ZnO-SiO$_2$ and Zn$_2$SiO$_4$ Synthesis Utilizing Oil Palm Leaves for Degradation of Methylene Blue Dye in Aqueous Solution

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Abstract

A new approach was developed for the green synthesis of ZnO-SiO$_2$ composite and Zn$_2$SiO$_4$ using zinc nitrate and sustainable silica precursor, oil palm (Elaeis guineensis) leaves (OPL). The products were synthesized at two different reaction temperatures through calcination in an open-air furnace at 500 and 1000 °C, respectively, and further identified with an X-ray diffractometry (XRD) analysis. The composite indicated by the presence of peaks at 2θ = 31.7°, 34.4°, 36.3°, 47.6°, 56.6°, and 62.9°, corresponds to ZnO and also revealed amorphous SiO$_2$ at 2θ = 21°. Conversely, Zn$_2$SiO$_4$ was acknowledged at 2θ 25.6°, 31.50°, 34.0°, 39.5°, 48.9°, 56.5° and 65.6°, with crystalline silica at 2θ = 21.9°. The results showed the morphology of both products exhibited similar agglomeration based on scanning electron microscopy (SEM) analysis. Both products (ZnO-SiO$_2$ composite and Zn$_2$SiO$_4$) possessed the capacity to degrade methylene blue (MB) under sunlight irradiation with efficiency of 85.9% and 69.3%, respectively.

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Keywords: Composite, Oil palm leaves, Silica precursor, ZnO-SiO$_2$, Zn$_2$SiO$_4$

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Introduction

The Synthesis of ZnO-SiO$_2$ composite and other ZnO and silica interactions, including the formation of ZnSiO$_4$ was extensively demonstrated in this research. An example involves the use of zinc sulfate as ZnO precursor mixed with SiO$_2$ in an ammonium hydroxide solution. The resulting product was due to the evaporation of water from the gel at 500 °C for 2 hours [1]. In addition, a combination of ZnO and Palash leaves powder in water/HCl was also employed at ambient temperatures. Interestingly, the product generated was effectively applied in the refinery to treat waste by photocatalytic approach [2, 3].

Further methods were developed to synthesize the composite on Si glass plates using zinc acetate and triethanolamine (TEOS) in the presence of diethanolamine base. Subsequently, amorphous ZnO/SiO$_2$ film formed after heating the plates at 400 °C, was useful in photodegradation and decolorization of methyl green under UV irradiation [4]. Moreover, the synthesis of ZnO-coated SiO$_2$ was conducted through monodispersed silica spheres prepared by using the Stober method and zinc acetate with ethanol-water solvent in the presence of triethanolamine [5]. Additional studies reported the composite was synthesized under the sol-gel system from TEOS and also with zinc acetate having specific photoluminescence [6].

The reaction between ZnO and SiO$_2$ precursors through other approaches provides additional products apart from the ZnO-SiO$_2$ composite being a successfully prepared available chemical, e.g. (TEOS) and zinc nitrate as SiO$_2$ and ZnO source, respectively. The resulting product is due to the sol-gel process in water-glycerol as solvent at 120 °C followed by heating to 400 °C. However, the further reaction occurred at elevated temperature (1000 °C) to finally form ZnSiO$_4$ [7]. On the other hand, ZnSiO$_4$ was also obtained using hydrothermal process at 130 - 180 °C without further treatment [8]. Moreover, amorphous silica and zinc nitrate in the presence of NaOH (to increase the pH reaction mixture and heated at the same temperature) is used to achieve pure ZnSiO$_4$ nanorods [9]. Also, other shapes are derived by a related process, but with variation in pH [10–11]. In similar hydrothermal method, the spindle-like ZnSiO$_4$ product was easily acquired by involving zinc nitrate and sodium silicate in the presence of sodium hydroxide after heating at 220 °C [12]. Additional techniques were developed using solid-state reaction between SiO$_2$ and ZnO or other precursors to form Zn$_3$SiO$_4$ at high temperature, i.e., the use of colloidal gel prepared from zinc nitrate and silica sol, heated at 1000 - 1400 °C [13]. In addition, use of zinc acetate and TEOS to form the sol-gel followed by thermal treatment at 800 – 1000 °C was also evaluated [14]. Recently, heating ZnO-SiO$_2$ composite (synthesized from ZnO and TEOS using the wet-chemical synthetic method) at 900 °C under open-air revealed the formation of Zn$_3$SiO$_4$ nanorods [15].

Based on results, several paths were involved in the synthesis of ZnO-SiO$_2$ and Zn$_3$SiO$_4$, but only few focused on biogenic silica from sustainable resources. Specifically, there have been limited studies concerned on the use of oil palm leaves as silica precursor in advanced material preparation. Therefore, this research intends to explore other possible means in the synthesis of both silica based compounds above (ZnO-SiO$_2$ and Zn$_3$SiO$_4$) using oil palm leaves as silica precursor by in situ degradation of Si-complexes. Furthermore, current products were also applied as photocatalyst to investigate their utility. In addition, the idea to make use of oil palm leaves (OPL) is greatly dependent on the outcome from other studies [16, 17].

Experimental Section

Zinc nitrate was acquired from Merck and used without further purification. OPL powder was prepared from the oil palm leaves from a plantation. Demineralized water served as solvent and washing material. The synthesis was carried out under solution-solid reaction. Typically, 50 mL of zinc nitrate (0.25 M) was moved into a crucible containing 4 g of OPL to form a paste after heating at 70 °C for 15 hours. Subsequently, heat was again applied to the mixture in a furnace at 500 °C for 4 hours to form a product called ZnSi-5. Similar procedure was initiated for other reaction mixtures heated at 1000 °C to produce other product called ZnSi-10. Meanwhile, the resulting solid materials were collected and characterized (XRD and SEM) in an attempt to verify the properties. Furthermore, catalytic activities of ZnSi-5 or ZnSi-10 were evaluated in order to remove MB following a slight modification in the process [24]. For instance, 5 mL of methylene blue (MB, 5 mg L$^{-1}$) and 25 mg of ZnSi-5 or ZnSi-10 were mixed in separate transparent bottles and kept for 1 hour for adsorption-desorption equilibrium. Both reaction mixtures were irradiated using sunlight for 3 hours (11.00 a.m. – 2.00 p.m.) together with control sample (MB solution without any catalyst). All photo-
catalytic degradation experiments were repeated twice and the MB photo-degradation was monitored by measuring absorbance at 664 nm with a spectrophotometer (UV/Vis) Agilent 60. The final concentration was calculated using calibration curve prepared from a series of MB concentrations (0; 1; 2.5; 5; 7.5; 10 ppm) with correlation coefficient \( R = 0.998 \). The photo-catalytic degradation efficiency has been calculated using \( \% \text{ degradation} (\% D) \):

\[
\% D = \frac{C_i - C_f}{C_i} \times 100\%
\]

The \( C_i \) and \( C_f \) corresponds to the initial and final concentration of dye before and after photo-irradiation.

**Results and Discussion**

A mixture of zinc nitrate solution and oil palm leaves powder was heated using hotplate magnetic stirrer to form a sticky paste. Figure 1 shows the further treatment of the paste at temperatures 500 and 1000 °C to generate two products with grey coloration which was then characterized by XRD.

Figure 1(a) shows significant peaks at \( 2\theta = 31.7^\circ, 34.4^\circ, 36.3^\circ, 47.6^\circ, 56.6^\circ, \) and \( 62.9^\circ \), clearly corresponds to zinc oxide, while the product revealed silica points were not observed, although existed in amorphous form. The XRD profiles of the current product showed similar patterns compared to previous results [7, 18–20] and JCPDS No. 36-1451. The formation of SiO\(_2\) in ZnSi-5 is caused by the degradation of silicon complexes in OPL, started by carbonization and subsequently in situ formation of amorphous silica for ZnO-SiO\(_2\) composite due to increasing temperature up to 500 °C.

The different phenomenon observed in Figure 1(b) was a product reaction at 1000 °C and the presence of crystalline silica at \( 2\theta = 21.9^\circ \). Zinc oxide peaks were not clearly indicated, meaning the compound already reacted with silica produced in situ from OPL. However, new peaks were discovered at \( 2\theta = 25.6^\circ, 31.5^\circ, 34.0^\circ, 39.5^\circ, 48.9^\circ, 56.5^\circ \) and \( 65.6^\circ \), predicted to be zinc silicate (Zn\(_2\)SiO\(_4\)) based on the JCPDS No. 37-1485, and also supported by XRD profiles generated, showing similarities to previous results reported [11, 18, 21].

The product of Zn\(_2\)SiO\(_4\), in the current approach, is explained by the interface reaction between Zn\(^{2+}\) and O\(^{-}\) with silica shell at high temperatures [11, 22]. Other studies mentioned that the formation of Zn\(_2\)SiO\(_4\) from ZnO and SiO\(_2\) started 700 °C and clearly identified at 800 °C [23]. Based on the current results and other previous studies, plausible formation reactions of ZnO-SiO\(_2\) and Zn\(_2\)SiO\(_4\) are as follow:

\[
\begin{align*}
\text{Si-complex} & \xrightarrow{(in \text{ oil palm leaves})} \text{SiO}_2 \\
\text{Zn(NO}_3)_2 & \xrightarrow{[500 \degree C]} \text{ZnO} \\
\text{ZnO + SiO}_2 & \xrightarrow{[1000 \degree C]} \text{ZnO-SiO}_2 \\
\text{ZnO-SiO}_2 & \xrightarrow{[500 \degree C]} \text{Zn}_2\text{SiO}_4
\end{align*}
\]

**Figure 1.** XRD pattern of reaction product (a) ZnSi-5 and (b) ZnSi-10.

Figure 2 provides information on further analysis of the synthesis not clearly distinguished using SEM. Subsequently, Figure 2 shows the product of ZnSi-5 indicating corresponding irregular particles, while for ZnSi-10, aggregates were formed in terms of morphology as captured in Figure 2(c) – (d). Hence, Zn\(_2\)SiO\(_4\) proves to be more agglomerate and compact.
Figure 2. SEM images of (a-b) ZnSi-5 and (c-d) ZnSi-10.

Figure 3. Visualization of MB 5 ppm of (a) without any treatment, (b) treated without catalyst under sunlight irradiation, (c) treated with ZnSi-5 under sunlight irradiation, and (d) treated with ZnSi-10 under sunlight irradiation.

Figure 4. Representative spectra of MB (a) without any treatment, (b) treated without catalyst under sunlight irradiation, (c) treated with ZnSi-5 under sunlight irradiation, and (d) treated with ZnSi-10 under sunlight irradiation.

Tabel 1. Effect of photocatalytic reaction conditions on MB degradation under sunlight irradiation.

<table>
<thead>
<tr>
<th>Reaction System</th>
<th>%D</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB treated without catalyst</td>
<td>16.5</td>
</tr>
<tr>
<td>MB treated with ZnSi-5</td>
<td>85.9%</td>
</tr>
<tr>
<td>MB treated with ZnSi-10</td>
<td>69.3%</td>
</tr>
</tbody>
</table>

The mechanism of photocatalysis processes may follows general approaches for the corresponding catalysts as proposed by other researchers [26, 32].
Both compounds (ZnO-SiO$_2$ and Zn$_2$SiO$_4$) are induced by sunlight irradiation producing valence bond holes (h$^+$) and electrons (e$^-$), thus revealed the intermediate ZnO$^+$-SiO$_2$ and Zn$_2$SiO$_4^+$, respectively. The holes (h$^+$) react with water or hydroxyl ions to form OH$^-$•, while the electrons (e$^-$) with oxygen to form O$_2$••. The active species, including OH$^-$•, O$_2$•• and h$^+$ react in situ with MB to form certain intermediate compounds as proposed by other reported results [32]. Furthermore, some possible intermediates such as N,N-dimethyl-para-phenylenediamine and 1,2,4-trihydroxybenzene were identified when MB was attacked by OH$^-$•, O$_2$•• and h$^+$ species [33], and subsequently converted to carbon dioxides and water by ring opening reactions.

Conclusions

A composite containing ZnO-SiO$_2$ was synthesized from zinc nitrate (synthetic precursor) with oil palm leaves powder (natural precursor) at 500 °C. The reaction carried out at 1000 °C, revealed ZnO further reacted with amorphous silica to form Zn$_2$SiO$_4$ along with the rest of amorphous silica changed to crystalline silica phase. Moreover, the Zn$_2$SiO$_4$ has lower activity than ZnO-SiO$_2$ in the degradation of MB under sunlight.

Conflict of Interest

The authors declare there is no conflict of interest.

References


