Titania Modified Silica from Sugarcane Bagasse Waste for Photocatalytic Wastewater Treatment

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Abstract. Photocatalytic oxidation is one of the technologies to overcome pollution that can be applied for air and water purification. TiO$_2$ has been widely used as a photocatalyst, however, several disadvantages of TiO$_2$ including low absorption of visible or solar radiation, rapid recombination of electron and hole as well as low stability limits its practical applications especially for wastewater treatment. Thus, to overcome this problem, this study aims to develop highly adsorbent photocatalyst using TiO$_2$/SiO$_2$ composites with sugarcane bagasse waste act as SiO$_2$ source. The experimental results show that the photocatalytic performance of TiO$_2$/SiO$_2$ composite in the decolorization of methyl orange exhibits three-fold enhancement compared to neat TiO$_2$. Several catalyst characterizations were obtained including X-ray diffraction (XRD), scanning electron microscopy (SEM), and X-ray fluorescence (XRF). Characterization data show that a phase transformation was obtained from amorphous to crystalline phase by increasing TiO$_2$ content. These results proved that the feasibility of SiO$_2$ from sugarcane bagasse waste coupled with TiO$_2$ can be utilized for wastewater degradation.

1. Introduction

In today's era, the world is witnessing a social economic revolution from various types of industries. However, the progress of this industry is not balanced between the processes contained in the industry and the waste produced, resulting in environmental pollution which is very dangerous for its sustainability. One of the largest industries in the world is the textile industry. Based on the process taking place in the textile industry, a lot of water, dyes and chemicals are used to produce textile products. Currently, about 10,000 types of dyes are used in the textile industry and more than 7x10$^5$ tons of dyes are produced annually worldwide which are widely used for textile dyeing, paper printing, color photography, and as additives in petroleum products[1]. It is estimated that 10–15% of these dyes are contained in industrial waste[1]. Due to the use of these materials, the end result of this process is a lot of waste that cannot be utilized. Consequently, this textile waste will be very dangerous for the environment if it is thrown away without being processed.

Among the existing technologies, photocatalytic oxidation is one of the promising technologies to overcome pollution issue that can be applied to water and air purification due to low-cost, environmentally friendly and sustainable technology. The basic principle of photocatalysis is the excitation of electrons from the valence band to the conduction band after being illuminated by light source (with the energy higher than band gap energy of semiconductor-based photocatalyst used). The electron in the conduction band react with oxygen to generate superoxide radical while the holes in the valence band react with water to form hydroxyl radical. These reactive radicals act as important role in
oxidizing organic pollutants, i.e. textile waste (dye). Among the various metal oxide semiconductors, titania (TiO$_2$) is a semiconductor frequently used due to non-toxic and cheap. However, the main drawback of TiO$_2$ is the wide band gap energy (3.0 – 3.2 eV), which limits its light response only in the UV region. In addition, other disadvantages of TiO$_2$ including agglomeration, the low efficiency of the catalyst, high electron-hole recombination rate, and low adsorption of organic pollutants[2]. In recent decades, several attempts have been reported that immobilization of TiO$_2$ into porous materials such as clay[3], zeolite[4], activated carbon[5], and silica[6-11] can increase photocatalytic activity.

In this study, we report on the developing silica-based material to support TiO$_2$ based photocatalyst due to its high specific surface area and high stability and good adsorption of organic pollutants capacity. Waste biomass, i.e. sugar cane bagasse is used as a silica source to synthesize TiO$_2$/SiO$_2$ composites due to its abundant, unutilized waste and high silica content. The effect of TiO$_2$/SiO$_2$ ratio is also examined for photocatalytic dye degradation and physiochemical properties of TiO$_2$/SiO$_2$ composites.

2. Methodology

2.1. Synthesis of Silica from Sugar Cane Bagasse

10 grams of sugar cane bagasse was cut, dried, cleaned and weighed. Bagasse was calcined at 600°C for 4 hours. Then the calcined sugar cane bagasse was washed using HCl to remove aluminium and iron contents. A total of 5 grams of bagasse ash was stirred and mixed with 50 ml of 1 M HCl for 2 hours at room temperature with a stirring speed of 200 rpm. The solid was then filtered with filter paper and the residual solid was washed with 20 ml of distilled water to remove metal ions. Finally, the residue was dried for 5 hours at 100°C for further processing.

2.2. Synthesis of TiO$_2$/SiO$_2$ composites

The preparation of TiO$_2$/SiO$_2$ composites is adopted from Fatimah and Lusi Sopia [12]. TiO$_2$ supported by silica bagasse ash was prepared using the impregnation method. Briefly, the source of TiO$_2$ was obtained from the dilution of TiO$_2$ P25 in isopropanol as a solvent followed by stirring at 750 rpm for 2 hours at room temperature before being dispersed into the silica suspension of bagasse ash in distilled water. The mixture was stirred at 750 rpm for 4 hours at room temperature followed by solvent evaporation until a dry powder was obtained at 90°C for 4 hours. The dry powder obtained was then calcined at 600°C for 4 hours. In this study, the ratio of TiO$_2$/SiO$_2$ molar ratio used are 1:0, 1:1, 1:3, 3:1, and 0:1.

2.3. Catalyst characterizations

The SiO$_2$ content of sugarcane bagasse was measured using wavelength dispersive X-ray fluorescence (WD-XRF, Rigaku Supermini 200). The crystal structure of the catalyst was determined in air by X-ray Diffraction using a Rigaku SmartLab X-Ray Diffractometer instrument. The samples were ground and sieved to obtain a fine powder of particle sizes <50 μm. Data were collected varying 2θ between 15° and 65° with a step size of 0.01°. The anatase and rutile ratio was estimated using Spurr equation:

$$X_R = \frac{1.26I_R}{I_A + 1.26I_R}$$

(1)

XR is the Rutile fraction and IR and IA are the strongest intensities in the Rutile ((110)) and Anatase ((101)) diffraction pattern, respectively. The morphologies of the samples were investigated by scanning electron microscopy (SEM), using a JEOL 6510 equipped with Energy Dispersive Spectrometry (EDS). Diffuse reflectance UV–Vis spectra were collected at ambient temperature on an Evolution 220 (Thermo Scientific) spectrometer, using BaSO$_4$ as a reference. Spectra were recorded in the wavelength range of 200–1000 nm.

2.4. Photocatalytic activity assessment
The photocatalytic activity of the prepared materials was tested in the decolorization reaction of Methyl Orange (MO) in the home-built reactor. The housing consists of an aluminum box with dimensions of 55 cm in height, 85 cm in width, and 50 cm in depth and four Philips black light tubes (F20 T8 BLB, 18W, 60 cm in length) for illumination. In a typical reaction, 50 mg of the catalyst was introduced into a beaker containing 50 ml of MO (20 mg/L). The suspension was ultra-sonicated for approximately 10 min and then placed into the reactor. Once in the reactor housing, the solutions were stirred for 30 min in the dark at room temperature to allow for complete chemisorption. Once this time had elapsed, a sample of the solution was taken, and the remaining reaction solution irradiated with UV light. Additional samples were taken every 20 min, filtered through a 0.2 mm PTFE Millipore membrane filter to remove suspended catalyst agglomerates, and finally analysed using a UV–Vis spectrometer 220 (Thermo Scientific) at the wavelength of 456 nm to determine the concentration of the dye.

The reaction rate constant (\(k_a\)) was then determined assuming quasi first order kinetics using the following equation:

\[
\ln \frac{C_0}{C} = k_a t
\]  

(2)

where \(C_0\) is the concentration of the dye in solution after chemisorption, \(C\) is the concentration at time \(t\), and \(k_a\) is the reaction rate constant.

3. Results and Discussion

3.1. Synthesis of Silica from Sugar Cane Bagasse

The SiO\(_2\) source in this study was sugarcane bagasse ash. The analysis of the compound compositions was carried out by WD-XRF analysis. The XRF spectra and analysis data of sugarcane bagasse ash are shown in Figure 1 and Table 1, respectively. The XRF results indicated that sugarcane bagasse ash was dominated by the SiO\(_2\) component as much as 92%. The SiO\(_2\) content increased after dealumination with 1 M HCl which helped to remove impurities in sugarcane bagasse ash [13]. The finding of XRF results in this study are in line with the research reported by Norsuraya et al. [13] which found that after acid treatment, the silica composition increased by 1.7 times from the initial composition of 53% to 88%. This silica content is also in accordance with the research of Worathanakul et al. [14] which reported that the acid treatment method was able to increase the silica composition in ash with the obtained silica composition by 89%. In addition, research reported by Drummond and Drummond [15] that the SiO\(_2\) composition obtained was 97% which is higher than the composition obtained in this study.

![Figure 1. XRF spectra of sugar cane bagasse after acid treatment.](image)
Table 1. XRF analysis data of sugarcane bagasse after acid treatment.

| Composition | %-weight |
|-------------|----------|
| Na₂O        | 0.420    |
| MgO         | 0.363    |
| Al₂O₃        | 0.618    |
| SiO₂        | 91.7     |
| P₂O₅        | 0.171    |
| SO₃         | 0.182    |
| Cl           | 0.740    |
| K₂O         | 4.86     |
| CaO         | 0.587    |
| Fe₂O₃       | 0.249    |
| CuO         | 0.0507   |
| ZnO         | 0.0235   |
| Rb₂O        | 0.0255   |

3.2. Catalyst characterizations

Figure 2a shows the XRD patterns TiO₂/SiO₂ composites with varying TiO₂/SiO₂ ratio compared with neat SiO₂ and TiO₂. The XRD pattern of neat TiO₂ samples shows peaks at 2θ = 25.3°, 37.9°, 48°, 54°, 55.1° and 62.7° which are characteristic of the (101), (004), (200), (105), (211), and (204) anatase phase crystal facets (JCPDS 84-1286), respectively, while peaks at 2θ = 27.5°, 36.1°, and 41.3° corresponded to the (110), (101), and (111) rutile phase crystal facets (JCPDS 88-1175). The XRD pattern of the neat SiO₂ was characterized by a broad peak at 2θ = 21.5° corresponded to the characteristic of amorphous SiO₂ phase. In addition, the peak at 2θ = 21.9°, 28.3°, and 40.5° are corresponded to the presence of distributed K₂O on the SiO₂ surface (JCPDS 47-1701) which is in agreement with the XRF results (Table 1). The diffraction peaks of TiO₂ with a main component of anatase phase and a small fraction of rutile phase can be observed for TiO₂/SiO₂ composites. The existence of amorphous SiO₂ phase was still observed in 1TiO₂-3SiO₂ and 1TiO₂-1SiO₂ composites indicating that there is a transformation of amorphous into crystalline phase by incorporating more TiO₂ content. The XRD patterns provide clear evidence that incorporation of Si atoms into the TiO₂ lattice, suggesting Ti-O-Si bonding is existed. The fraction of anatase and rutile phase was calculated by using Spurr equation. Based on the Figure 2b, it can be seen that the ratio of rutile phase fraction (Xₐ) to anatase phase fraction (Xₐ) increased by increasing SiO₂ content.

Figure 2. (a) XRD patterns and (b) ratio of rutile phase to anatase phase fraction (Xₐ/Xₐ) for TiO₂-SiO₂ composites compared to the neat TiO₂ and SiO₂.
Figure 3 provide representative SEM images and particle sizes distribution of the TiO$_2$/SiO$_2$ composites compared with neat TiO$_2$ and SiO$_2$ catalysts. The SEM images of SiO$_2$ from sugarcane bagasse ash (Figure 3a) show that the particles were found to be irregular-shaped with pre-dominantly tubular-shaped and rich in porous particles with fibrous morphology. For the neat TiO$_2$ samples (Figure 3b), the particles cluster consisting of agglomerated nanoparticles and can be identified as a non-ordered and porous structures. In the case of 3TiO$_2$-1SiO$_2$ (Figure 3c), 1TiO$_2$-1SiO$_2$ (Figure 3d), and 1TiO$_2$-3SiO$_2$ (Figure 3e) depicts that amorphous SiO$_2$ (in the form of mainly tubular-shaped) is interspersed and surrounded highly crystalline agglomerated spherical TiO$_2$ nanoparticles. It is also show that the majority of the TiO$_2$-SiO$_2$ particles are also well-dispersed nanospheres within a lightly compacted aggregate and with a broad particle size distribution. Larger tubular-like shape amorphous SiO$_2$ particles were present with TiO$_2$ particles are being observed on/in those particles.

Figure 3 SEM image of (a) SiO$_2$ (from sugarcane bagasse) (b) TiO$_2$ (c) 3TiO$_2$-1SiO$_2$ (d) 1TiO$_2$-1SiO$_2$ (e) 1TiO$_2$-3SiO$_2$ in magnification of 500 times.

3.3. Catalytic activity assessment

The photocatalytic activity of the TiO$_2$/SiO$_2$ composites synthesized at different TiO$_2$/SiO$_2$ ratio was evaluated in the decolorization reaction of Methyl Orange (MO) as depicted in Figure 4. Figure 4a clearly shows that MO is a very stable dye which is resistant to self-photo degradation. Neat SiO$_2$ exhibited negligible activity as expected given by the insulating properties of the material. Marginal activity was displayed by TiO$_2$. For TiO$_2$/SiO$_2$ composites, the photocatalytic activity of 1TiO$_2$-3SiO$_2$, 1TiO$_2$-1SiO$_2$, and 3TiO$_2$-1SiO$_2$ enhanced by 1.8, 2.8, and 3-folds compared with neat TiO$_2$. The enhanced of photocatalytic activity might be due to several aspects: (i) TiO$_2$/SiO$_2$ composites provide higher adsorption capacity and specific surface area compared to neat TiO$_2$ which can promote strong surface adsorption ability to dye molecules and thus reactive radicals can easily react with dye molecules adsorbed on catalyst surface[16]. (ii) TiO$_2$/SiO$_2$ composite possess more hydroxyl group on the surface than neat TiO$_2$ which can capture photoinduced holes to generate reactive hydroxyl radicals[17]. (iii) TiO$_2$/SiO$_2$ composite promote generation of Ti$^{3+}$ which can lower band gap energy and trap photoinduced electron to superoxide radicals[9, 18, 19]. In addition, the role of hydroxyl and superoxide anion radicals can be determined and quantified using isopropyl alcohol (IPA) and benzoquinone (BQ) as quenchers/scavengers, respectively[20]. It has been proved that both radicals play significant roles in the photocatalytic degradation of methyl orange[21].
3.4. Proposed mechanism

A schematic depicting photocatalytic degradation of methyl orange over TiO$_2$/SiO$_2$ composite has been proposed, derived from the catalyst characteristics, experimental findings and relevant literatures. Initially, UV light promote the excitation of electron from valence band to the conduction band. Then, electron in the conduction band react with oxygen to generate superoxide radical (•O$_2^-$) and holes in the valence band react with water to form hydroxyl radicals (•OH). Since the adsorption capacity of TiO$_2$/SiO$_2$ composites is higher than neat TiO$_2$ and neat SiO$_2$ [16], thus the methyl orange either in the interface of TiO$_2$ and SiO$_2$ particles or SiO$_2$ particles react with both radicals (•O$_2^-$ and •OH). In addition, the TiO$_2$/SiO$_2$ composite possess more surface hydroxyl groups than the neat TiO$_2$ and neat SiO$_2$ sample so that surface hydroxyl groups can capture the photoinduced holes to produce active hydroxyl radicals and prevent electron–hole recombination, simultaneously[17]. This proposed mechanism clearly highlights that modification of TiO$_2$ photocatalyst with SiO$_2$ (sourced from sugarcane bagasse waste) could enhance photocatalytic efficiency.

**Figure 4.** (a) Photocatalytic degradation of methyl orange and (b) the apparent rate constant without a presence of catalyst (orange), neat SiO$_2$ (black), neat TiO$_2$ (red), 1TiO$_2$-3SiO$_2$ (blue), 1TiO$_2$-1SiO$_2$ (pink), and 3TiO$_2$-1SiO$_2$ (green) under UV light irradiation.

**Figure 5.** Schematic mechanism of photocatalytic degradation of methyl orange on TiO$_2$/SiO$_2$ composite.
4. Conclusion

TiO₂–SiO₂ composites was successfully synthesized by sol-gel method using sugarcane bagasse ash waste as a silica source. By increasing the addition of TiO₂ content, the transformation phase from amorphous to crystalline phase was obtained and amorphous SiO₂ is interspersed by highly crystalline TiO₂ nanoparticles. The small amount of silica addition, i.e. 3TiO₂–1SiO₂ can enhance photocatalytic efficiency for MO degradation by 3-folds compared with the neat TiO₂. The study clearly demonstrates the power of renewable silica source (i.e. from sugarcane bagasse ash waste) and the potential it holds as a useful approach to advancement photocatalyst performance in the future research for efficient, cheap and abundant catalysts for photocatalytic degradation of organic pollutant.

5. References

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