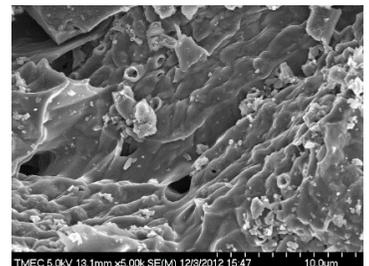
(d) Activated carbon (AC)



Mag.  $\times 250$

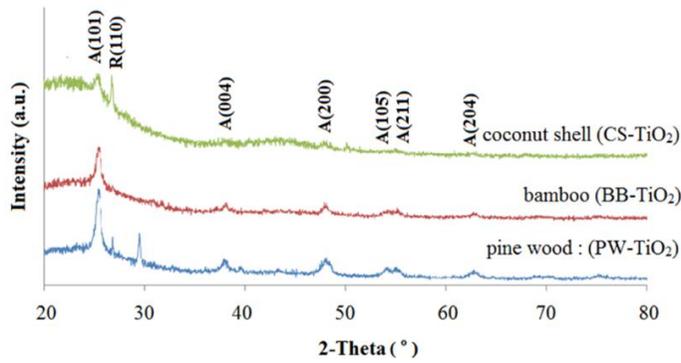


Mag.  $\times 1000$



Mag.  $\times 5000$

**Fig. 2.** Surface morphology of various biomasses for (a)PW (b)BB (c)CS and (d) AC at magnifications of 250, 1000, 5000

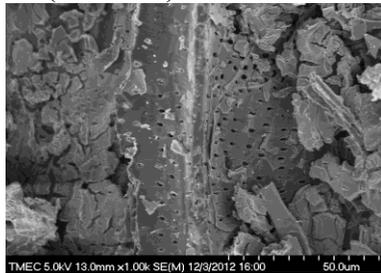


**Fig. 3.** XRD patterns of TiO<sub>2</sub> at various biomass charcoals.

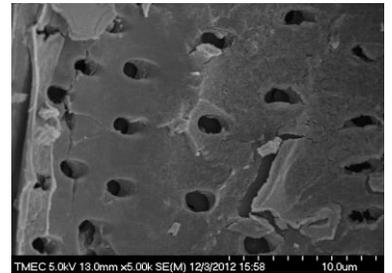
(a) Pine wood charcoal TiO<sub>2</sub>-coated (PW-TiO<sub>2</sub>)



Mag. ×250

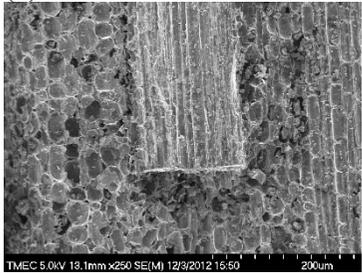


Mag. ×1000



Mag. ×5000

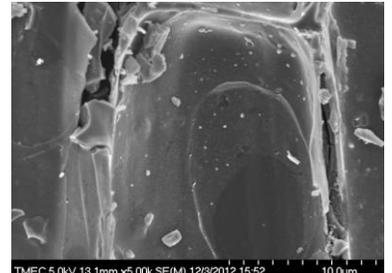
(b) Bamboo charcoal TiO<sub>2</sub>-coated (BB-TiO<sub>2</sub>)



Mag. ×250

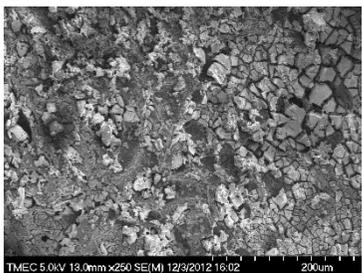


Mag. ×1000

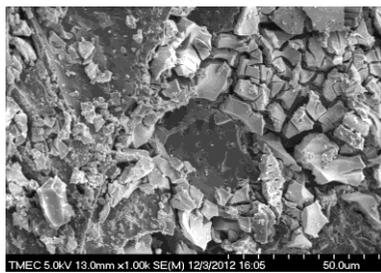


Mag. ×5000

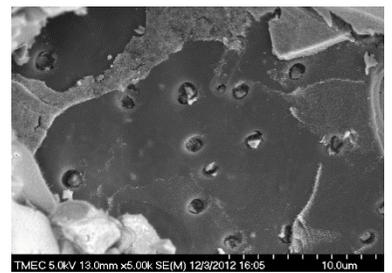
(c) Coconut shell-charcoal TiO<sub>2</sub>-coated (CS-TiO<sub>2</sub>)



Mag. ×250



Mag. ×1000



Mag. ×5000

**Fig. 4.** Surface morphology of TiO<sub>2</sub> on various biomasses for (a) PW-TiO<sub>2</sub> (b) BB-TiO<sub>2</sub> and (c) CS-TiO<sub>2</sub> at magnifications of 250, 1000 and 5000.

Fig. 2 shows SEM images of (a) pine wood-charcoal (PW), (b) bamboo-charcoal (BB), (c) coconut shell-charcoal (CS) and (d) activated carbon (AC). PW had large pores all over surface but had no small holes inside. CS had smooth surface when compared to another other biomass but under high magnification, it showed the very small holes. BB had large pores surface with the tube shape due to phloem and xylem that showed the many small holes, resulting in high absorption. Consequently, the order of volume absorption of adsorbents is  $BB > CS > PW$  with a little difference value.

From the results in Table 1 and Fig. 2, AC had high surface area, small holes, volume absorption of iodine number (693 mg/g) and volume absorption of methylene blue (141 mg/g) so it was often used as adsorbent for solve the problems caused by the toxic substance. However, AC was adsorption process. On the contrary, photocatalytic application has been decompose of toxic substance, thus resulting in their complete degradation into small inorganic species. Therefore, this research was to develop the synthesis of  $TiO_2$  impregnated biomass charcoals.

### 3.2 Crystalline and Feature of $TiO_2$ films on biomass charcoals

Fig. 3 shows the result of XRD pattern of  $TiO_2$  at various biomass charcoals. The result showed that  $TiO_2$  on biomass charcoals appeared crystalline structure of mixed phases of anatase and rutile phases. XRD pattern demonstrated the main peaks of anatase phase of A(101), A(004), A(200), A(105) and A(204) while the main peaks of rutile phase was R(110). The result presented that anatase phase ratio were CS- $TiO_2$ , BB- $TiO_2$  and PW- $TiO_2$ , respectively. Anatase has a large band gap that increases the oxidation “power” of electrons and facilitates electron transfer from the  $TiO_2$  to adsorbed molecules in photocatalytic reaction [22].

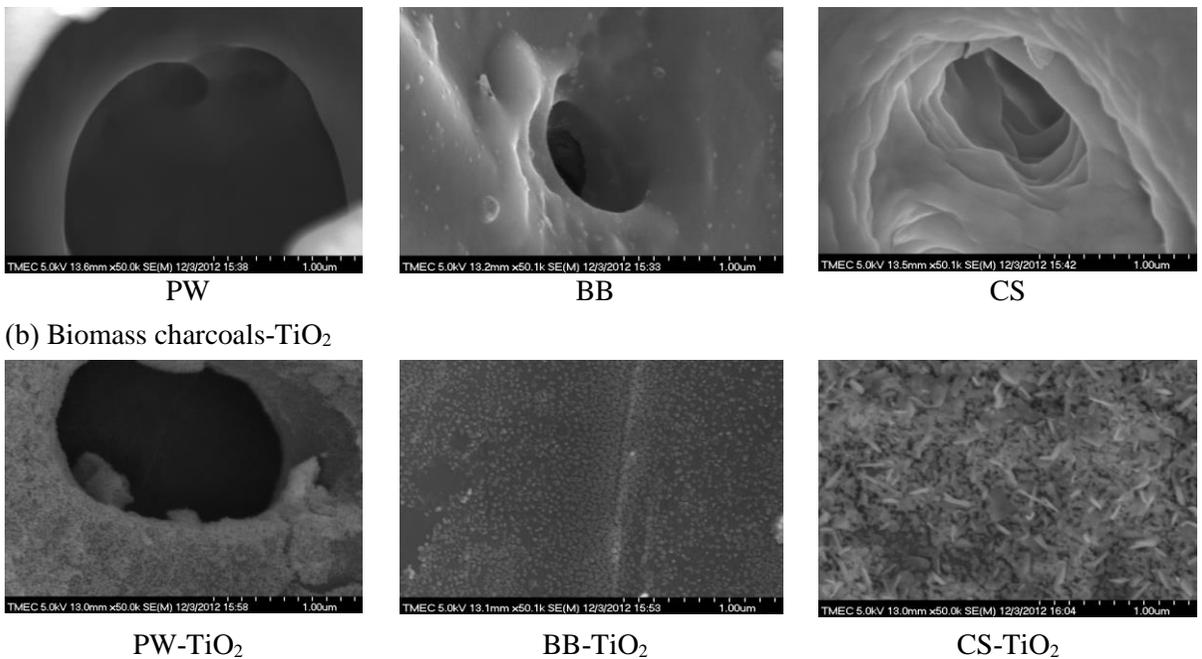
Fig. 4 shows SEM images of  $TiO_2$  that were coated on (a) pine wood-charcoal (PW-  
(a) Biomass charcoals

$TiO_2$ ), (b) bamboo-charcoal (BB- $TiO_2$ ) and (c) coconut shell-charcoal (CS- $TiO_2$ ).  $TiO_2$  thin films distributed in the pores and covered on biomass charcoals. BB- $TiO_2$  and CS- $TiO_2$  showed high covering films of  $TiO_2$  on surface and filled full in the small pores but PW- $TiO_2$  still had many large pores. Comparisons for porous morphology of (a) biomass charcoals and (b) biomass charcoals- $TiO_2$  were shown in Fig. 5. This  $TiO_2$  surface on charcoals can inhibit the probability of electron hole recombination, and also promote photocatalytic reaction [3,4, 23-26].

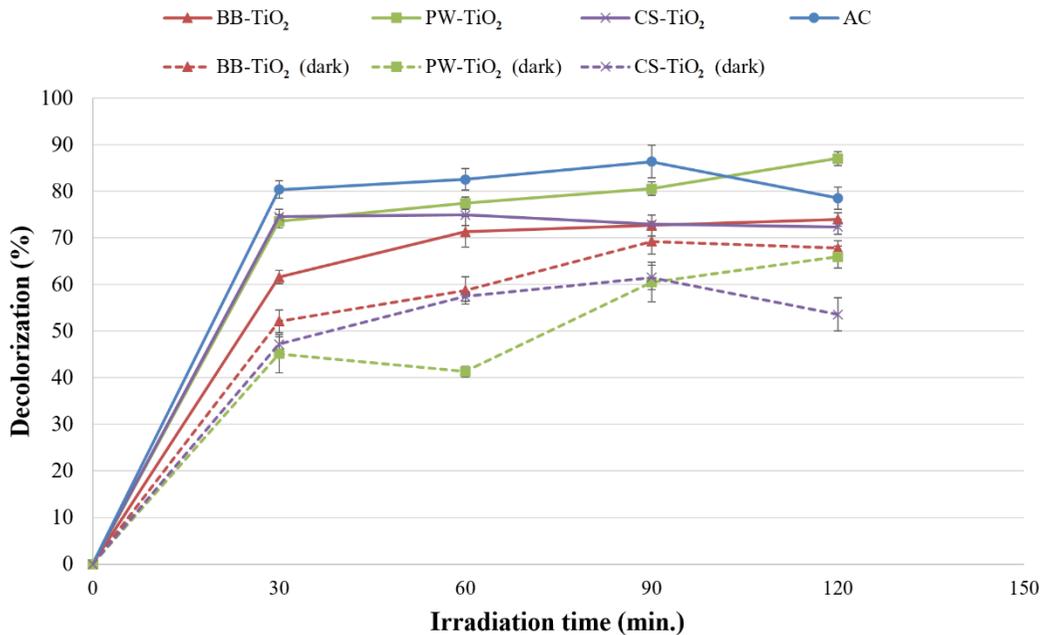
### 3.3 Photocatalytic decolorization tests

Fig. 6 shows percentages of decolorization of wastewater from textile dye for biomass- $TiO_2$  and activated carbon (AC). Wastewater under treatment was kept to measured absorption every 30 min over 2 h. The figure shows that decolorization of biomass- $TiO_2$  were CS- $TiO_2$ , BB- $TiO_2$  and PW- $TiO_2$ , respectively. The results were consistent with anatase phase ratio of biomass charcoals in XRD pattern. At 120 min., percentage decolorization of PW- $TiO_2$  was reach to 87.02%, because photocatalysis process of  $TiO_2$  decomposed dye on PW- $TiO_2$  surface. Nevertheless, biomass- $TiO_2$  in dark condition were low decolorization because they occurred low photocatalysis process [27]. Briefly, when biomass- $TiO_2$  is irradiated in light energy,  $OH^\bullet$  radical attack and breaking of the dye molecule. The decolorization by  $OH^\bullet$  radical as shown by Eq. (3.1) – Eq. (3.9)

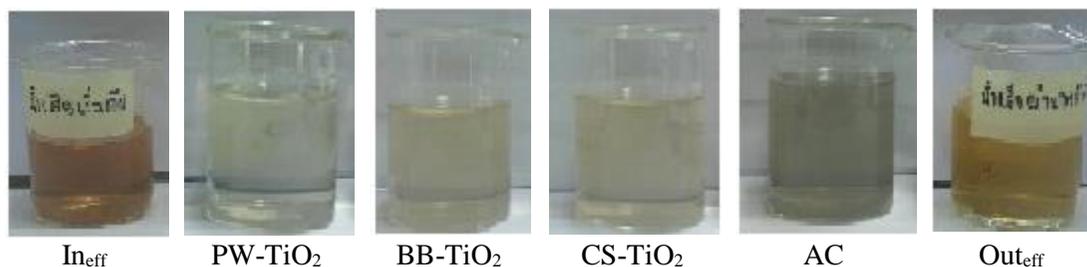
In addition, the decolorization of AC were 80.37, 82.55, 88.01 and 78.54% for UV irradiation time of 30, 60, 90, and 120 min., respectively. In the other word, percentage decolorization for AC decreased as UV irradiation time increased. The result suggests that, adsorption takes place rapidly at the initial stage on the external surface of AC followed by a slower internal diffusion process and decreased due to desorption [8-10].



**Fig. 5.** Porous morphology of (a) biomass charcoals and (b) biomass charcoals-TiO<sub>2</sub> at magnification of 50000.



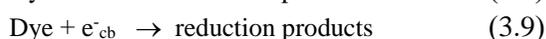
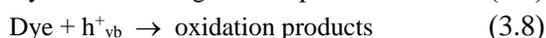
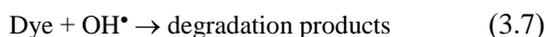
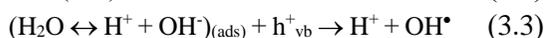
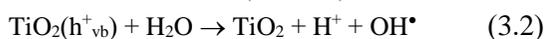
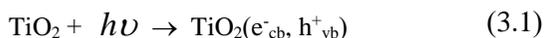
**Fig. 6.** The percentages of decolorization of wastewater from textile dye for biomass-TiO<sub>2</sub> and AC. Error bars presented are mean values of  $\pm$  standard deviation of triplicates of three independent experiments.



**Fig. 7.** Comparisons for the color of influent and effluent wastewater under biomass-TiO<sub>2</sub> and AC treatment.

Moreover, PW-TiO<sub>2</sub> showed highest decolorization because it still had many large pores. These observation suggest that, the enhanced photocatalytic efficiency is attributed due to the synergistic effects of absorptive properties and the photocatalytic activity of PW-TiO<sub>2</sub> [4]. This indicates that PW-TiO<sub>2</sub> has effective absorbent nearby commercial AC. Furthermore, photocatalytic application has been decompose of toxic substance, resulting in high percentage of removal on long-term. Comparisons for the color of influent and effluent wastewater under biomass-TiO<sub>2</sub> treatment were showed in Fig. 7.

The photocatalytic reaction under UV light, for decolorization of basic dyes occurred under electron hole pair ( $e^-_{cb}$ ,  $h^+_{vb}$ ) that produced by UV light. The recently proposed basic dyes degradation mechanism for the irradiated TiO<sub>2</sub> system as follows Eq. (3.1) – Eq. (3.9) [28-30]. The holes are subsequently trapped by surface hydroxyl group ions or adsorbed H<sub>2</sub>O to yield  $\cdot$ OH radicals. After generation of  $\cdot$ OH radicals, the degradation of dyes molecules occurs, which finally yields CO<sub>2</sub> gas *via* many oxidation steps.



#### 4. Conclusions

Decolorization of wastewater from real textile industry with biomass-TiO<sub>2</sub> was investigated. Biomass-TiO<sub>2</sub> was prepared by the sol-gel and dip-coating technique. The real wastewater from textile dyes was used as wastewater on photocatalytic test. The order of decolorization is PW-TiO<sub>2</sub> > AC > BB-TiO<sub>2</sub> > CS-TiO<sub>2</sub> > PW > BB > CS. The photocatalytic tests indicated that PW-TiO<sub>2</sub> has the highest decolorization ( 87. 02% ) within 120 minutes because of the synergistic effects of absorptive properties and TiO<sub>2</sub> high generated  $\cdot$ OH radicals. These radicals were strong oxidizing agents that can easily attack the adsorbed dye molecules. Using biomass charcoals, such as PW, BB, and CS, to produce absorbent, providing a less expensive raw material.

#### Acknowledgements

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