Utilization of Coal Fly Ash and Rice Hull Ash as Geopolymer Matrix-cum-Metal Dopant Applied to Visible-Light-Active Nanotitania Photocatalyst System for Degradation of Dye in Wastewater

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Abstract: Geopolymer (GP) spheres made from coal fly ash (FA) and rice hull ash (RHA) waste products are utilized as both support matrix and dopant applied to titania (TiO$_2$) photocatalyst for organic dye degradation in wastewater. Processing of FA and RHA via suspension-solidification method resulted in GP spheres with nanoporous morphology. The nanocrevices enabled low-energy sol-gel TiO$_2$ coating technique because they served as anchoring sites on the geopolymer surface that favored rigidity and larger surface area. The GP-TiO$_2$ system has been characterized by infrared spectroscopy, X-ray diffraction and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy. Diffuse reflectance spectroscopy revealed a narrowing of the GP-TiO$_2$ system optical band gap due to the interaction of metal dopants contained in RHA and FA with TiO$_2$, thus making the GP-TiO$_2$ system a visible-light-active photocatalyst, as confirmed by methylene blue dye degradation measured through UV-Vis spectroscopy.

Keywords: geopolymer; titania; sol-gel; dye degradation in water

1. Introduction

Titania (TiO$_2$) is a nontoxic, inexpensive and stable ultraviolet photocatalyst used in wastewater treatment facilities that produces reactive hydroxyl (·OH) and superoxide (O$_2^-$·) radical species when it comes in contact with water and oxygen that converts organic dyes into nontoxic anionic by-products [1]. Two of the most common forms of titania are anatase and rutile crystal phases with band gap energies of ~3.2 and ~3.0 eV, respectively [1,2]. Among the two polymorphs, anatase TiO$_2$ has better photocatalytic activity than rutile despite its wider band gap due to its crystallographic orientation that allows better exciton transport and faster charge carrier migration on its surface, which leads to the formation of more radical species that facilitates the oxidative degradation process [3,4]. In general, solar light, which is the conventional photocatalytic activator of titania, produces low conversion efficiency due to the fact that the absorption range of anatase (λ = 385 nm) constitutes only 3–5% of the solar spectrum. However, these issues can be addressed by (1) particle size reduction and (2) doping [5]. Particle size reduction creates defect sites within the solid state structure that reduces the electron
creates added energy states that narrow the optical band gap width to produce a visible-light-active TiO$_2$ [6–12].

Another drawback in using TiO$_2$ powder in photodegradation of dyes in wastewater is its agglomeration, phase transformation and high filtration costs for recovery, which are addressed by supporting TiO$_2$ on a solid medium [13]. One type of material that may serve as a TiO$_2$ support matrix is fly ash [14–16] and its processed derivative, geopolymer. Geopolymers are inorganic polymers made of aluminum–silicon–oxygen cross-links, produced at temperatures lower than 100 °C by chemical activation of an aluminosilicate-rich waste material [17].

Figure 1 shows an overview of the process used in this study for the photodegradation of organic dye in wastewater, starting with the geopolymer synthesis employing rice hull ash (RHA) as the activator and fly ash (FA) as the aluminosilicate source. RHA is a silica-rich waste generated by rice-producing countries such as the Philippines, which may be used as a substitute to commercial water glass solution (WGS) since the production of commercial WGS involves high-temperature calcination (at about 1400–1500 °C) of sodium carbonate (Na$_2$CO$_3$) and quartz sand/silica (SiO$_2$) that generates various gaseous pollutants such as CO$_2$, dust and sulfur oxides [18]. FA, correspondingly, is also a waste material that is generated by coal powerplants and typically consists of silicon dioxide (SiO$_2$), aluminum oxide (Al$_2$O$_3$), ferric oxide (Fe$_2$O$_3$) and calcium oxide (CaO) [19]. These precursors are abundant waste materials produced in various industrial processes and are considered practical and suitable starting materials for the preparation of porous geopolymer spheres. Recently, TiO$_2$ nanobelts were grown on the geopolymer surface via vapor growth, where the stability of geopolymer spheres to TiO$_2$ deposition has been established [20]. However, the high-temperature deposition process in the study opposes the aim of creating an environment-friendly functional material. It is, therefore, necessary to search for a practical, minimal-energy coating method that may be replicated on the industrial scale, such as sol-gel. Sol-gel technique is a low-temperature method of producing solid molecules in nanoscale with high purity [21]. The green chemistry approach in its synthesis, as well as its nontoxic nature, qualify the sol-gel process as a sustainable coating technique for the in situ formation of anatase TiO$_2$ on the geopolymer surface. Furthermore, the metal components of the precursor waste materials will serve as dopants to anatase TiO$_2$ that will make the photocatalyst system visible-light-active.

Figure 1. Schematic diagram of the overall process employed in this study for the photodegradation of organic dye in wastewater using visible-light-active titania.

In this paper, geopolymer spheres are synthesized using suspension-solidification method [22], utilizing a synergistically-mixed system of two abundant waste products, fly ash and rice hull ash. The resulting spherical geopolymer with a porous surface provides greater surface area for rigid in situ anatase TiO$_2$ growth via the minimal-energy, low-waste and nontoxic sol-gel coating technique. The visible light catalytic activity of the TiO$_2$-coated geopolymer (GP) spheres are then confirmed against methylene blue dye degradation.
2. Results

2.1. Synthesis of Geopolymer Spheres Using Rice Hull Ash as an Activator

With the aim of producing an environmentally-friendly material, we opted to synthesize our own water glass solution using rice hull ash, since the commercially-available WGS involves high amounts of energy for its production. In our previous study [20], we reported the optimum conditions for maximum extraction of silicate species in rice hull ash. Table 1 presents the chemical composition of rice hull ash used in this study, where the ~70% SiO$_2$ content makes it suitable to be used as chemical activator. Figure 2a shows the infrared profile of commercial WGS and RHA-based WGS, with comparable peaks at 1641 cm$^{-1}$ and 1014 cm$^{-1}$, which are assigned to OH and Si–O–Si stretching peaks, respectively. Furthermore, the infrared profile of the GP spheres synthesized using the WGS (Figure 2b) show similar peaks as well, demonstrating that the FA, with 2.5:1 ratio of SiO$_2$–Al$_2$O$_3$ (Table 1), was effectively activated using the RHA-based WGS. The formation of a geopolymer results in broadening, a shift to a higher wavenumber of the Si–O–Si stretch at 1082 cm$^{-1}$ and a decrease of the O–H stretch at 1600 cm$^{-1}$ due to the formation of the Si–O 3D network in the GP system [23]. This 3D network system is further evidenced by the appearance of the characteristic Al–O–Al and Si–O–Al stretching bands at 849 and 778 cm$^{-1}$, respectively. Thus, the WGS derived from RHA is a suitable substitute for the commercial WGS in producing GP spheres. From here on, the term geopolymer pertains to GP spheres synthesized using the RHA-derived WGS.

Table 1. Chemical composition from X-ray fluorescence (XRF) of fly ash (FA) and rice hull ash (RHA).  

| Analyte          | Fly Ash | Rice Hull Ash |
|------------------|---------|---------------|
| Fe$_2$O$_3$      | 50.2%   | 8.2%          |
| SiO$_2$          | 18.18%  | 72.2%         |
| CaO              | 18.01%  | 7.1%          |
| Al$_2$O$_3$      | 7.14%   | -             |
| K$_2$O           | 1.55%   | 8.5%          |
| Others           | 4.85%   | 4.0%          |

Figure 2. Infrared profile of (a) water glass solution (WGS) and (b) geopolymer (GP) sphere prepared using (-) commercial and (--) extracted WGS.

Figure 3a presents scanning electron microscopy (SEM) analysis of a GP bead showing an uneven surface with nonuniform pores, where its corresponding energy dispersive x-ray (EDX) analysis reveals mainly oxygen and silicon elemental composition, as well as trace amounts of aluminum, iron, magnesium and calcium metals. These pores and crevices are key points in providing maximized active sites suitable for the in situ growth of TiO$_2$.
Figure 3. Scanning electron microscopy (SEM) image (left) and energy dispersive x-ray (EDX) spectra (right) of (a) geopolymer (GP) and (b) TiO$_2$-coated GP (GP + TiO$_2$). (Inset of SEM image: actual image of GP spheres).

The X-ray diffraction (XRD) profile of RHA and FA, presented in Figure 4, shows an amorphous nature with crystalline phases of quartz, magnetite, alumina and calcite units. On the other hand, the diffraction patterns of the GP sphere show sharper peaks than its precursors that result from the geopolymerization (formation of ordered Si–O–Si and Si–O–Al 3D networks) of FA and RHA.

Figure 4. X-ray diffraction (XRD) pattern of (a) rice hull ash (RHA), (b) fly ash (FA), (c) geopolymer (GP), (d) titania (TiO$_2$) and (e) TiO$_2$-coated GP sphere (GP + TiO$_2$). 1—quartz; 2—magnetite; 3—alumina; 4—K$_2$O; 5—calcite; 6—anatase. Peaks are assigned based on their corresponding Joint Committee on Powder Diffraction Standards (JCPDS) diffraction data.
2.2. TiO$_2$ Coating of the GP Sphere via Sol–Gel Synthesis

The mechanism of nanotitania formation via sol–gel technique involves a series of hydrolysis and condensation reactions. Figure 5 shows a schematic of the titania formation process using titanium isopropoxide (TTIP) as a precursor, via sol–gel technique, on the GP surface. Initially, the GP spheres were sonicated in water and isopropanol to remove any adsorbed species. They were then transferred to a colorless solution of TTIP and isopropanol and allowed to establish a sorption equilibrium by vigorous stirring. The slow addition of a solution of water and isopropanol into the GP and TTIP solution facilitated the slow hydrolysis of TTIP, enabling the chain hydrolysis–condensation reactions to happen on the GP surface. Figure 6 shows the infrared spectra profile of TiO$_2$, GP and GP + TiO$_2$. The decrease in ~3400 and ~1600 cm$^{-1}$ bands is due to the surface adsorbed H$_2$O being replaced with TiO$_2$ species; while the disappearance of ~2900 and ~1300 cm$^{-1}$ bands is due to the removal of carbon groups (formed from the reaction of atmospheric CO$_2$ and unreacted NaOH originally present in the geopolymer surface) when the sample was annealed at 500 °C. Furthermore, the characteristic Si–O–Si vibration at 1087 cm$^{-1}$ and 799 cm$^{-1}$ for the GP sphere is shifted to a lower wavenumber (1012 cm$^{-1}$) and decreased in intensity for both GP and TiO$_2$, which is attributed to the formation of Si–O–Ti coordination that distorts the SiO$_4$ tetrahedra due to TiO$_2$’s larger ionic radius [24]. Additionally, the expected 950 cm$^{-1}$ Ti–O–Si vibration is overlapped in the broad Si–O–Si vibration at 1150 cm$^{-1}$, while the distinct 540 cm$^{-1}$ Ti-O–Ti vibration causes broadening in the 500–600 cm$^{-1}$ area in the GP + TiO$_2$ IR spectra.

![Figure 5. Schematic diagram of the hydrolysis–condensation reaction of titanium isopropoxide (top) in solution and (bottom) on the GP surface.](image)

![Figure 6. Infrared profiles of TiO$_2$, geopolymer and TiO$_2$-coated geopolymer sphere.](image)
The X-ray diffraction data of sol–gel synthesized TiO$_2$ and TiO$_2$-coated GP sphere presented in Figure 4 reveal that the in situ synthesis of TiO$_2$ on the geopolymer surface by the sol–gel technique produced TiO$_2$ in the anatase phase and that the sol–gel process and sample annealing did not change the GP molecular structure. Furthermore, the anatase TiO$_2$ grew on the GP surface, with spherical morphology with an average diameter of 200 nm, as shown in Figure 3b. Its corresponding EDX data reveal O, Si, Ti and various trace elemental components present in the GP + TiO$_2$ system, which complements its diffraction profile in Figure 4.

Figure 7a shows the diffuse absorbance spectra of anatase TiO$_2$ (synthesized using the same sol–gel method performed sans GP sphere) and GP + TiO$_2$ system that reveal its optical properties. The spectra of TiO$_2$ showed an intense absorption in the ultraviolet region, while a further increase and red shift (beyond 400 nm) for the GP + TiO$_2$ absorbance is observed. This indicates narrowing of the band gap width, as shown in the Tauc plot (Figure 7b), where it was calculated that $E_g = 3.195$ eV for TiO$_2$ was narrowed to $E_g = 3.145$ eV for the GP + TiO$_2$ system. The calculated band gap width from the diffuse reflectance ultraviolet-visible spectra (DRS) data, together with the FTIR, EDX and XRD data, indicate that the components in the GP sphere from RHA and FA precursors served as dopants to anatase TiO$_2$ that resulted in a visible-light-active photocatalyst system via sol-gel coating of TiO$_2$ on the GP sphere. The metal components, as characterized by EDX (Figure 3), are said to narrow the optical band gap of TiO$_2$ due to interstitial (Ca [25,26]) and substitutional (Mg [27,28], Fe [29,30]) doping in the TiO$_2$ lattice based on their respective ionic radius.

![Graph](image_url)

**Figure 7.** (a) UV-Vis diffuse absorbance spectra and (b) Tauc plot of TiO$_2$ and GP + TiO$_2$.

### 2.3. Photocatalytic Degradation of Methylene Blue

To demonstrate the visible light activity of the GP + TiO$_2$ system, the photocatalytic degradation of methylene blue (MB) experiment was performed. The adsorption-desorption equilibrium between methylene blue and the GP + TiO$_2$ system was first established to eliminate calculation errors due to the initial physical adsorption of MB on the TiO$_2$ surface. Figure 8 shows the change in concentration at varying times of MB with the GP + TiO$_2$ system stirred in the dark, where it was found that 30-min equilibration time is sufficient for the actual photodegradation experiment.
Figure 8. Adsorption–desorption equilibrium of methylene blue (MB) on GP and GP + TiO\textsubscript{2} surfaces at varying times under dark conditions.

Figure 9a displays the absorbance spectra of MB solution (5 ppm) in varying durations of exposure (0–8 h) to the TiO\textsubscript{2}-coated GP catalyst. In the Figure 9a inset, the actual color intensity based on the presence/degradation of MB is seen. It can be noted in Figure 9b that the optimal and practical exposure time is at 8 h, which registered 48.18% degradation efficiency as the plateaued value was observed. Furthermore, the TiO\textsubscript{2}-GP system was subjected to reusability testing (cycle 2), which resulted in 42.5% degradation efficiency at an optimal 8-hour exposure time.

3. Materials and Methods

3.1. Chemicals

Rice hull ash (RHA) and fly ash (FA) were obtained from a materials recovery facility and a coal-fired power plant in Central Luzon Region in the Philippines, respectively, and were used as received. Sodium hydroxide (NaOH), titanium isopropoxide (TTIP), anhydrous 2-propanol, polysorbate 80, 50% hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}) and polyethylene glycol (average molecular weight = 600 g/mol, PEG-600) (Sigma-Aldrich, St. Louis, MO, USA) were used without further processing or purification.

3.2. Synthesis of Geopolymer (GP) Spheres

The geopolymer spheres were synthesized by modification of the suspension–solidification method procedure [22], wherein the WGS was synthesized by base-extraction of silicates in rice hull
ash, following a previously reported procedure [20]. The as-received RHA was refluxed with 12 M NaOH (3:1 wt%) and 100 mL distilled water at 90 °C for 4 h, and the resulting clear brown filtrate was reduced to 50% vol by heating to 95 °C. This activating solution (AS) was then added to the as-received FA in 1:2 AS–FA wt% and was mixed for several minutes. Then, pore-forming agents 1.5% polysorbate solution and 50% H₂O₂ were also added and mixed. The resulting slurry was loaded on a 10 mL needleless syringe and dropped on a 90 °C PEG–600 solution at a rate of 1 drop/min. The formed geopolymer spheres, with average diameter of 0.50 cm, were harvested, washed twice in distilled water and oven dried at 60 °C for 24 h.

3.3. Synthesis of Titania-Coated GP (GP + TiO₂) Sphere

One hundred pieces of GP spheres (~8 g) were cleaned by sonicating in water and isopropanol for 30 minutes each. They were then added to a solution of 2 mL TTIP and 100 mL isopropanol and stirred at 600 rpm. Then, a solution of 2 mL H₂O in 100 mL isopropanol was dropped at a rate of 1 drop/min. The resulting colorless solution was heated to 60 °C, forming a clear gel. It was heated in an oven at 200 °C for 24 h and annealed at 450 °C for 5 h.

3.4. Material Characterization and Measurement

The chemical composition of the precursor and final products were determined using X-ray fluorescence (XRF) analysis via EDX–720 (Shimadzu, Kyoto, Japan) with 50 kV and a current of 35 A. Fourier transform infrared (FTIR) analysis was done on a Nicolet Magna IR–550 (Thermo Fisher Scientific, Waltham, MA, USA) instrument in KBr disc. X-ray diffraction (XRD) analysis was done using Ultima IV (Rigaku, Tokyo, Japan) diffractometer using CuKα (λ = 1.452 Å), where the samples were scanned from 5–90° (2θ) at a rate of 0.02°/min. The XRD diffractograms were analyzed using the powder diffraction file database from the Joint Committee of Powder Diffraction Standards (JCPDS). Morphological and elemental analysis was performed using scanning electron microscope coupled with energy dispersive x-ray (SEM–EDX) analysis on a Phenom XL 2015 LR1 (Thermo Fisher Scientific, Waltham, MA, USA), where the samples were coated with gold and then placed on carbon tape. Diffuse reflectance ultraviolet-visible spectra (DRS) were measured using a UV-3600 (Shimadzu, Kyoto, Japan) by diluting the sample in KBr powder and were converted to a Kubelka–Munk function. Optical band gap calculation was done by Tauc plot of the DRS data.

3.5. Photocatalytic Experiment

The photocatalytic testing was done in triplicate using a self-made photoreactor employing an indoor fluorescent white light (60 W, full spectrum) that was 12 inches away from the reaction cell. Four TiO₂-coated spheres (total surface area = 3.14 cm²) were placed in 50 mL of 5 ppm MB solution. Then, the absorption-desorption equilibrium was determined for each test by stirring in the dark, obtaining 3 mL aliquots every 15 minutes. After establishing the absorption-desorption equilibrium, the coated spheres were irradiated with visible light for 8 h, where the final absorbance was measured using a U-2900 UV-Vis spectrophotometer (Hitachi High-Technologies Corp., Tokyo, Japan). The photocatalytic efficiency was calculated by:

\[
\text{% efficiency} = (1 - C/C_0) \times 100\%
\]

where \(C_0\) and \(C\) represent the initial MB concentration and final MB concentration at time \(t\), respectively.

To test for reusability, the TiO₂-coated spheres were regenerated by rinsing with water prior to reuse.

4. Conclusions

Rice hull ash and fly ash waste products can be utilized to produce spherical geopolymer matrices with porous nanoscale crevices which provide maximized surface area for in situ formation of photocatalytic TiO₂ coating. Furthermore, the stated structural properties of the matrix enable the
minimal-energy, low-waste and nontoxic sol-gel anatase TiO$_2$ outer layer formation. Moreover, it is also determined that the metal components found in rice hull ash and fly ash act as dopants that narrow the optical band gap of the geopolymer-TiO$_2$ system, thereby resulting in a visible light photocatalyst. The RHA-FA geopolymer matrix and dopant applied to the catalytic TiO$_2$ is deemed to be a synergistic and sustainable system ideal for degradation of organic pollutants in murky waters where low-light energy is beneficial to activate photocatalysis.

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