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TiO_2 Supported on Brick Waste as Low Cost Photocatalyst for Dye Photodegradation

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Photocatalysis is one of the most important technology for treating water pollutants effectively. The method is better compared to adsorption method in that photocatalysis gives advance destroying organic contaminants and has better reusability. In other side, textile industry including Batik's industry is a potential source of wastewater contaminated with dyes which can cause serious environmental problems. For photocatalysis purposes, TiO_2 is the popular material. In order to enhance both economic and photocatalytic activity of TiO_2, supporting TiO_2 into solid material is interesting effort. In this research, brick waste was chosen as low cost and effective support for TiO_2. TiO_2 supporting onto brick waste by impregnation method was carried out. The composite of TiO_2/Brick waste (TiO_2/BW) was conducted by dispersing titanium tetraisopropoxide as TiO_2 precursor followed by calcination. Characterization of TiO_2/BW was performed by XRD analysis, Diffuse Reflectance UV-Vis and FTIR analysis. For photocatalytic activity, experiments on photocatalysis and photooxidation of rhodamine B solution were examined. Prepared Ti-BW exhibits the formation of TiO_2 in mixed anatase and rutile phases as presented by XRD pattern. From the DRUV-Vis analysis, it is found that the band gap energy of composite material lays in UV-Visible region. TiO_2/BW showed high photoactivity as represented by faster degradation rate of rhodamine B over photooxidation and photocatalysis compared to adsorption method. From the data simulation, it is revealed that rhodamine B degradation over photocatalysis mechanism follow pseudo-first order while over photooxidation the kinetic obey pseudo-second order.

1. Introduction

Synthetic dyes are mostly used in industries such as textile, paint, and other handicraft such as batik to color their final products. The effluents of batik and textile dying are usually darkly colored because of the presence of dyes that are not easily biodegradable (Hassena, 2016). In fact, mostly dyes are considered carcinogenic and harmful to aquatic living organisms and human life since it can undergo bioaccumulation. Some methods are attempted for the removal of dye from wastewater including ozonation, coagulation, flocculation, chemical oxidation, bio-degradation, adsorption, and reverse osmosis. Among the mentioned methods, adsorption is easy and economical for the removal of dyes from aqueous systems but further step is required for handling saturated adsorbent. In advance, the combination of adsorption and photodegradation are proposed (Deng and Zhao, 2015). Photodegradation process is based on photocatalysis mechanism in that the dye molecule will be oxidized based on radicals formed from the interaction between photocatalyst and photon. In this case, TiO_2 or called as titania is the most popular material due to its photoactivity, non-toxic and low-cost properties. The combined adsorption-photocatalysis mechanisms can be achieved by preparing composite of TiO_2 and porous materials such as clay, zeolite, MCM-41 and silica and alumina materials (Wang et al., 2011). Table 1 lists some investigations in synthesis of TiO_2 composite and their successful application of dye or organic degradations. In order to preserve low cost photocatayst material for small or home scale industry, an effort to synthesize TiO_2 composite with low cost material is interesting topic. The use of fly ash, natural clay and natural zeolite have been reported.

In other side, brick is important building material that usually also become construction waste during building renovation. Chemically, brick contains some minerals that are preserve porous structure for adsorption mechanism. From precious investigation, it was reported that brick waste shows adsorption capability for some

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dyes and heavy metals (Kooli, 2015). Due to the mineral composition and the porous structure of brick waste, in this research TiO_2 supporting into brick waste for photocatalysis mechanism is conducted. The objective of the present work was to investigate physicochemical character of prepared material and it photoactivity for dye degradation. As dye model, rhodamine B (RhB) was used for simulation.

Table 1: Some investigation on TiO_2 support for photocatalysis applications

TiO_2 support	Degraded Dye/Organic molecule	Result	Reference
Bentonite	Cationic Red GTL	High photocatalytic activity of composite and effect of H_2O_2 addition to the activity.	(Sun et al., 2002)
Montmorillonite	Methylene blue and *Eschericia coli*	The kinetics of methylene blue photodegradation indicate the significant role of prepared material as photocatalyst as well as in *E.coli* inactivation. Photodegradation of methylene blue over prepared material shows the fitness to Langmuir-Hinshelwood model.	(Fatimah, 2012)
Clay	Anionic reactive blue 19	The effect of UVA and solar irradiation (UV-solar) was studied at room temperature. TiO_2–clay demonstrated an effective degradation of RhB 19 under both types of irradiation. Moreover, in this study, the effects of various oxidants such as hydrogen peroxide (H_2O_2), potassium peroxodisulfate($K_2S_2O_8$) and sodium. carbonate(Na_2CO_3) were thoroughly investigated.	(Bel et al., 2014)
Zeolite	2-propanol	photocatalytic performances of composites due to the improvement of hydrophobicity of Y-zeolite as a support	(Kamegawa et al., 2013)
MCM-41	RhB and Phenol	RhB was adsorbed instead of being degraded by TiO2/MCM-41 due to the large specific surface area of MCM-41, while most of phenol was degraded.	(Tian et al., 2012)
Activated carbon	Direct Blue-199	The degradation efficiencies of the synthesized (Singh et al., 2016) composites for Blue-199 dye shows very active and efficient process.	(Singh et al., 2016)
Activated carbon	Tartrazine	Better performances with this promising material –TiO2 deposited onto AC – compared with TiO2 powder could be explained by the vicinity of photocatalytic and AC adsorption sites.	(Andriantsiferana et al., 2013)
Al_2O_3	CO, CO_2, HC, and NOX	Loading on Al_2O_3 improved photocatalytic effect of TiO_2 modified with Fe^{3+}, and the best purification effect was achieved when the loaded content of TiO_2 was 10 %. The degradation rates of CO, CO_2, HC, and NO_X were 6.9 %, 13.8 %, 21.4 %, and 49.2 %, respectively, under UV light condition.	(Andriantsiferana et al., 2013)

2. Materials

Brick waste was obtained from domestic area in Sleman District, Yogyakarta Province, Indonesia. The brick waste was washed, crushed and screened until 200 mesh. Titanium tetraisopropoxide, RhB and H_2O_2 were purchased from Merck, Germany. Preparation of TiO_2 supported in brick waste (furthermore called as TiO_2/BW) was carried out by dispersing titanium isopropoxide solution in isopropanol solvent into brick waste powder suspension in water (10 % w/v). Theoretic content of titanium was 5 %. The mixture obtained was then stirred for overnight before was dried in oven at 100°C for 8 h followed by calcination at 400°C for 4 h. Prepared material was characterized by using x-ray diffraction (XRD), scanning electron microscope (SEM-EDX) and attenuated-Fourier Transform Infra-Red (FTIR). A Philips Benchtop x-ray diffractometer with radiation source of Ni-filtered Cu-Kα was utilized for analysis. Phenom-X microscope and Perkin Elmer ATR-FTIR were employed for SEM-EDX and FTIR analysis respectively. Photocatalytic degradation of RhB performed in photocatalytic reactor with the scheme presented in Figure 1. Initial concentration of RhB was varied.

3. Results and discussion

Figure 2 shows the XRD pattern of Ti/BW. The major peaks are associated with quartz (Q), anatase (A), rutile (R) and muscovite mica (M) in agreement with the results of SEM-EDX analysis in Figure 2. Strong diffraction peaks at 25° and 48° indicating TiO_2 in the anatase phase while the peaks at 27° and 550 are correspond to the presence of rutile (JCPDS no.: 88-1175 and 84-1286) (Thamaphat et al., 2008). Other peaks are related to quartz (Q), muscovite and kaolinite. The presence of kaolinite and quartz can be attributed to the raw material of brick that are natural kaolinite minerals (Monteiro et al., 2005). The pattern indicates that TiO_2 was formed during composite synthesis. It is also confirmed by surface profile data as well as elemental analysis results listed in Table 2.

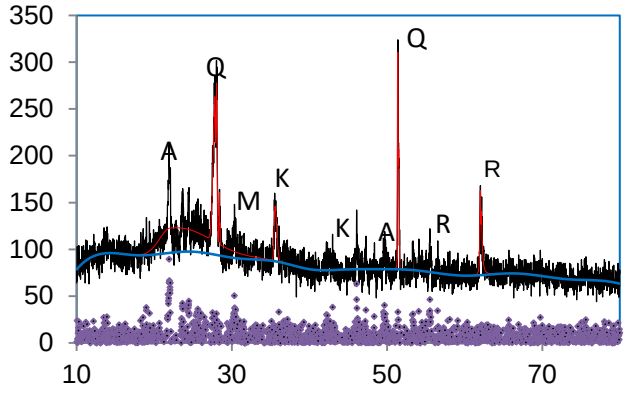

Figure 2: XRD pattern of TiO_2/BW

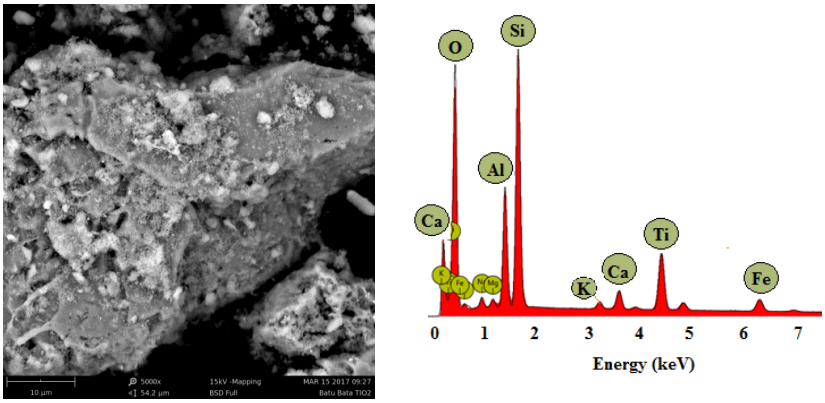

Figure 3: SEM-EDX profile of TiO_2/BW

Table 2: Elemental analysis result of Ti/BW

Element	Percentage (%wt.)
Silicon	11.9
Oxygen	71.9
Aluminum	6.9
Titanium	4.0
Calcium	1.0
Iron	1.5
Potassium	0.4
Sodium	1.6
Magnesium	0.7

As TiO_2 in the composite is functionalized as photocatalyst, the band gap energy is important parameter. Analysis of band gap energy is presented by DRUV-Vis spectra in Figure 4.

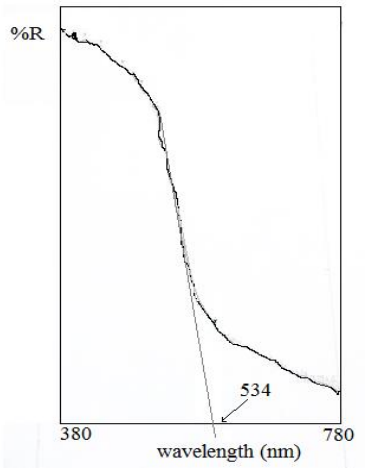

Figure 4: DRUV-Vis spectra of TiO_2/BW

From the pattern of spectrum, it is found that the material absorb light in the UV and visible region of spectrum and the edge wavelength obtained is at 534 nm correspond to 2.32 eV value of the band gap. The value is smaller than the theoretic band gap energy value of anatase (3.2eV) and also rutile (3.0 eV).
Photocatalytic performance of TiO_2/BW is presented by kinetic curve of RhB degradation in Figure 5.

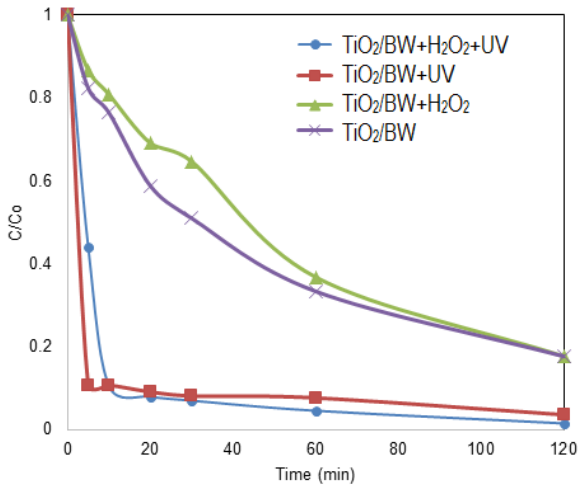

Figure 5: Kinetic curve of rhodamine B over varied treatment using TiO_2/BW

The kinetic curve displays the different pattern of rhodamine B degradation over varied treatment. The treatment of TiO_2/BW with the addition of H_2O_2 and UV light exposure means the photooxidation mechanism while the similar treatment without H_2O_2 means photocatalysis process. The presence of H_2O_2 is aimed to accelerate the oxidation process since H_2O_2 is easy to produce hydroxyl radicals from homolitical bond cleavage under UV exposure by mechanism Eq(1) to (6):

$TiO_2 + hv \longrightarrow TiO_2 + e^-(CB) + h^+_{(VB)}$ …. (1)
$^-OH + h^+ \longrightarrow \bullet OH$ ……. (2)
$O_2 + e^- \longrightarrow O_2^-$ ……. (3)
$O_2^- + H^+ \longrightarrow HO_2$ ……. (4)
$HO_2 \longrightarrow H_2O_2$ ……. (5)
$H_2O_2 + e^- \longrightarrow \bullet OH + {}^-OH$ ……. (6)

The presence of H_2O_2 will accelerate the oxidation by activating step (6) in the mechanism.
From the kinetic curves, it is found that the degradation of RhB from photocatalytic degradation and photooxidation mechanism is not significantly different, meanwhile that the initial rates are quite similar. Moreover, the reduction of RhB concentration over adsorption and addition of H_2O_2 are slower compared to both mechanisms. The photocatalytic activity of prepared material is revealed from the difference between the kinetic of photocatalysis and adsorption (TiO_2/BW only) and also the room temperature oxidation (TiO_2/BW+ H_2O_2).
Kinetics of the RhB degradation over varied treatments are studied by utilizing four models:
First-order model with Eq(7) to (10):

$$ln\left(\frac{C_o}{C_t}\right) = kt \quad \ldots\ldots\ldots \tag{7}$$

Second order model:

$$\left(\frac{1}{C_t} - \frac{1}{C_0}\right) = kt \ldots\ldots \tag{8}$$

Modified Freundlich model:

$$\left(\frac{C_0 - C_t}{C_0}\right) = kt^b \quad \ldots\ldots\ldots\ldots \tag{9}$$

and parabolic diffusion model:

$$\frac{\left(1-\frac{C_t}{C_0}\right)}{t} = kt^{1/2} + \alpha \tag{10}$$

with C_o and C_t are initial RhB concentration and concentration at certain time t , respectively, k is kinetics constant, t is time of sampling, b is coefficient of modified Freundlich model and α is coefficient of parabolic model (Rahman et al., 2014).
Calculations to the data presented in Figure 5 give the results as listed in Table 2. From the It is found that photooxidation and oxidation with the H_2O_2 addition obey second-order model while photocatalysis and adsorption kinetics follow modified-Freundlich model and first order model, respectively. Second order kinetics of the processes is an indication of the role of RhB and H_2O_2 to give influence for the reaction rate, meanwhile from the photocatalysis mechanism which fit to modified-Freundlich model, it is concluded that adsorption mechanism is also taking part as the influencing factor for the dye degradation (Laysandra et al., 2017). The graphs from related models are depicted in Figure 6 and the kinetics parameters are tabulated in Table 3.

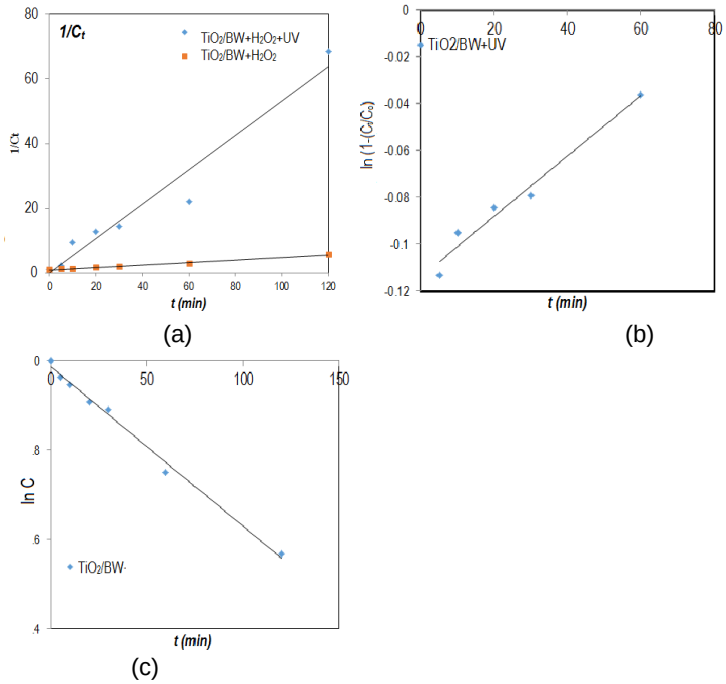

Figure 6: Kinetics model of RhB using (a) TiO_2/BW+H_2O_2+UV and TiO_2/BW+ H_2O_2 (b) TiO_2/BW+UV + H_2O_2 (c) TiO_2/BW

Table 3: Results of Kinetics evaluation of RhB degradation

Treatment	Kinetics equation (R^2)	Initial Rate (ppm/min)
TiO_2/BW+H_2O_2+UV	$\frac{1}{C_t} = 0.53t - 0.021$	4.654
TiO_2/BW+H_2O_2	$\frac{1}{C_t} = 0.038t - 0.910$	4.590
TiO_2/BW+UV	$\ln C_t = -69.43t - 3.62$	2.450
TiO_2/BW	$\left(\frac{C_0 - C_t}{C_0}\right) = 5.13t^{7.31}$	1.764

4. Conclusion

The results of the present study demonstrate that TiO_2 supported brick waste was successfully synthesized. The material consists of formed TiO_2 in mixture of anatase and rutile phases and has the band gap value of 2.2 eV. The material exhibits the photocatalytic activity of in rhodamine B degradation.

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