

## Enhancement of Titanium Dioxide by Bagasse Silica for Photocatalytic Degradation of Dyes

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### Abstract

The utilization of an alternative silica source from agriculture products such as bagasse from sugar and biofuel industries is considered as a zero-waste management. In this work, silica extracted from bagasse was introduced as a support for titanium dioxide (TiO<sub>2</sub>) to enhance photocatalytic degradation. TiO<sub>2</sub> precursor prepared by sol-gel from titanium butoxide was dispersed on bagasse silica with 10, 20, and 30 %wt loading by impregnation method. The photocatalysts were further investigated the physicochemical properties by several techniques. Interestingly, DR-UV-Vis results showed that band gap energy of TiO<sub>2</sub>/BGS was lower than that of bare TiO<sub>2</sub>. For catalytic testing, the degradation of methyl orange (2 ppm of initial concentration) as an anionic dye from bare TiO<sub>2</sub> (48%) was better than from composite TiO<sub>2</sub>/BGS (12 -16%) due to an electrostatic repulsion from negatively charge on silica surface to anionic species. However, photodegradation of methylene blue (1 ppm of initial concentration), which was represented to cationic dye, from TiO<sub>2</sub>/BGS composites (45 -71%) were better than bare TiO<sub>2</sub> (29%) due to a higher surface area of active phase. 20 %wt of TiO<sub>2</sub>/BGS was the best photocatalyst for this route. Therefore, BGS played a crucial role to improve the photocatalytic activities and also was one of the most promising strategies to use the worthless material of bagasse.

**Keywords:** Photocatalysis; Titanium dioxide; Silica; Bagasse

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### 1. Introduction

Bagasse is one of agriculture residue from several industries such as electricity, sugar, molasses, and bioethanol. Approximated 280-290 kg of bagasse generates from 1000 kg of sugarcane. Although, it is mainly used a fuel to produce the electricity through water steaming process, but some inorganic compounds such SiO<sub>2</sub>, K<sub>2</sub>O, and Na<sub>2</sub>O are still considered unused materials. Utilization of those inorganic compound is important in order to achieve a zero-waste management. Several reports explored that bagasse or its ash contain high SiO<sub>2</sub> content

about 90 %wt which could be used as an alternative source for further application (Worathanakul *et al.*, 2009, Saputera *et al.*, 2021). Among various methods of extracting SiO<sub>2</sub> from raw agriculture residue, our previous work has been reported that acid leaching provided a relatively high purity and yield of extracted SiO<sub>2</sub> from rice husk (Rongchapo *et al.*, 2013). This route was done by refluxing a raw material in a mild acid concentration and then calcination at 600°C. Typically, the extracted SiO<sub>2</sub> has high surface area and

good adsorption ability which are essential properties to use a supporting material for catalytic fields.

Titanium dioxide (TiO<sub>2</sub>) is common and effective photocatalyst to degrade several organic pollutants under UV irradiation (Rasalingam *et al.*, 2014). However, TiO<sub>2</sub> is classified to non-porous or microporous material led to lower adsorption ability and catalytic activity. Moreover, an issue of particle agglomeration can arise with a direct use. One of solving methods is to disperse TiO<sub>2</sub> onto supporting materials to increase surface area and reduce particles gathering. In previous work, TiO<sub>2</sub> on SiO<sub>2</sub> from rice husk was studied for photocatalytic degradation of paraquat. The 30%wt SiO<sub>2</sub> supported catalyst which enhancement from the dispersion showed a higher activity than the bare TiO<sub>2</sub> (Rongchapo *et al.*, 2016). In addition to similar strategy, SiO<sub>2</sub> from Bagasse improved the photocatalytic activity of commercial TiO<sub>2</sub> P25 for methyl orange degradation (Saputera *et al.*, 2021). Therefore, in this work, SiO<sub>2</sub> extracted from bagasse by acid-leaching method was introduced as a support for TiO<sub>2</sub> to investigate photocatalytic characteristics and decolorization of methylene blue and methyl orange.

## 2. Materials and Methods

### 2.1 Preparation of photocatalysts

Silica was prepared from bagasse by acid leaching method modified from the literature (Khemthong *et al.*, 2007 and Manzano *et al.*, 2015). The bagasse was refluxed in 3 M hydrochloric acid (37% HCl, Carlo-Erba) for 6 h, washed with deionized water (DI water), dried and calcined at 600°C for 3 h. The obtained white powder was silica with estimated particle size between 25 – 330 μm, namely BGS and further used as a support material with titanium dioxide (TiO<sub>2</sub>). The TiO<sub>2</sub> and 10 20 and 30 wt% TiO<sub>2</sub>/BGS composites were prepared by our previous report (Rongchapo *et al.*, 2016). Sol solution containing Titanium butoxide (99% C<sub>16</sub>H<sub>36</sub>O<sub>4</sub>Ti, Acros) in 40 mL of 1 M

HNO<sub>3</sub> acid (65%, Carlo Erba) was diluted with 10 mL of DI water and adjusted to pH 3 with NaOH (99%, Qrec) to give a turbid colloid. Subsequently, BGS was added and agitated for 2 h. The composite was washed with DI water, separated by centrifugation, dried at 105°C overnight and calcined at 300°C for 1 h.

### 2.2 Characterization of photocatalysts

The resultant photocatalysts were further investigated the physicochemical properties by X-ray diffraction (XRD) using a Bruker-AXS diffractometer D5005 with Cu Kα radiation, N<sub>2</sub> adsorption-desorption analysis using a Micromeritics ASAP 2010 analyzer, UV-Vis-NIR spectrophotometer for optical diffuse reflectance spectroscopy (DRS) using Carry 5000, inductively coupled plasma optical emission spectrometer (ICP-OES) using Optima 8000, PerkinElmer, energy dispersive X-ray fluorescence (EDXRF) spectrometer using an Oxford ED2000 and X-ray Photoelectron Spectroscopy (XPS) using a PHI5000 VersaProbe II XPS instruments (ULVAC-PHI, Japan) (Monochromatic X-ray of Al Kα, 1486.6 eV) at Synchrotron Light Research Institute (SLRI), Thailand.

### 2.3 Photocatalytic testing

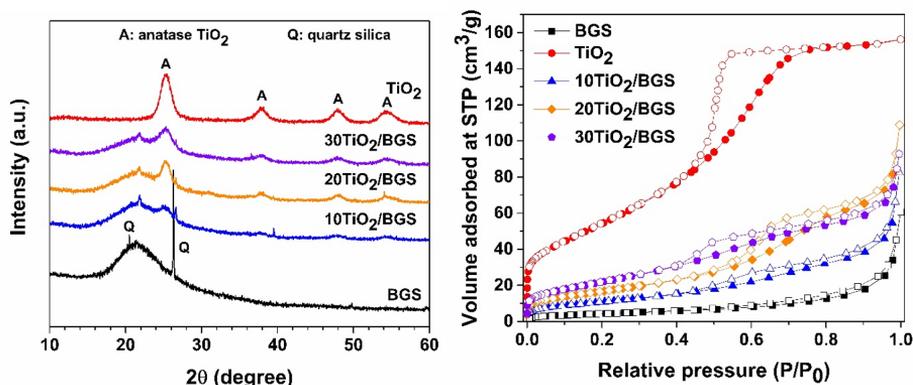
25 mg of photocatalyst and 250 mL of dye solution which is 1 ppm of methylene blue (99%, Qrec) or 2 ppm methyl Orange (99%, Qrec) was placed in 1-L beaker. The mixture was stirred at room temperature for 30 min in the dark and then irradiated by 3 lamps of 18-W fluorescent black light in the range of 300-400 nm for 120 min. At interval time, the sampling suspension mixtures were separated by a 0.45 μm polypropylene filter to remove solid and the filtrate were determined by UV-Vis spectroscopy using a Varian Cary 1E UV/Visible spectrophotometer at 668 nm for methylene blue and 446 nm for methyl orange. All reactions were repeated at least three times.

### 3. Results and Discussion

#### 3.1 Characterization of photocatalysts

XRD pattern of all sample including BGS, bare TiO<sub>2</sub> and their composites were displayed in Figure 1 (left). BGS displayed two sharp peaks at 20.8 and 26.3 degree corresponding to the plane (100) and (011) of quartz SiO<sub>2</sub>, respectively (JCPDS PDF No. 46-1045). Meanwhile, synthesized TiO<sub>2</sub> sample showed peaks at 25.3, 38.0, 47.9 and 54.4 degree related to the plane (101), (112), (200), and (105 and 211) of anatase TiO<sub>2</sub> (Rasalingam *et al.*, 2014). Both characteristic peaks of BGS and synthesized TiO<sub>2</sub> were obtained in the composite samples and phase transformation did not observe. Moreover, peak intensities of anatase phase increased with increasing of percent loading from 10 to 30 wt%.

Porosities of all samples were shown in Figure 1 (right) and Table 1. Like other silica derived from plants, BGS exhibited a non-porous or microporous material with 15.6 m<sup>2</sup>/g of surface area (Worathanakul *et al.*, 2009). The bare TiO<sub>2</sub> showed a mesoporous nature corresponding to type IV with H2 hysteresis loop of N<sub>2</sub> adsorption-desorption isotherm with surface area of 201.9 m<sup>2</sup>/g. Nitrogen sorption analysis suggested that micro- and mesopores were observed in the TiO<sub>2</sub>/BGS composites. BET results indicated that surface area mainly derived from TiO<sub>2</sub> species and increased with increasing TiO<sub>2</sub> loading in composite materials. When amount of TiO<sub>2</sub> loading was considered, surface areas per TiO<sub>2</sub> was significantly improved implied that TiO<sub>2</sub> particles were well dispersed in BGS and composite materials had more active site for further photocatalytic testing.



**Figure 1.** XRD patterns (left) and Nitrogen adsorption (filled)–desorption (empty) isotherm (right) of all prepared catalysts.

**Table 1.** Physicochemical properties of prepared photocatalysts.

Sample	TiO <sub>2</sub> (%wt) <sup>a</sup>	Surface area (m <sup>2</sup> /g) <sup>b</sup>	Band gap energy (eV) <sup>c</sup>	Surface area per TiO <sub>2</sub> <sup>d</sup>
BGS	-	15.6	-	-
TiO <sub>2</sub>	-	201.9	3.10	2.02
10TiO <sub>2</sub> /BGS	8.01	40.4	3.08	3.09
20TiO <sub>2</sub> /BGS	15.9	61.6	3.05	2.89
30TiO <sub>2</sub> /BGS	26.5	81.6	2.93	2.49

<sup>a</sup> ICP-OES

<sup>b</sup> N<sub>2</sub> adsorption-desorption analysis with BET method

<sup>c</sup> obtained from DR-UV-Vis result of the plot of  $[F(R)/h\nu]^{1/2}$  versus photon energy ( $h\nu$ )

<sup>d</sup> calculated from TiO<sub>2</sub> surface area divided by weight percent of TiO<sub>2</sub> and assumed that surface area of BGS was constant at 15.6 m<sup>2</sup>/g; for example, 10TiO<sub>2</sub>/BGS, (40.4-15.6)/8.01

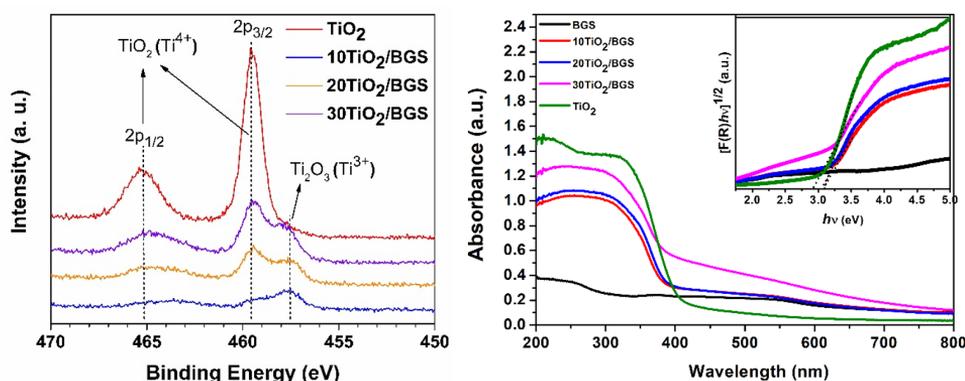
XPS technique was used to identify oxidation state of titanium on surface of photocatalysts as shown in Figure 2 (left). Binding energies at 459.6 (Ti2p<sub>3/2</sub>) and 465.2 eV (Ti2p<sub>1/2</sub>) assigned to Ti<sup>4+</sup> species were found in TiO<sub>2</sub> and its composites. In addition, Ti<sup>3+</sup> species indicated by binding energy of 57.5 eV were detected in TiO<sub>2</sub>/BGS composites. This species might be referred to Ti<sub>2</sub>O<sub>3</sub> formation on oxygen vacancies of surface silica (Bharti *et al.*, 2016). Regarding to peak area, Ti<sup>3+</sup> species did not significantly increase while photoactive phase of Ti<sup>4+</sup> species clearly increase with the TiO<sub>2</sub> loading. Band gap energies (E<sub>g</sub>) were evaluated by Kubelka-Munk plot from DR-UV-Vis spectra as shown in Figure 2 (right). E<sub>g</sub> of three TiO<sub>2</sub>/BGS composites had lower value compared to bare TiO<sub>2</sub>. Typically, the lower E<sub>g</sub> values give the better photocatalytic activity due to the lower excitation energy are required.

### 3.2 Photocatalytic activity

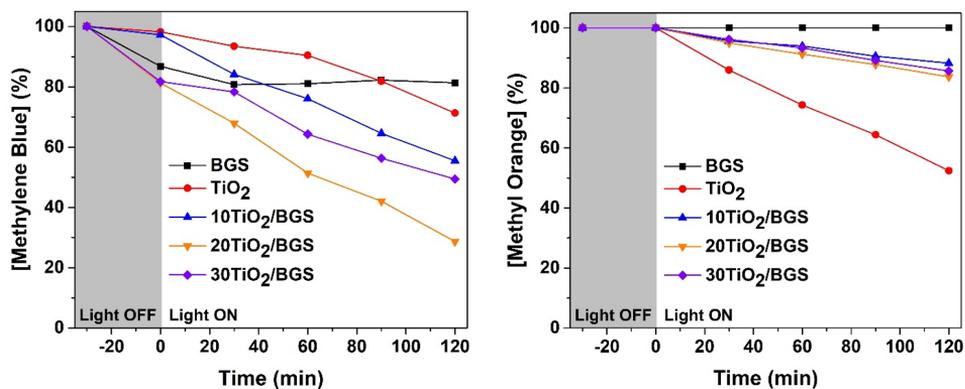
Photocatalytic degradation pathway was explained based TiO<sub>2</sub> material. Photocatalyst absorbs an excitation energy which is UV. Then, electrons from valence band (VB) are promoted into conduction band (CB) resulting in the formation of excited electrons in CB that can create reactive oxygen species (ROSs) or directly reduce organic molecules and the formation of positive holes in VB that can create hydroxyl radical or directly oxidize organic molecules for decolorization of MB

(Houas *et al.*, 2001) and MO (Saputera *et al.*, 2021), respectively. Photocatalytic activities of all prepared photocatalysts were shown in Figure 3. Photocatalytic degradation of dyes was not obtained from BGS indicated that BGS only acted as support material. In case of MB degradation, bare TiO<sub>2</sub> achieved 29% of photodegradation, meanwhile the TiO<sub>2</sub>/BGS composites had better degradation performance about 45%, 51% and 71 % from 10%wt, 30%wt and 20%wt of TiO<sub>2</sub> loading, respectively. However, in MO degradation, all TiO<sub>2</sub>/BGS composites had smaller percentage of dye degradation around 15% compared to bare TiO<sub>2</sub> about 48%. These unexpected results could be explained by adsorption behavior. The cationic molecules of MB can closely diffuse to negatively charge of catalyst surface confirmed by the decreasing of MB concentration in dark condition. Therefore, BGS played a crucial role to improve the photocatalytic activities. On the other hand, the anionic molecules of MO might be difficult to adsorb on the catalyst regarding to a constant concentration of MO in dark condition. So, bare TiO<sub>2</sub> had a higher change to come across with MO and resulting in the better photocatalytic activity.

According to Saputera *et al.*, (2021), although the catalyst preparation, phase of TiO<sub>2</sub>, and the amount of TiO<sub>2</sub> used in catalytic reaction were obviously different, their composite material showed around 22 to 33% of degradation and had better catalytic performance compared to bare TiO<sub>2</sub> P25 at around 13%. These opposite results compared



**Figure 2.** XPS photoemission spectra of Ti 2p (left) and DR-UV-Vis spectra (right) with extrapolation of the band gap energy (inset) of photocatalysts



**Figure 3.** Photocatalytic activity of all photocatalysts for methylene blue (left) and methyl orange (right) degradation.

to our MO degradation indicating that phase of active species and catalyst preparation were also important. In addition, zeta potential on surface catalyst was affected by a calcination temperature which directly involved the adsorption features (Shah and Rather, 2021). The best photocatalyst among the prepared catalyst was 20 %wt of  $\text{TiO}_2/\text{BGS}$  because  $\text{TiO}_2$  particles might be accumulated at high amount of loading.

#### 4. Conclusion

BGS was successfully extracted from waste bagasse by acid leaching method and use as a support for prepared  $\text{TiO}_2$  with 10, 20, and 30 %wt loading by impregnation method. The investigation of physicochemical properties revealed that  $\text{TiO}_2/\text{BGS}$  composites showed both characteristic nature from parent  $\text{TiO}_2$  and BGS. Surface areas of loading  $\text{TiO}_2$  in composites were enhanced. The band gap energies, an essential optical property for photocatalysis, narrowed in the composites. The photocatalytic testing under UV light was consistent with characterization. Photodegradation of methylene blue from  $\text{TiO}_2/\text{BGS}$  composites (45-71%) were better than bare  $\text{TiO}_2$  (29%). However, the degradation of methyl orange from bare  $\text{TiO}_2$  (48%) was better than composite  $\text{TiO}_2/\text{BGS}$  (12-16%). 20 %wt of  $\text{TiO}_2/\text{BGS}$  was the best photocatalyst among the prepared catalyst. The results indicated that BGS played a crucial role on photocatalytic activity via adsorption effect. Nevertheless, the utilization

of BGS as an alternative silica source is promising ideal to treat the agricultural residues.

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