Research Article

Synthesis and Characterization of Mesoporous Silica SBA-15 and ZnO/SBA-15 Photocatalytic Materials from the Ash of Brickyards

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SBA-15 has been successfully synthesized from ash of brickyard with the surface area of 700.100 m²/g, pore volume of 0.813 cm³·g⁻¹, and pore size of 7.5 nm. SBA-15 material has been modified by a simple impregnation method, and the ZnO/SBA-15 obtained material retains the hexagonal structure of SBA-15, but the hexagonal capillary tube size is reduced, in which the surface area, volume of pores, and pore size is 212.851 m²·g⁻¹, 0.244 cm³·g⁻¹, and 3.7 nm, respectively. The ZnO/SBA-15 materials were investigated by the photodegradation of methylene blue under ultraviolet light and exhibited significant photocatalytic activity with the reached MB removal efficiency about 96.69%.

1. Introduction

SBA-15 is a mesoporous silica sieve based on uniform hexagonal pores with a narrow pore size distribution and a tunable pore diameter of between 5 and 15 nm [1]. The important properties of SBA-15 such as high surface area of typically 400–900 m²·g⁻¹, high thermal and mechanical stability, inert, and not harmful to the environment make SBA-15 a well-suited material for various applications. It can be used in environmental treatment for adsorption and separation [2, 3], as a support material for catalysts [4, 5] and as a template for the production of ordered mesoporous carbon [6].

SBA-15 is usually synthesized in a cooperative self-assembly process under acidic conditions using the triblock copolymer pluronic 123 (EO20PO70EO20) as template and tetraethoxysilane (TEOS) as the silica source [1–7]. However, high cost of complex TEOS processing motivates the development of alternative silica source. The recent studies are the synthesis of highly siliceous SBA-15 from inorganic silica sources as sodium silicate [8] and the silica inorganic precursor with the presence of impurities of industrial waste product which typically consist of metal oxide containing 42 wt% SiO₂ [9].

In this paper, the ash of brickyards was used as the silica precursor for preparation of mesoporous silica SBA-15 because its main component was the rice husk ash that has high silica content. In Vietnam, the rice husk ash of brickyards is an abundantly available waste material; therefore, SBA-15 synthesized by using rice husk ash as the silica source will bring economic efficiency.

Moreover, the mesoporous silica SBA-15 materials are particularly interesting as host matrices for loading metals and semiconductor nanoparticles. These supported metal oxide particles have important applications in photocatalysis [10, 11]. In this study, to further improve the efficiency of the treatment of dyers, ZnO has been chosen to develop on internal and external surfaces of SBA-15 materials by the impregnation method. Recent studies have demonstrated the good photocatalysis of ZnO in the decomposition reactions of toxic organic compounds in wastewater due to high quantum efficiency, redox potential, high physicochemical stability, nontoxicity, and low cost [12–14].
2. Materials and Methods

2.1. Preparation of SBA-15. The ash of brickyard was cleaned and stirred in concentrated NaOH solution at 100 °C for 3 hours. Then, the mixture was filtered with activated carbon to obtain a transparent solution (solution A). SBA-15 was synthesized under strong acidic condition (pH = 1) using the triblock copolymer pluronic 123 (EO_{20}PO_{70}EO_{20}) as the template [1] and solution A as the silica source.

2.2. Preparation of ZnO/SBA-15. ZnO/SBA-15 was synthesized by impregnating SBA-15 with zinc acetate solution. 0.901 g Zn (CH_{3}COO)_{2}.2H_{2}O was dissolved in 42 mL of ethanol solvent along with stirring at 70 °C for 2 hours. The obtained solution was cooled down to room temperature, and then was added 0.5 g SBA-15 with strong stirring. The resulting mixture was dried at 80 °C for 24 hours to remove the solvent. Then, the obtained samples were calcinated in air by raising the temperature from room temperature to 550 °C over 1 hour period and holding at 550 °C for 1 hour.

2.3. Structural Characteristics Analysis. FTIR spectra were obtained by using a FTIR-8400S Shimadzu spectrometer. X-Ray diffraction patterns were recorded by the D2 Phaser system using Cu K{\alpha} radiation (λ = 1.54 Å) with 2θ of 10° to 80°. With Brucker D8 Advance using Cu Kα radiation (λ = 1.54 Å) with 2θ of 0.1° to 10°. The nitrogen adsorption/desorption isotherms were surveyed by a Quantachrome Nova 2000e meter, measured isothermal adsorption N2 at 77 K and the adsorption rate of desorption P/Po from 0.01–0.99, by taking surface area from 0.05–0.35. The structure of materials is observed via TEM images and recorded on a JEOL apparatus (model: JEM-1400, Japan) with 100kV voltage. The sample preparation technique is used for recording scanning electron microscopic images (SEM) and analyzing EDS on the same device. The sample recorded image on JSM-IT200 InTouchScope™ scanning electron microscope.

2.4. Experimental Protocol of Methylene Blue Removal. In this section, the light of the ultraviolet lamp 50 W was chosen to investigate the photocatalytic activities of ZnO/SBA-15 materials because ZnO is appropriate for short wavelength optoelectronics [11–13].

The experiments were carried out in 100 mL Erlenmeyer flask by mixing 25 mg ZnO/SBA-15 adsorbents and 50 mL of MB solution with 56 ppm of initial concentration. The solution was stirred at 600 rpm on a stirrer at a constant temperature for 10 min in the dark to equilibrate and then stirred for 60 min under ultraviolet light. After shaking the solution, the reaction mixtures were centrifuged, and the filtrate was analyzed using a spectrophotometer. The adsorbed quantity and removal efficiency of MB were calculated using equations (1) and (2), respectively:

\[ q_e = \frac{(C_o - C_e)V}{m}, \]  
\[ \text{% removal} = \frac{C_o - C_e}{C_o} \cdot 100, \]  

where \( q_e \) is the amount of dye in mg per gram of adsorbent. \( C_o \) and \( C_e \) are, respectively, initial concentration and equilibrium time of MB (mg·L^{-1}). \( V \) is the volume of solution. \( m \) is the mass of adsorbent.

2.4.1. Effect of Photocatalytic Time on MB Removal Capability. 5 mg ZnO/SBA-15 was added to 50 mL MB solution with initial concentration, \( C_o = 56 \) ppm. The mixture was stirred for 10 min in the dark to equilibrate and then stirred for 30 min to 360 min under ultraviolet light.

2.4.2. Effect of Solid/Liquid Ratio on the Adsorption and Photocatalytic Capacity of ZnO/SBA-15. The solid/liquid ratio is determined by the following formula:

\[ \sigma = \frac{m_{\text{ZnO/SBA-15}}}{V_{\text{MB}}}, \]  

where \( m_{\text{ZnO/SBA-15}} \) is the weight of ZnO/SBA-15 and \( V_{\text{MB}} \) is 50 mL methylene blue solution.

The solid/liquid ratios of 0.1 to 3 were selected to investigate the removal capacity of ZnO/SBA-15. The mixture was stirred for 10 min in the dark and 60 min under ultraviolet light.

3. Results and Discussion

3.1. Structural Characteristics of SBA-15 Materials. SBA-15 synthesized from rice husk ash was analyzed using the FTIR infrared spectrum is shown in Figure 1. In the FTIR pattern, a broad peak at 3500 cm\(^{-1}\) is the O-H bond stretching vibration of the silanol groups and the remaining absorbed water molecules in the samples. The presence of a weak peak at 2890 cm\(^{-1}\) is supposed to be C-H stretching vibration, and it suggests that almost all surfactant was ousted. The bending vibration of the O-H of water appears at wavenumber 1635 cm\(^{-1}\). The strong characteristic peak of siloxane (\(-\text{Si-O-Si}-\)) appears at 1082 cm\(^{-1}\). The Si-OH bond stretching vibration of the silanol groups is observed at 961 cm\(^{-1}\), and the Si-O bond rocking vibration was shown at 490 cm\(^{-1}\). These functional groups correspond to the FTIR pattern of SBA-15 from TEOS [1].

XRD pattern of the SBA-15 sample is shown in Figure 2. Figure 2(a) shows the small-angle XRD patterns of SBA-15, scan range of 2 theta degrees of 0.5° to 10°. The typical XRD pattern for SBA-15 exhibits three characteristic peaks relative to the (100), (110), and (200) planes at 2θ of 0.96°, 1.45°, and 1.7°. These peaks characterize the two-dimensional hexagonal structure of SBA-15 which matches SBA-15 synthesized using TEOS as the silica source. So, SBA-15 material was successfully synthesized from the ash of brickyards.
The high-angle XRD pattern of SBA-15, scan range 2θ of 10°–80° is shown in Figure 2(b) shows that there is no SiO₂ crystal phase in SBA-15, so we can confirm the porous structure of SBA-15 is SiO₂ amorphous.

The porosity and capillary structure of SBA-15 and ZnO/SBA-15 materials were studied by nitrogen adsorption/desorption isotherms and are shown in Figures 3 and 4. IUPAC adsorption isotherm of type IV shows that SBA-15 belongs to mesoporous material with mesopore size. In addition, the hysteresis type of H1 is characteristic of mesoporous materials with cylindrical pores and has a uniform pores size. Figure 3(b) shows the SBA-15 synthesized from the ash of brickyards with uniform pore size and concentrated in 6–12 nm.

From the data obtained by the BET method to calculate the surface area of the SBA-15 is 700.10 m²/g, the volume of pores and pore size, respectively: 0.813 cm³/g and 7.5 nm. On the contrary, the molecule methylene blue is seen as a rectangular box with dimensions 17.0 × 7.6 × 3.3 Å [15]. Therefore, SBA-15 synthesized from the rice husk ash with size suitable for good adsorption of methylene blue.

TEM images of SBA-15 are shown in Figure 5 with the parallel, uniform channels (Figure 5(a)), and hexagonal structure has formed with uniform pore size, about 7.8 nm (Figure 5(b)).

3.2 Structural Characteristics of ZnO/SBA-15 Materials. Figure 6(a) displays the high-angle XRD patterns of ZnO/SBA-15. XRD patterns show the peaks at 2θ = 31.77°; 34.42°; 36.25°; 47.50°; 56.60°; 62.86°; 66.38°; 67.96°; 69.10°; and 72.86°, corresponding to the reflection from (100), (002), (101), (102), (110), (103), (200), (112), (201), and (004) planes of the standard ZnO crystal (JCPDS 36-1451). This result is consistent with the UV-Vis absorption spectra of SBA-15 and ZnO/SBA-15 (Figure 6(b)). In the UV-Vis absorption spectrum, ZnO/SBA-15 presents an amorphous and a crystalline ZnO phase shown by an absorption band in the region 240–420 nm.

Small-angle XRD patterns of the ZnO/SBA-15 and SBA-15 samples are shown in Figure 7. ZnO/SBA-15 material still has 3 peaks of (100), (110), and (200) planes of the hexagonal space group, indicating that the introduction of ZnO into SBA-15 did not collapse the mesoporous structure of a two-dimensional hexagonal structure.

TEM images of SBA-15 and ZnO/SBA-15 are shown in Figure 8. Figure 8(b) shows that the ZnO/SBA-15 material
retains a tubular structure like SBA-15 (Figure 8(a)). Figure 8(d) shows that ZnO/SBA-15 retains the hexagonal structure of SBA-15, but the hexagonal size is reduced due to ZnO covering the inner surface of the capillary, making the capillary wall thickening and capillary tube size is reduced. The obtained results of the BET and BJH method show that the surface area, volume of pores, and pore size of ZnO/SBA-15 is 212.851 m$^2$·g$^{-1}$, 0.244 cm$^3$·g$^{-1}$, and 3.7 nm, respectively (Figure 4).

The surface of ZnO/SBA-15, SBA-15, and mass percent of elements in the materials were observed by SEM and EDS...
The EDS patterns (Figures 9(a) and 9(b)) show the presence of zinc elements in the SBA structure-15. SBA-15 surface (Figure 9(c)) is the bond of large arrays, while the surface of ZnO/SBA-15 (Figure 9(d)) has the bond of smaller particles. The mass percent of elements of SBA-15 and ZnO/SBA-15 materials are listed in Table 1.

Therefore, ZnO has been successfully dispersed on the surface of SBA-15 which synthesized using the ash of brickyards without collapsing the mesoscopic order of a two-dimensional hexagonal structure.

3.3. MB Removal Capacity of Materials

3.3.1. Effect of Photocatalytic Time on MB Decomposition Capability. The optimal photocatalytic time in the MB treatment of ZnO/SBA-15 was investigated and shown in Figure 10. This investigated result shown that during the photocatalytic period from 30 to 60 min, MB concentration decreased rapidly, from 60–180 min, MB concentration fell slowly. In the period of 180–360 min, the concentration of MB is almost unchanged because the mixture was saturated. So, the optimal photocatalytic time to decompose MB (96.69% removal efficiency) is 180 mins.

3.3.2. Effect of Solid/Liquid Ratio on the Adsorption and Photocatalytic Capacity of ZnO/SBA-15. The optimal solid/liquid ratio of ZnO/SBA-15: MB was investigated and shown in Figure 11. The results showed that when the ratio of solids/liquids was adjusted in the range of 0.1–3.0, the removal efficiency of MB increased slowly (95.84%–96.75%). The efficiency was reached the highest when the ratio was 0.1 (corresponding to 5 mg ZnO/SBA-15) and decreased sharply when the solids ratio increased. The reason may be due to the light shielding effect between particles in the suspension, and this shielding is greater when the concentration of particles in the suspension is high [16]. Therefore, the solid/liquid ratio of 0.1 was chosen to use in experimental of methylene blue decomposition in solution. The maximum amounts of
Figure 8: TEM images of SBA-15 (a, c) and ZnO/SBA-15 (b, d).

Figure 9: EDS spectra and SEM images of materials: (a) EDS spectrum of SBA-15; (b) EDS spectrum of ZnO/SBA-15; (c) SEM images of SBA-15; and (d) SEM images of ZnO/SBA-15.
MB adsorbed (Q, mg·g⁻¹) by ZnO/SBA-15 along with other adsorbents is shown in Table 2. In comparison with other adsorbents, ZnO/SBA-15 is promising material for removal of the MB from aqueous solutions.

3.3.3. Efficient Catalyst Reuse. After each decomposition experiment, the ZnO/SBA-15 catalyst was recovered by filtration, washing with water, and dried for reuse. The efficient catalyst reuse of ZnO/SBA-15 material after reusing 5 times are shown in Figure 12. The investigated result indicates that the MB removal efficiencies of ZnO/SBA-15 after reusing 5 times were reached more 94%.

4. Conclusions

SBA-15 mesoporous material was successfully prepared by using the ash of brickyards. The SBA-15 material has the surface area of 700.100 m²·g⁻¹, pore volume of 0.813 cm³·g⁻¹, and pore size of 7.5 nm. These results were determined by the analysis methods as FTIR, XRD, TEM, EDS and BET, BJH.

The results of the structural characteristic methods (FTIR, UV-Vis, XRD, SEM, TEM, EDS, BET, and BJH) shown that the material ZnO/SBA-15 was successfully synthesized. The mesoporous channels of SBA-15 is also retained in ZnO/SBA-15 with surface area, pore volume, and pore size, respectively: 212.851 m²·g⁻¹, 0.244 cm³·g⁻¹, and 3.7 nm.

The methylene blue removal capacity of ZnO/SBA-15 was generally investigated. The MB removal efficiency of ZnO/SBA-15 was reached 96.69% with initial concentration of MB of 56 ppm; the photocatalytic time of 180 mins and the optimal solid/liquid ratio of 0.1. Especially, the MB removal efficiencies of ZnO/SBA-15 after reusing 5 times were reached more 94%.

Data Availability

The data used to support the findings of this study are included within the article.
Conflicts of Interest
The authors declare that they have no conflicts of interest.

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