TiO$_2$/ZnO nanocomposite photocatalyst: Synthesis, characterization and their application for degradation of humic acid from aqueous solution

Muhammad Ali Zulfikar$^{1*}$, Anggia D. Chandra$^1$, Rusnadi$^1$, Henry Setiyanto$^1$, Nurrahmi Handayani$^1$, and Deana Wahyuningrum$^2$

$^1$ Analytical Chemistry Research Group, Bandung Institute of Technology, Bandung, Jawa Barat, 40132 Indonesia

$^2$ Organic Chemistry Research Group, Bandung Institute of Technology, Bandung, Jawa Barat, 40132 Indonesia

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Abstract

In this study, TiO$_2$/ZnO nanocomposite (TZC) photocatalysts were successfully prepared through a sol-gel process followed by calcination. TZC photocatalyst characterization was performed by XRD, FTIR, SEM, TEM and UV-vis diffuse reflectance spectroscopy (DRS). The photocatalytic activity of the TZC photocatalyst is studied systematically by the degradation of humic acid (HA) from aqueous solutions under visible light irradiation. Photodegradation of HA from aqueous solutions shows excellent photocatalytic activity. The rate of photocatalytic degradation increases with increasing catalyst loading and light intensity. From kinetic studies, it showed that HA photodegradation using TZC photocatalysts can be explained by the pseudo-first-order kinetic model. The results also show that this method has excellent potential to remove HA from peat water.

Keywords: humic acid, photocatalytic degradation, nanocomposite, TiO$_2$/ZnO, photocatalyst

1. Introduction

Humic materials are the major organic compounds contained in the peat water (Stevenson & Goh, 1971). Humic compounds can be described as negatively charged polyelectrolyte macromolecules because of the carboxylic and phenolic functional groups which are contained in their structure (Abbt-Braun, Frimmel, & Schulten, 1989). This property cause these compounds are difficult to degrade and potentially produce the other compounds with carcinogenic properties (Zouboulis, Chai, & Katsoyiannis, 2004). The compounds also have aromatic functional groups which contribute to the presence of color in the peat water (Moore, 1985). Conventional treatment processes include coagulation and flocculation (Lee, Morad, Teng, & Poh, 2012; Matilainen, Vepsäläinen, & Sillanpää, 2010; Ng et al., 2012), membrane filtration (Lamsal, Montreuil, Kent, Walsh, & Gagnon, 2012; Metsämäinen, Sillanpää, Bhatnagar, & Mänttäri, 2014), photocatalysis (Ng, Kho, Liu, Lim, & Amal, 2014; Philippe et al., 2010) and adsorption techniques (Zulfikar et al., 2016; Zulfikar, Afriyansih, Nasir, & Handayani, 2017; Zulfikar, Afrita, Wahyuningrum, & Ledystuti, 2016; Zulfikar, Wahyuningrum, Makti, & Setiyanto, 2016) have been developed to remove these substances.

ZnO is being considered as an alternative material to TiO$_2$ because they have similar properties as a semiconductor. Moreover, ZnO exhibits a higher electron mobility and longer photo-generated electron lifetime than TiO$_2$, which is beneficial for photocatalytic degradation of dyes (Huang et al., 2013). It can be synthesized by various synthesis methods (Huang et al., 2013, Song, Zhang, Wu, & Wei, 2012; Uddin et al., 2012; Wang et al. 2011). However, it can only absorb a
very small ultraviolet part of the solar spectrum because of its wide band gap, which is similar to TiO$_2$. Therefore, it is essential to develop new photocatalysts with a smaller band gap to harvest visible light.

In the present work an attempt was made to enhance the photocatalytic activity of ZnO by synthesizing of TiO$_2$/ZnO using a sol-gel process followed by calcination treatment. Photocatalytic activity of TiO$_2$/ZnO nano composite (TZC) photocatalyst was evaluated by measuring the photodegradation of humic acid (HA) under visible light irradiation.

2. Materials and Methods

2.1 Materials

All materials were commercial reagent grade and used as received without further purification. The reagents used for the preparation of TZC photocatalyst were tetraethyl ortho titanate (TEOT) (Sigma-Aldrich), zinc acetate dehydrate (Sigma-Aldrich), citric acid (Sigma-Aldrich), ethylene glycol (EG) (MW = 36,000) (Sigma-Aldrich). Deionized water was used in all experiments. For the photodegradation evaluated, humic acid (HA) (Sigma-Aldrich) was chosen as the model organic pollutant.

2.2 TiO$_2$/ZnO nano composite photocatalyst fabrication

A series of ZnO combined TiO$_2$ catalysts (abbreviated as TZC) with different concentration of TiO$_2$ were prepared by changing the quantity of TEOH added to the ethanol. First, TEOH with various concentrations of Ti (1%, 3%, and 5%) in ethanol were mixed with 25 mmol of citric acid and stirred. Subsequently, a portion of Zn(CHR)$_2$CoO$_2$·2H$_2$O was added dropwise to the solution by sufficiently ultrasonic dispersing for 1 h at 80 $^\circ$C to obtain a homogeneous solution. During the reaction, 5% (w/w) of polyethylene glycol (PEG) solution was added and stirred continuously until a light yellow sol was formed. The addition of PEG as additive was carried out to increase the nano composite performances (Khodadadi, Sabeti, Moradi, Azar, & Farshid, 2012). The catalysts were designated as TZC-X where “X” represents the nominal mass percentage content of TiO$_2$ in ZnO. Pure TiO$_2$ was prepared by the same procedure but by replacing the ZnO with another material (TZC-1). The morphology of the TZC photocatalyst was investigated using scanning electron microscope (SEM) (JEOL JSM 6360) and using high resolution transmission electron microscope (HRTEM, JEOL Model JEM 1400). The diffuse reflectance UV-Vis spectra (DRS) were recorded on a Thermo Scientific Evolution 220 system equipped with a Labsphere diffuse reflectance accessory to obtain the reflectance spectra of the catalysts over a range of 200-800 nm. BaSO$_4$ (Labsphere USRS-99-010) was used as a reference in the measurement. The measured spectra were converted from reflection to absorbance by the well-known Kubelka–Munk method.

2.4 Photocatalytic activity studies

The photocatalytic degradation of humic acid (HA) from aqueous solution in the presence of TZC photocatalyst was performed in a self-designed photo reactor at room temperature. Photocatalytic studies were performed to investigate the effect of TiO$_2$ composition in the photocatalyst, pH solution, distance of lamp from the material, power of lamp, and the comparison between photolysis, adsorption, and photocatalytic.

2.4.1 The effect of TiO$_2$ composition in the nanocomposite

Initially, a 100 mL of aqueous HA solution (25 mg/L) and 0.08 g TZC-1 were placed inside the reactor and was continuously stirred for 1 h and irradiated under Hg lamp (Philips) at 15 W. The HA solution was separated from the photocatalysts by centrifugation for 20 min to determine the concentration of HA using UV-Vis spectrophotometer model 1601 (Shimadzu, Japan) in the wavelength of 254 nm at various times of light exposure (0.5; 1; 1.5; 2; 2.5; and 3 h). The same procedure was carried out by changing TZC-1 with another material (TZC-3, TZC-5 and ZnO). The percentage of degradation efficiency was calculated by following Equation 1:

$$\%D = \left(\frac{C_0 - C_t}{C_0}\right) \times 100\%$$

where %D was percentage of degradation, and $C_0$ and $C_t$ were the HA concentration which were measured initially and at a certain time after irradiation, respectively.

2.4.2 Influence of the dosage of catalyst material

A 100 mL of HA solution (25 mg/L) was stirred continuously and irradiated by a Hg lamp (15 W) for 1 h. The measurement of HA concentration after irradiation was performed for each of dosages variation (in the range of 0.02-0.20 g) by UV-Vis spectrophotometer at 254 nm.

2.4.3 Effect of pH

A 100 mL of HA solution (25 mg/L) with various pH (pH 1-12) were added with TZC-1 (in accordance with the results obtained in testing of the nanocatalyst’s amount effect). The photocatalytic process was carried out under Hg lamp (15 W) with continuously stirring for 1 h. HA concentration was measured by using UV-Vis spectrophotometer in the wavelength of 254 nm.
2.4.4 Effect of lamp distance from the surface of solution

A 100 mL of HA solution (25 mg/L) was mixed with TZC-1 (in optimum pH and dosage), continuously stirred for 1 h, and irradiated under Hg lamp (15 W). The test was carried out with varying the distance of lamp with the material surface (7.5; 11.5; and 15 cm). Concentration of HA was measured by using UV-Vis spectrophotometer in the wavelength of 254 nm.

2.4.5 Influence of Hg lamp power

A 100 mL of HA solution (25 mg/L) was mixed with TZC-1 (in optimum pH, dosage, and distance of lamp with the surface), continuously stirred for 1 h, and irradiated under Hg lamp (15 W). The test was carried out with varying the power of lamp (8; 10; and 15 W). Concentration of HA was measured by using UV-Vis spectrophotometer in the wavelength of 254 nm.

2.4.6 Comparison of photolysis, adsorption, and photocatalytic

A 100 mL of HA solution (25 mg/L) was continuously stirred and treated as follows: a) For photolysis, HA solution only stirred without nanocatalyst material addition and no irradiation; b) For adsorption, HA solution was added with TZC-1 0.08 g, without irradiation; c) For photocatalytic, HA solution was added with TZC-1 0.08 g and irradiated under Hg lamp (15 W). HA concentration measurements were performed on the three different conditions for 0.5; 1; 1.5; 2; 2.5; and 3 h by using UV-Vis spectrophotometer at 254 nm.

2.5 HA photodegradation from peat water (real sample)

Peat water samples containing HA as coexisting anions were collected from Rimbo Panjang, a sub district of Kampar in Riau Province, Indonesia, which is a source for water supply. Photodegradation of HA from peat water samples was performed using the batch systems and similar procedure described earlier. The peat water samples at original pH were fed onto the photo reactor and irradiated for various time of light exposure (0.5; 1; 1.5; 2; 2.5; and 3 h). Table 1 shows the characteristics of the peat water.

<table>
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<tr>
<th>Parameters</th>
<th>Unit</th>
<th>Result</th>
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</thead>
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<td>Color</td>
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<tr>
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<tr>
<td>pH</td>
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<tr>
<td>Manganese</td>
<td>mg/L</td>
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<tr>
<td>Calcium</td>
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<tr>
<td>Magnesium</td>
<td>mg/L</td>
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</tbody>
</table>

Figure 1. a) XRD patterns of ZnO and TZC photocatalyst; b) FTIR spectrum of ZnO (black) and TZC photocatalyst (red); c) DRS spectrum of TZC photocatalysts.

3. Results and Discussion

3.1 Characterization of nano composite photocatalyst

3.1.1 XRD analysis

Investigation by X-ray diffraction was carried out to analyze the phase composition and crystallite size of the samples. The addition of Ti to ZnO affects the formation of the material.

Figure 1a shows the XRD pattern of both ZnO and TZC photocatalyst samples. The peak appears at 2θ =31.61°, 34.36°, 36.25°, 47.75°, 56.55°, 62.05°, 67.87°, 68.84°, and 72.54° correspond to the ZnO reference pattern (PDF: 96-230-114). In the TZC-3 and TZC-5 samples, after increasing the titanium oxide molar ratio, Ti and Zn were doped and the new
intense peaks were detected. The XRD line at 35.17° corresponds to Zn$_2$TiO$_4$, or to ZnTi$_{1.5}$O$_4$ (JCPDS 04-006-5709).

3.1.2 FTIR analysis

FTIR spectra of ZnO and TZC-1 are shown in Figure 1b. The broad band at 3400 cm$^{-1}$ and the small band at 1600 cm$^{-1}$ are related to the water and hydroxyl groups physically adsorbed in the sample (Ullah, Khan, & Khan, 2014; Pozan & Kambur, 2014; Khodadadi, Sabeti, Moradi, Azar, & Farshid, 2012). Absorption bands between 400 and 750 cm$^{-1}$ are associated with symmetrical and asymmetrical stretching frequencies of the Zn-O and Ti-O vibrational bands (Ullah et al., 2014; Stoyanova et al., 2013).

3.1.3 UV-vis diffuse reflectance spectra analysis

The UV-vis diffuse reflectance spectra (DRS) of TZC-1, TZC-3 and TZC-5 were compared (Figure 1c). Using the well-known Kubelka-Munk equation, the band gap of pure ZnO and TZC-1, TZC-3 and TZC-5 were 3.22, 3.17, 3.18, and 3.18, respectively. There is a slight change in the band-gap energy among the TZC as prepared at different TiO$_2$ compositions. However, the decrease in TZC photocatalyst band gap energy can be attributed to the synergistic effect between the conduction bands of ZnO and TiO$_2$. Some sub-bands are formed by introducing impurities and defects to the forbidden band of TiO$_2$ thereby reducing the band-gap energy (Pei & Leung, 2013; Perkgoz et al., 2011; Štengl, Bakardjieva, & Murafa, 2009).

3.1.4 SEM and TEM analysis

Morphology of the TZC photocatalyst was characterized by SEM as shown in Figure 2. The beam energy used in SEM experiments was 20 kV, which has been marked in the SEM image. The surface of as-spun, randomly oriented, TZC photocatalyst appears relatively smooth and uniform. In TZC-5, with a further increase in TiO$_2$, several large aggregations of different sizes were dispersed that decreased the photocatalytic activity.

TZC morphology in different TiO$_2$ compositions was also characterized by HRTEM. The surface morphology and size of the samples vary depending on the composition of Ti as shown in Figure 3. The TZC consists of compactly packed nanocrystallites surface and randomly oriented. Diameter of the nanocrystallites was calculated from HRTEM image (see Figure 3a-c). The diameter ranges from 84.22 to 185.95 nm for TZC-1, 62.53-134.81 nm for TZC-3 and 67.63-111.02 nm for TZC-5.

3.2 Photocatalytic studies

3.2.1 Effect of TiO$_2$ composition toward photocatalytic process

The photocatalytic activity of the pure ZnO and TZC was evaluated by the photocatalytic degradation of HA under visible light irradiation. From Figure 4a, it can be seen that the percentage of degradation decrease with increasing the TiO$_2$ content. The degradation percentage of ZnO, TZC-1, TZC-3, and TZC-5 were 80.63%, 89.43%, 88.58%, and 81.23%, respectively. In the TZC catalyst, photogeneration electron transfer occurs from the conduction band of light-activated ZnO to the conduction band of light-activated TiO$_2$ and, conversely, the transfer of holes can occur from the valence band of TiO$_2$ to the ZnO valence band (Pei & Leung, 2013; Sukharev & Kershaw, 1996). Meanwhile, due to the...
differences in the energy band position, there exists a synergetic relationship between ZnO, anatase and rutile to reduce the band-gap energy (Pei & Leung, 2013) and this could increase the photocatalytic activity of TZC. However, the addition of a high dose of the TiO$_2$ to ZnO causes the formation of photoinactive Zn$_2$TiO$_4$ compound (such as XRD analysis confirmed above) which will reduce photocatalytic activity (Jantabar-Darzi & Mahjoub, 2009; Moradi, Azar, Farshid, Khorrami, & Givianrad, 2012; Wang, Xu, Wang, & Zhao, 2005).

From the results, it indicates that the nano-photocatalyst material with the most excellent photocatalytic ability is TZC-1.

### 3.2.2 Effect of catalyst dosage

The effect of catalyst dosage on photocatalytic activity is represented in Figure 4b. From the graph, the optimum dosage of catalyst which can be added during the photocatalytic process is 1.4 g/L. From 0.02 to 1.14 g/L, the percentage of HA degradation increase, but immediately decreased after adding more TZC-1. Under a low catalyst dosage, the degradation efficiency is enhanced by increasing the catalyst dosage due to the increasing number of active sites on the photocatalyst surface. Beyond a certain limit of catalyst dosage, the solution becomes turbid and thus blocks light radiation for the reaction to continue and therefore the percentage degradation starts to decrease (Pei & Leung, 2013). In addition, an increase in the amount of catalyst causes catalyst particle aggregation and this ends up in reducing the available surface area for light absorption. Similar results have been reported by (Evgenidou, Fytianos, & Poulios, 2005; Pei & Leung, 2013; Nagaveni, Sivalingam, Hegde, & Madras, 2004; Sobana & Swaminathan, 2007).

### 3.2.3 Effect of pH

The pH of an aquatic environment plays an important role in photocatalytic degradation of organic compounds because it determines the surface charge of the catalyst and the size of aggregate formed. Therefore, the pH of the solution can play a key role in photocatalytic oxidation of pollutants (Bansal, Chaudhary, & Mehta, 2015). The effect of pH value in the range from 4 to 10 on visible radiation degradation of HA was investigated under photoreaction with an initial HA concentration of 25 mg/L, 14 mg of TZC-1 and the results are shown in Figure 4c. The rate of degradation decreases with increasing pH. The efficiency of degradation in aqueous medium is related to the surface charge properties of the TZC-1. The point of zero charge (pzc) for ZnO/TiO$_2$ is at pH 6 (Zuas, Budiman, & Hamim, 2013). The surface charge is positive at pH value lower than pH pzc, neutral at pH pzc and negative at higher pH pzc value. The surface of photocatalyst is positively charged in an acidic solution and negatively charged in alka-
line solution (Bansal et al., 2015). HA consist of many phenolic and carboxylic functional groups. As is known, phenolic and carbonyl functional group can be ionized in aqueous medium and may acquire a negative charge in aqueous medium. On the other hand, the HA molecule becomes more negatively charged as pH value increases due to ionization of carboxylic and phenolic groups of humic acid (Zulfikar et al., 2016). As a result, this will reduce the electrostatic attraction between the surfaces of TZC-1 and HA compounds and thus decrease the degradation efficiency of HA.

### 3.2.4 Effect of light distance

The influence of light distance from the surface of solution in the photocatalytic process is shown in Figure 4d. From the figure, by approaching the distance of light to the surface of the solution, the degradation percentage of HA becomes larger which indicates that the photocatalytic activity increases. It may be occurred because the light intensity is even greater if the distance of light and catalyst material becomes closer. The higher intensity facilitates the formation of hydroxyl radicals and initiates to increase the photocatalytic activity.

### 3.2.5 Effect of lamp power

The power of lamp also gives an effect on the photocatalytic activity which represented in Figure 4e. By increasing the power of the lamp, the degradation percentage of HA increases. Lamp power (Watt or J/s) is the amount of energy per unit of time which means the power is proportional to energy. In other words, the greater of power used will generate a large of energy (photon) that induces more electron-hole pairs on the surface catalyst which results in the higher of photocatalytic activity.

### 3.2.6 Comparison of photocatalytic, adsorption, and photolysis activity

According to Figure 5, by increasing the time of reaction, the percentage of degradation in photolysis curve suffered only slight changes. It can be concluded that with the conditions used in the test, HA is not degraded by the photolysis process. Different things can be seen in the adsorption curve which the percentage of HA degradation is 45.15% after 3 h of reaction indicating that ZnO can act as an adsorbent. However, when compared to the photocatalytic curve, the percentage of HA degradation gives a higher value after 3 h, i.e. 89%. These results indicate that the photocatalytic reactions show the best performance compared to photolysis and adsorption process to degrade the humic acid solution.

### 3.2.7 Kinetics modeling

The photocatalysis degradation kinetics of HA were studied by conducting reactions at various contents of TiO$_2$. Photocatalyst with as prepared samples can be expressed by degradation kinetics using the Langmuir-Hinshelwood model as follows:

\[
\ln (C_0 - C) = k \cdot t 
\]

(2)

where \(k (\text{hour}^{-1})\) is the apparent reaction rate constant, \(C_0\) and \(C\) are concentration of HA (mg/L) at time \(t = 0\) and at a given time \(t\), respectively. The pseudo first order reaction rate constant \(k\) was calculated from the graph as shown in Figure 6 and the results are given in Table 2.

When the HA concentration is reduced to 50% of its initial value, half-life \((t_{1/2})\) of the photodegradation of the HA is calculated by substituting \(C = \frac{1}{2}C_0\) into Equation 3:

\[
\ln 2 = k \cdot t_{1/2} \text{ or, } t_{1/2} = 0.693/k
\]

(3)

The half-life \((t_{1/2})\) is summarized in Table 2. From the table we may conclude that the photocatalytic rate under visible radiation is directly influenced by the TiO$_2$ content in nanocomposite photocatalyst.

### 3.3 Photocatalytic activity on the real sample (peat water)

The content of peat water is dominated by humic acids which gives it a brownish color. Photocatalytic activity on the peat water was carried out by using optimum condi-
tions that has been obtained (1.40 g/L; pH 3; 15 W; the time of reaction was 3 hours; and the distance of lamp from the solution surface was 7.5 cm). Degradation of HA plot is shown in Figure 7. Photocatalytic processes can degrade the organic compounds in peat water with a percentage of degradation of 89.34%. This could imply that the concentration of organic compounds in the peat water reduces with this value. After the reaction is complete, the color of the solution changes from brownish to colorless (Figure 8) and this indicates that HA has been successfully degraded. This may indicate that photocatalytic by using nanocatalyst based TiO$_2$/ZnO into the peat water was successfully done.

![Figure 7. Photocatalytic activity on the peat water.](image)

![Figure 8. Photographs of change in the color of peat water: (a) before, and (b) after treatment.](image)

4. Conclusions

In summary, TZC photocatalysts have been successfully prepared through a sol-gel process and used for photodegradation of HA in suspension. The photocatalytic degradation rate increases with increasing catalyst dosage and light intensity. The results of the kinetic studies show that the photodegradation of HA using TZC photocatalyst could be described by the pseudo-first order kinetic model. The present study demonstrates that the TZC photocatalyst with optimal Ti content (1% of Ti) is a potential viable photocatalyst in degrading HA and possibly other pollutants (e.g. organics in water) with degradation percentage of 89.34% under visible light irradiation.

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References


