Research Paper

Physicochemical characteristics and photocatalytic performance of Tin oxide/montmorillonite nanocomposites at various Sn/montmorillonite molar to mass ratios

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A B S T R A C T

Nanocomposites of tin oxide immobilized in montmorillonite (Mt) with various Sn/Mt mole-to-mass ratios were prepared for photocatalysis application. The prepared samples were characterized by x-ray diffraction, transmission electron microscopy, N₂ adsorption-desorption analysis, and diffuse reflectance UV-visible spectroscopy. The relationships between the physicochemical characteristics and photocatalytic activities of the materials were evaluated in terms of rhodamine B photocatalytic degradation. From the results, the samples showed that the Sn/ Mt. mole-to-mass ratio affects the increase in the interlayer space of the montmorillonite structure, and the particle size of the dispersed SnO₂ nanoparticles increases with increasing ratio, ranging from 10 to 50 nm. The BET specific surface area, pore volume, and band gap energy of the nanocomposites are related with the structural changes, which are closely related with the SnO₂ content. The materials exhibit excellent photocatalytic activity as indicated by their higher turnover number and degradation efficiency than those of SnO₂ and related photocatalysts. Statistical optimization of the effect of the physicochemical characteristics of the photocatalyst on photocatalytic activity by using the logit model revealed that SnO₂ and pH affect the degradation efficiency and initial rate of rhodamine B degradation.

1. Introduction

Metal-oxide-supported clays and clay minerals, including pillared clay, are composite materials for applications such as catalysis and adsorption, as well as for many other functional purposes. Many advantages are designed and obtained by improving the physicochemical properties of these materials from those of their raw forms for applications to obtain properties such as a high surface area, chemical stability, and enhancement of specific characteristics related to homogeneous distributions (Molina et al., 2011). The modification of a metal oxide photocatalyst into a heterostructure and composite is an important strategy to develop photocatalytic activity (Tang et al., 2016; Bai et al., 2018). Pillarization of clay minerals using metal oxides of aluminum, titanium, zirconium, chromium, zinc, tin, and others has been reported (Abdelmoula et al., 2016; Ahmad et al., 2013; Undabeytia et al., 2013a; Kar et al., 2014). The most significant issue for all these studies is that the enhancements of the physicochemical characteristics and catalytic activity are related to the homogeneous dispersion of active catalysts in the clay structure.

In a more specified application, the modification and pillarization of clays with TiO₂, ZnO, and ZrO₂ was attempted for photocatalysis applications owing to their potency in the photocatalysis mechanism (Papoulis et al., 2009; Undabeytia et al., 2013b; Zyoud et al., 2019). Aside from those metal oxides, SnO₂ is one of the potential photocatalysts. In an effort to enhance the photocatalytic activity of materials, various techniques and modifications of SnO₂ have been reported (Wang and Rogach, 2014). The modifications consist of metal-doping, particle size manipulation, and forming SnO₂ composites with other oxides or inorganic supports. The formation of metal oxide nanocomposites by utilizing silica and silica-alumina materials was reported to be effective for photocatalysis applications due to the increasing surface porosity for the supporting photocatalysis mechanism. Previously, a series of studies have been conducted for the preparation of SnO₂-pillared or SnO₂-immobilized clay minerals. However, to the best of our knowledge, there are only a few studies on this and the photocatalytic activity. Some of these studies are on the pillarization of
montmorillonite with SnO₂ for the photocatalytic degradation of dyes and antibacterial agents (Vidal and dos Santos, 2015; Gu et al., 2018; Babu and Antony, 2019; Honaramoud et al., 2020). On the other hand, photocatalysis is also a promising technique for environmental remediation technology, particularly for dye degradation in textile wastewater treatment.

To move this promising application forward, we studied the physicochemical characteristics and synthesis of SnO₂ immobilized in montmorillonite (Mt). The photocatalytic performances of the synthesized materials were evaluated by studying the photocatalytic degradation of rhodamine B dye under UV light irradiation. Based on several studies on the relationship between the physicochemical characteristics and photocatalytic activity of the metal oxide nanocomposite, the role of the Sn/Mt mole-to-mass ratios on the materials' photocatalytic activity is important to study.

2. Materials and methods

2.1. Materials

Natural montmorillonite samples were procured from East Java, Indonesia, and purified by the sedimentation method using distilled water to collect the < 2 μm fraction. The composition of the clay determined by gravimetric analysis methods was as follows: SiO₂: 59.98%; Al₂O₃: 21.11%; Fe₂O₃: 2.34%; MgO: 1.02%; and CaO: 0.69 wt%; LOI: 15.51%. Tin chloride dihydrate (SnCl₂·2H₂O), sodium hydroxide (NaOH) pellets, ethanol, and rhodamine B were purchased from Merck. All the chemicals were of analytical grade and used as received without any further purification.

2.2. Preparation of materials

A tin oxide precursor solution was made by the slow titration and vigorous stirring of a tin chloride solution with a sodium hydroxide solution to achieve an Sn/OH ratio of 1:1. A metal precursor solution was added to the montmorillonite suspension and stirred continuously for 1 h before refluxing for 4 h. The result obtained from reflux was separated and washed with water until the filtrate was free from Cl⁻ by testing with AgNO₃. The solid was dried in an oven and then calcined at 600 °C for 3 h. To evaluate the effect of the Sn content on the physicochemical characteristics of the material, the Sn molar-to-Mt mass ratios of 1.0, 2.5, 5.0, 7.5, and 10.0 mmol/g were applied, and with these variations, the obtained materials were designated as Sn1.0/Mt, Sn2.5/Mt, Sn5.0/Mt, Sn7.5/Mt, and Sn10.0/Mt, respectively.

2.3. Physicochemical characterization

X-ray diffraction (XRD) studies were carried out with a Rigaku diffractometer (Tokyo, Japan) using Ni-filtered Cu Kα radiation. The continuous scan mode was used to collect 20 data from 3 to 65° with a 0.1° sampling pitch and a 2° min⁻¹ scan rate. Scanning electron microscopy-energy dispersive X-ray (SEM-EDX) analyses were performed with a Phenom-X instrument (Singapore). N₂ adsorption-desorption analyses were conducted with a NOVA 1200 instrument (Singapore) to determine the BET specific surface area, pore volume and pore radius, and for each analysis, degassing at 100 °C for 6 h was carried out. Diffuse reflectance UV-visible (UV-DRS) spectrophotometry was performed on a JASCO V760 instrument (Tokyo, Japan) to determine the band gap energy. Transmission electron microscopy was performed using a JEOL JEM 2100F instrument (JEOL, Tokyo, Japan) operated at an acceleration voltage of 200 kV (wavelength λ = 2.51 pm). X-ray photoelectron spectroscopy (XPS) was performed using a ULVAC instrument (Quantera SXM, Japan).

2.4. Photocatalytic experiments

The photocatalysis experiments were conducted using a water-jacketed batch photocatalytic reactor equipped with a UV lamp (20 W, 360 nm). Photocatalytic degradation was conducted by mixing a photocatalyst with 500 mL of RhB solution under stirring and UV lamp illumination. For photocatalytic oxidation, 10⁻² M H₂O₂ was added to the mixture. The pH of the solutions and photocatalyst dose were varied. The concentrations of RhB in the initial and treated solutions were analyzed by UV-visible spectroscopy by using either the wavelength scan analysis or the standard curve colorimetric method. To elucidate the degradation mechanism, LC-ESI-MS was performed on a HUPAC instrument. Citric acid and methanol (1:1) were used as the mobile phase and introduced with a flow rate of 1.0 mL/min and injection volume of 20 μL. The MS analysis was performed with a spray voltage of 3.5 kV, a capillary temperature of 325 °C, a capillary voltage of 50 V, and a tube lens voltage of 120 V, and the detected mass range was from 50 to 600 m/s.

3. Results and discussion

3.1. Physicochemical characteristics of the materials

From the XRD patterns (Fig. 1a), it is seen that the raw bentonite shows a d₀₀₁ reflection located at 20° (2) = 5.71, which corresponds to a basal spacing of 15.49 Å, and other peaks at 20 = 19.99° and 35.6°, which correspond to (011) and (004) reflections, respectively. In addition to the reflections indicating the montmorillonite structure, the peak at 27° represents the quartz that usually exists in natural minerals. The presence of immobilized SnO₂ in the Sn/Mt samples is confirmed by the EDX analysis (Table 1). The data showed that 4.30 wt% SnO₂ was immobilized in the Sn0.0/Mt sample, which was obtained from the molar-to-mass ratio of 1.0, and the immobilized SnO₂ content increased with increasing the ratio. For all the samples, the calculated weight percentages were less than the total theoretical content attributed to the intercalation molar ratio. For example, for Sn1.0/Mt, approximately 15 wt% SnO₂ should be present, as all Sn precursors were immobilized.

These low amounts are related to the general mechanism of the intercalation step, which is the chemical equilibrium process. In this case, please refer to a previous work (Vidal and dos Santos, 2015), wherein the Sn precursor solution consisted of Sn(OH)₂, SnO₂, and Sn₄(OH)₆Cl₄, which are the possible ions in cation-exchange equilibrium with the native cations in the montmorillonite interlayer spaces. The equilibrium condition does not permit all the cations to enter and replace the cation positions in the interlayer region to release the unreacted Sn₂⁺ from the mixture.

The small angle XRD pattern depicted in Fig. 1b shows that pillaring with Sn molar ratios of 1 and 2.5 mmol/g affects the increase in the d₀₀₁ basal spacing. The increase in the d₀₀₁ basal spacings are shown by the shift in the d₀₀₁ reflection to 20° (2) = 5.32 and 5.58, implying that the basal spacings are 17.24 and 15.91 Å, respectively. In addition, Sn molar-to-clay mass ratios, the d₀₀₁ reflection is identified to shift to a higher angle and have a lower intensity. These d₀₀₁ reflections shifted to smaller angles represent the formation of SnO₂ pillars in the interlayer space of montmorillonite. These results are similar to those reported by previous works. However, the d₀₀₁ value in this work is lower than that of the SnO₂-montmorillonite prepared by Gu et al. (2018). The lower d₀₀₁ value presented in this study is probably due to the lower Sn molar ratio used in pillariization; that is, the molar ratio of 7.8 mmol/g was applied by Gu et al. (2018b). The noticeable pattern comes from increasing the Sn molar ratio to 5 mmol/g or more, which is demonstrated by the new peaks at 2θ = 26.2°, 33.8°, 36.2°, and 51.6°, which are attributed to the (110), (101), (200), and (211) planes of crystalline SnO₂, respectively. Meanwhile, those peaks are absent for the molar ratio of 2 mmol/g. The low content of intercalation species, which are the Sn₃⁺ polyhedrons, may affect the homogeneously
montmorillonite and other smectite minerals. Furthermore, SnO$_2$ modification seems to affect the evolution of the surface, as represented by the irregular spherical particles deposited on the surface, which are noticeably from Mt. The higher Sn content represents the more regular spherical forms, which are particularly distinctive in Sn7.5/Mt. and Sn1.0/Mt. These forms are associated with the SnO$_2$ particles, as the observed patterns are similar to patterns of SnO$_2$ nanoparticles prepared in previous studies (Gnanam and Rajendran, 2010; Abiz et al., 2012; Herrmann et al., 2019). These morphological changes are confirmed from the TEM profile (Fig. 3). (See Fig. 4.)

The TEM images show the detailed views of lattice fringes and corresponding increased spacings occurring as a result of pillerization. The lattice fringe spacings observed from the TEM image of Mt. ranged from 1.2 to 1.4 nm and increased after pillerization. The lattice fringe spacings are in the range of 1.4–1.6 nm for Sn1.0/Mt., 1.6–1.8 nm for Sn2.5/Mt., and 1.5–1.6 nm for Sn5.0/Mt., which are considerably higher than the lattice fringe spacings of Mt., which is consistent with the spacings obtained from the small angle XRD pattern presented in Fig. 1b. At a high Sn content, the SnO$_2$ particles are more visible than the interlayer space as a consequence of the formation of external SnO$_2$ particles and aggregates instead of the formation of metal oxide as pillar of the interlayer structure. The aggregate profile in these TEM images is in line with the SEM images, which exhibit the distinctive SnO$_2$ particles at high Sn contents. In addition, Sn10.0/Mt. exhibits a spherical form of the particles with sizes in the range of 10–80 nm. The sizes coincide with the SnO$_2$ crystallite mean sizes calculated using Scherrer’s formula (Eq. 1) and are listed in Table 1. The tendency of SnO$_2$ aggregation and nanoparticle formation in the dispersed form within the pillar structure by increasing the metal content is attributed to the chemical equilibrium during the intercalation process. The cation exchange capacity of montmorillonite could not accommodate the introduced amount of Sn metal precursor within the interlayer space, which leads to the formation of external aggregates. This was similarly reported for the immobilization of TiO$_2$ and ZnO into the montmorillonite structure (Chen et al., 2012; Kalmakhanova et al., 2019) (Abdenouri et al., 2016; de Lucas-Gil et al., 2020).

The surface evolution is also characterized by the change in adsorption/desorption and pore distribution profiles presented in Fig. 4. The calculated parameters include the BET specific surface area, external surface area, pore volume, and pore radius (Table 2). Increasing parameters were found for all the Sn/Mt. samples, and the BET specific surface area becomes larger with decreasing the additional Sn molar ratio. The trend of the parameters can be confirmed from the pore distribution obtained from the desorption profile.

The N$_2$ gas adsorption/desorption isotherms expressed by Mt. and Sn/Mt. are characterized as type IV with H2 and H4 hysteresis loops, according to the IUPAC classification. The Sn1.0/Mt., Sn2.5/Mt., and Sn5.0/Mt. samples are characterized by H2 hysteresis loops, which are associated with narrow slit-like pores. On the other hand, Sn7.5/Mt. and Sn10.0/Mt. demonstrate the H4 hysteresis loop pattern. The narrow slit-like pores characteristic of the H2 type correspond to the presence of channels with a smaller pore mouth than the pore body, whereas the type H3 hysteresis loop is characteristic of a very wide

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**Table 1**

Results obtained from the elemental analysis, XRD and UV-DRS analysis results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Component (%)</th>
<th>Component (wt.)</th>
<th>d$_{am}$</th>
<th>Crystallite size</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mt</td>
<td>2.34</td>
<td>27.98</td>
<td>68.11</td>
<td>1.64</td>
<td>nd</td>
</tr>
<tr>
<td>Sn1.0/Mt</td>
<td>9.66</td>
<td>25.54</td>
<td>67.69</td>
<td>0.36</td>
<td>4.30</td>
</tr>
<tr>
<td>Sn2.5/Mt</td>
<td>6.64</td>
<td>32.64</td>
<td>56.93</td>
<td>0.34</td>
<td>4.84</td>
</tr>
<tr>
<td>Sn5.0/Mt</td>
<td>9.22</td>
<td>21.12</td>
<td>55.66</td>
<td>0.61</td>
<td>21.61</td>
</tr>
<tr>
<td>Sn7.5/Mt</td>
<td>9.75</td>
<td>17.27</td>
<td>42.24</td>
<td>0.47</td>
<td>38.53</td>
</tr>
<tr>
<td>Sn10.0/Mt</td>
<td>9.21</td>
<td>14.09</td>
<td>38.27</td>
<td>0.64</td>
<td>46.77</td>
</tr>
</tbody>
</table>

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**Fig. 1.** a. XRD patterns of the Sn/Mt. samples compared with the Mt. pattern. (b). Small angle XRD patterns of Mt., Sn1.0/Mt. and Sn2.5/Mt.
distribution of the pore size, and the type H4 hysteresis loop corresponds to small amounts of mesopores that are domination by micropores. These expressions agree with the pore size distribution (Fig. 4c); that is, Sn5.0/Mt. shows a significantly changed pore size distribution for the sizes of 10–50 Å. According to the distribution and data calculation, Sn5.0/Mt. has the highest BET specific surface area since it has a higher volume capacity than the other samples in all the pore size ranges. This is also closely related with the profile of the TEM image, showing the combination of increasing the interlayer region and the formation of SnO2 aggregates that are smaller than those represented in Sn7.5/Mt. and Sn10.0/Mt.

To investigate the absorption properties of the Sn/Mt. samples, diffuse reflectance spectroscopy was performed. The spectra are depicted in Fig. 5. The band gap energy values of the samples were calculated using the absorption coefficient near the fundamental absorption edge, which is given by the following eq. (1):

\[(\alpha h\nu)^{n} = A (h\nu - E_g)\]  

(1)

where \(\alpha\) is the absorption coefficient, \(h\nu\) is the photonic energy, \(n\) is 2 for SnO2, and \(A\) is a constant related to the material. Based on the UV-DRS spectra shown in Fig. 5a, the plot of \((\alpha h\nu)^{2}\) vs \(h\nu\) in Fig. 5b was used to determine the \(E_g\) values presented in Table 1.
The data shows that the $E_g$ values range from 2.49 to 3.18 eV depending on the Sn content of the materials; however, all the values are lower than that of bulk SnO$_2$ (3.6 eV). The band gap energy values of Sn1.0/Mt., Sn2.5/Mt., Sn5.0/Mt., Sn7.5/Mt., and Sn10.0/Mt. were estimated to be 2.49, 2.58, 2.92, 3.18, and 3.18 eV, respectively. These values were lower than that of bulk SnO$_2$ but similar to the values reported by supporting SnO$_2$ in activated carbon and SnO$_2$/montmorillonite (Babu and Antony, 2019). The low band gap energy may be attributable to the defects in the crystalline system with a low SnO$_2$ content, in which oxide formation in the interlayer region is not as facile as that in the outside interlayer region with a high SnO$_2$ content. The defects give the possibility of oxygen vacancies, which can lead to a low electron recombination rate.

These low band gap energy values are advantageous for rapid electron excitation from the valence band to the conductance band to accelerate the formation of radicals for the oxidation step. A similar phenomenon was also reported by doping SnO$_2$ with vanadium, in which the large amount of dopant reduced the band gap energy (Ledli et al., 2019). However, the values obtained in this work are higher than those reported previously, even for a high SnO$_2$ content (1.5-2.4 eV) (Babu and Antony, 2019).

3.2. Photocatalytic activity

The photocatalytic activities of the materials were evaluated in terms of RhB photocatalytic oxidation, and their kinetics plots are compared in Fig. 6a. The significant effect of the photocatalysts can be seen from the decolorization process occurring faster in the photocatalysis system than the photocatalytic oxidation (with Sn1.0/Mt., without UV illumination, and without H$_2$O$_2$), photocatalytic degradation (with Sn1.0/Mt. and without H$_2$O$_2$ addition), UV-assisted oxidation (without Sn1.0/Mt., with UV, and without H$_2$O$_2$), and photolysis (with UV illumination, without Sn1.0/Mt. and without H$_2$O$_2$) occurring in the adsorption system. It is seen that performing an adsorption treatment for 30 min prior to the photon exposure reduces 10% of the initial concentration, which is insignificantly changed during the adsorption process until 120 min has passed.

The comparison of the initial rate of RhB decolorization (Fig. 6b) suggests the role of Sn2.5/Mt. as a photocatalyst, which is approximately noticed from initial decolorization rate achieved with photocatalysts being significantly higher (by 24-fold) than the decolorization rate achieved under UV-illumination-assisted oxidation. Moreover, the combination of the photocatalyst, UV illumination, and H$_2$O$_2$ addition
Fig. 4. (a)-(b) N₂ gas adsorption-desorption isotherms of the materials and (c) pore size distribution of the materials.

Table 2
Surface parameters of the materials, as obtained from the N₂ adsorption-desorption profile.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Specific surface area (m²/g)</th>
<th>External surface area (m²/g)</th>
<th>Pore volume (cc/g)</th>
<th>Pore radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mt</td>
<td>68.9</td>
<td>18.3</td>
<td>1.08 × 10⁻²</td>
<td>10.3</td>
</tr>
<tr>
<td>Sn1.0/Mt</td>
<td>114.2</td>
<td>44.1</td>
<td>2.13 × 10⁻²</td>
<td>13.2</td>
</tr>
<tr>
<td>Sn2.5/Mt</td>
<td>134.8</td>
<td>50.3</td>
<td>2.29 × 10⁻²</td>
<td>13.1</td>
</tr>
<tr>
<td>Sn5.0/Mt</td>
<td>147.6</td>
<td>55.8</td>
<td>3.78 × 10⁻²</td>
<td>12.9</td>
</tr>
<tr>
<td>Sn7.5/Mt</td>
<td>94.1</td>
<td>20.1</td>
<td>6.07 × 10⁻³</td>
<td>14.3</td>
</tr>
<tr>
<td>Sn10.0/Mt</td>
<td>88.7</td>
<td>18.7</td>
<td>1.98 × 10⁻³</td>
<td>13.8</td>
</tr>
</tbody>
</table>

results in a 34-fold higher initial rate than the decolorization rate achieved under UV-illumination-assisted oxidation. Meanwhile, there is no significant change in the RhB concentration under the adsorption and photolytic systems.

The presence of a degradation mechanism is verified from the change in the UV-visible spectra and LCMS analysis results presented in Figs. 6c and 7. The absorbance at the maximum wavelength (554 nm) is diminished with increasing treatment times, and a hypochromic shift occurs from 554 to approximately 528 nm. These changes imply the de-ethylisation mechanism of the RhB structure (He et al., 2009; Yu et al., 2009). De-ethylisation is identified from the de-ethylated intermediate by mass peaks at m/z 443, 415, 387, 359, and 331. The UV-visible pattern and MS analysis are similar to the identification of RhB degradation over other NaBiO₃ and TiO₂-supported activated carbons (He et al., 2009; Yu et al., 2009; Xu et al., 2010; Sengami and Dharmannj, 2012a, 2012b). The possible mechanism is presented in Fig. 8.
3.3. Effect of the physicochemical characteristics on the photocatalytic activity

A comparative study on the photocatalytic activities of materials was performed by achieving photocatalytic oxidation with $H_2O_2$ addition ($10^{-3}$ M), and the kinetics plot is shown in Fig. 9a. In general, it is seen from the kinetics plot that the photocatalytic activities of the materials are in the following order: Sn7.5/Mt $>$ Sn10.0/Mt $>$ Sn5.0/Mt $>$ Sn2.5/Mt $>$ Sn1.0/Mt.

The order of the photocatalytic activity is related to the combination of the physicochemical characteristics of the material since Sn7.5/Mt has neither the highest specific surface nor the highest SnO$_2$ content. The combination of the high band gap energy, SnO$_2$ content and provided specific surface area plays an important role and supports the photocatalytic activity. The benefit of the combination can be seen by the turnover numbers (TONs) obtained by the use of the composite being higher than that obtained by the use of SnO$_2$. As a reference, the photocatalytic activity of SnO$_2$ seems to be similar to that of Sn2.5/Mt.
A quantitative comparison is conducted by calculating the turnover numbers (TON) based on the degradation efficiency at 60 min per SnO$_2$ percentage using the following eq. (2):

$$\text{TON} = \frac{\text{DE}_{\text{at min}}(\%)}{\text{SnO}_2(\%)}$$

Eq. (2)

Fig. 9b shows the comparison; it can be inferred that the immobilization of SnO$_2$ into the clay structure enhances the catalytic efficiency. Compared with other SnO$_2$-based photocatalysts, the DE value obtained from the photocatalytic process over Sn5.0/Mt. is considered excellent. With the photocatalyst dose of 25 mg/L, the use of Sn7.5/Mt. gives a DE of 80%, which higher than the DE values obtained at 55-75% of RhB photodegradation over SnO$_2$-TiO$_2$, SnO$_2$-ZnO, SnO$_2$-Y NPs and SnO$_2$-V$_2$O$_5$ at the dose of 1 g/L and same initial concentration of RhB (Jiao et al., 2018; Hassan et al., 2019; Letifi et al., 2019). This DE value of Sn5.0/Mt. is comparable with that obtained with the use of SnO$_2$ nanoparticles (75-88%), indicating that the Sn/Mt. materials prepared with a low content of the SnO$_2$ photocactive material exhibit a high TON (Sengami and Dharmaraj, 2012a, 2012b; He and Zhou, 2013).

The calculation showed that all the kinetics plots obey the pseudo-first-order kinetics, as shown by the linear plots in Fig. 9a, which refer to the calculation based on the following Eq. (3):

$$C_t = C_0 e^{-k_{\text{app}} t}$$

Eq. (3)

where $C_t$ and $C_0$ are the RhB concentrations at time $t$ and at the initial condition, respectively, and $k_{\text{app}}$ is the apparent kinetics constant. The fit to the pseudo-first-order kinetics model was in agreement with that reported from RhB photocatalytic degradation using several photocatalyst composites. In general, photocatalysts on the composite is usually directed by the adsorption of a dye onto the surface of a photocatalyst, a mechanism that is assumed to be attributable to the reaction system being in dynamic equilibrium (Ollis, 2018; Sun et al., 2018; Ateia et al., 2020).

Several investigations on photocatalysis using high surface photocatalysts showed that the reaction is surface-mediated, and competition between the intermediate products and reactive species for the occupation of the catalyst active sites is not limiting. From this assumption, the Langmuir-Hinshelwood mechanism was considered in reference to
the following eq. (4):
\[
\frac{1}{k_{\text{exp}}} = \frac{1}{kk_{LH}} + \frac{C_0}{k}
\]

where, \( k_{\text{exp}} \) is the calculated kinetics constant in eq. 4, \( C_0 \) is the initial concentration of RhB (mg/ L), \( k \) is the rate constant of the surface reaction (mg/ L min\(^{-1}\)), and \( k_{LH} \) is the Langmuir–Hinshelwood adsorption equilibrium constant (L mg\(^{-1}\)).

Fig. 10b and Table 3 show that the L-H plot is fit to all the photocatalysts and was obtained by compiling the initial rate from the various initial concentrations of RhB. The \( R^2 \) values confirm the applicability of the Langmuir–Hinshelwood mechanism to the kinetics data. Furthermore, from the comparison of the \( k_{LH} \) values, which are lower than \( k \) for all the photocatalysts, it is observed that the adsorption mechanism is not more dominant than the surface reaction.

3.4. Effect of pH

that pH is an important factor for the applicability of photocatalysis, the effect of pH on the photocatalytic activity was evaluated by plotting the initial rate at various pHs (Fig. 11a). RhB is a cationic dye and is easily adsorbed on the surface under acidic conditions; however, under a very acidic condition, electrostatic competition and the destruction of the catalyst surface may occur. The increase in pH leads to the increase in the OH\(^-\) concentration and potentially affects the deprotonation of both the catalyst surface and RhB. These assumptions are related to the fact that an optimum surface interaction occurs at the point of zero charge (PZC) of the photocatalyst, which is achieved at approximately a pH of 4.6, as shown in Fig. 11b.

3.5. Reusability of the photocatalyst

The reusability of the photocatalyst is one of the most important
characteristics, especially for photocatalyst applications at the industrial scale. Fig. 12 presents the reusability performance, which was identified by measuring the DR at 60 min and the kinetics constant \( k \) until 10 photooxidation cycles were performed, and Sn7.5/Mt. was the most active photocatalyst. The regeneration of the photocatalyst in each cycle was performed by centrifugation, washing with ethanol and calcining at 200 °C for 1 h. It is seen that the DR is insignificantly changed during the photooxidation cycles and has values in the range of 97–98%. However, from the kinetics constant values, the performance of Sn7.5/Mt. decreases as the number of cycles increases, indicating that the photocatalytic mechanism is influenced by the change in the photocatalyst performance.

To determine the possible reason for this reduction, the evolution of the physicochemical characteristics of Sn7.5/Mt. was evaluated by determining the BET specific surface area and Sn content. Due to the kinetics constant decreasing stepwise, the BET specific surface area and Sn content were determined after the 2nd, 7th and 10th cycles and compared to those of the initial condition. The data presented in Table 4 suggest that both the SnO2 content and SSA are reduced after the cycles. Although the values decrease by no more than 10% with respect to the initial value, these changes are responsible, since, by modeling the photocatalytic activity, SnO2 plays as an important role in photocatalytic oxidation. The SnO2 content decreases due to the washing and calcining steps involved in the recycling process, which potentially detaches external SnO2 particles from the surface (Ngoh and Nawi, 2016). Meanwhile, the decreasing specific surface area is consequently related to the adsorbed dye on the surface blocking the pores, which is the accompanying mechanism in photocatalysis (Sathakala et al., 2019).

Further identification of the change in the physicochemical characteristics of the material after use was conducted by XPS. The survey scan spectrum depicted in Fig. 13 presents some peaks of Si, Al, Fe, Sn, O and Na in the photocatalysts before and after their use. The presence of Sn clearly indicates the presence of SnO2 in Sn/Mt. The deconvolution of the Sn 3d spectrum shows two peaks at 486.9 and 495.3 eV, which can be assigned as the Sn 3d5/2 and Sn 3d3/2 spin-orbit peaks. Note that the distance between the two peaks is 8.4 eV, which confirms the formation of the Sn4+ oxidation state in SnO2. The Sn 3d5/2 peak of the photocatalyst after it was reused for 10 cycles is obviously broadened. The spectrum (Fig. 13c) was deconvoluted into two peaks centered at 486.9 and 485.8 eV, which belong to the Sn4+–O and Sn4+–O bonds. This suggests that the partial transition of Sn4+ to Sn2+ occurred (Jin et al., 2015; Singh et al., 2020).

Furthermore, the deconvoluted O 1 s spectra demonstrates two peaks centered at 530.2 and 531.8 eV (Fig. 5c), which belong to the Sn–O and O–H bonds and are maintained after use. These results imply that self-reduction by photocatalytic interactions occurs; meanwhile, the Sn–O bonds in the composite structure are unchanged. A similar phenomenon also occurred on several photocatalysts based on WO3, Ag, and Fe (Liu et al., 2009; Jin and Tao, 2013; Dong et al., 2016).

### 3.6 Modeling the photocatalytic activity

As theoretically shown in many papers, the photocatalytic degradation of dyes and organic compounds is affected by various factors, such as the photocatalyst dose and pH. From the photocatalyst perspective, the specific surface area, band gap energy, crystallite size, and photocatalyst active material are the main parameters affecting the
kinetics and mechanism of photocatalysis (Piellä et al., 2015; Singh et al., 2013). The role of the photocatalyst properties, on the surface area is associated with the fit of the Langmuir–Hinshelwood mechanism, which is also confirmed by Sn7.5/Mt. having the highest rate of photocatalytic degradation. Meanwhile, the role of the band gap energy is clarified by Sn7.5/Mt. achieve a higher photocatalytic degradation rate than Sn5.0/Mt and Sn2.5/Mt. From these comparisons, it can be shown that the higher degradation rate referred to the higher band gap energy, which stabilizes the excited electrons in the conduction band and delays recombination. However, this justification does not agree with the data obtained for Sn7.5/Mt and Sn10.0/Mt. Based on these facts, statistical modeling was used to predict the important factors for the rate of photocatalytic oxidation and the photocatalytic activity. Physical parameters of the photocatalysts such as the BET specific surface area, SnO2 content, SnO2 crystallite size, and band gap energy were chosen as the predictors. The data of the initial rate (\( \varphi / \text{mgL}^{-1} \text{h}^{-1} \)) and degradation efficiency (DE / %) calculated from 30-min reactions were determined from the photocatalytic oxidation experiments performed by varying the reaction conditions, which include the pH, catalyst dose, and photocatalyst. The parameters are listed in Table S1, and the compiled data are presented in the Supplementary Information S1.

Analysis of the correlation between DE and \( \varphi \) gives a Pearson correlation of 0.973 using the following eq. (5):

\[
DE = 6.08 + 0.978 \varphi
\]

The values in the parentheses are the statistic-t, with the P-values approaching zero. The equation means that both values are representative for the evaluation of the photocatalytic degradation reaction.

The statistical evaluation of the physical parameters shows that all the parameters except \( \varphi \) are significant to the DE and \( \varphi \) of the reaction. More specifically, m is not significant to the DE but is significant to \( \varphi \). The pH and SnO2 content significantly affect the DE, and both the pH and SnO2 content interact with each other. C is also a significant parameter and is correlated with SnO2, as presented by the correlation value of 0.877 with a P-value of 0.01. The SSA is not an important factor given that a high SSA results in neither high nor low \( \varphi \) and DE values. Moreover, the SSA is not correlated with the C and SnO2 parameters. It is seen that the SSA becomes a maximum for Sn5.0/Mt. and decreases with increasing the SnO2 content.

From the DE values, the pH and SnO2 content are crucial parameters and are correlated with each other; meanwhile, m significantly affects...
Table 4
The change in the SnO₂ content and SSA at the initial condition and after uses.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Initial</th>
<th>After 2nd cycle</th>
<th>After 7th cycle</th>
<th>After 10th cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂ (wt%)</td>
<td>38.5</td>
<td>38.2</td>
<td>37.3</td>
<td>55.1</td>
</tr>
<tr>
<td>SSA (m²/g)</td>
<td>94.1</td>
<td>95.3</td>
<td>91.6</td>
<td>90.4</td>
</tr>
</tbody>
</table>

the DE. At various ranges, a low pH increases the DE as well as νₚ, and a similar pattern is obtained for all the various catalyst doses. The linear model representing the SnO₂ content and pH can be written using the following eq. (6):

\[ DE = 3.20 - 3.14 \, \text{pH} + 4.58 \, \text{SnO}_2 - 0.068 \, \text{SnO}_2^2 \]  

(6)

The values in the parenthesis are the statistic-t, with the P-values approaching zero. The equation means that the pH affects the DE linearly, whereas SnO₂ affects the DE quadratically. By deriving the equation, the optimum value was calculated with eq. (7):

\[ \frac{d[DE]}{d[\text{SnO}_2]} = 4.58 - 0.132[\text{SnO}_2] = 0 \]  

(7)

and the optimum value of SnO₂ was 34.69 wt%.

Eq. (7) is a linear model that has drawbacks for estimating the DE, which must be in the range of 0 ≤ x ≤ 100. From this equation and with SnO₂ = 34.69 and 0 ≤ pH ≤ 14, the x values range from 226.41 to 270.37, and these are unreal. To overcome this, a logistical model is obtained by transforming the dependent variable using the following eq. (8):

\[ Y = \ln \frac{DE}{1 - DE} \]  

(8)

The transformation assumes that the DE values are in the range of 0–100. The equation is as follows in eq. (9):

\[ Y = -1.20 - 0.222 \, \text{pH} + 0.310 \, \text{SnO}_2 - 0.00454 \, \text{SnO}_2^2 \]  

(9)

in which the p-values for all the coefficients approach 0. Both the pH and SnO₂ parameters in this model are similar to those in the linear model, which means that pH affects the DE linearly, whereas SnO₂ affects the DE quadratically toward the Y variable. The determination coefficient is also obtained from Eq. (9) to be 83.4%. With this equation, the optimum condition was solved, leading to a SnO₂ content of 34.14 wt%, a low pH (0), and a Y value of 3.99185 or DE (%) of 98.19. The model is acceptable, even though the condition of a pH of 0 is questionable for the photocatalytic degradation system. It can be concluded that a lower pH gives a higher DE.

Based on the νₚ data, a similar trend in which SnO₂ is the influencing factor is obtained. By using the logistical model, the following equation is obtained (10):

\[ Y_2 = -4.61 + 0.422 \, \text{SnO}_2 - 0.00639 \, \text{SnO}_2^2 \]  

(10)

with Y_2 = \ln \frac{\text{DE}}{1 - \text{DE}}.

Based on the model, the maximum value of νₚ is reached with 33.02 wt% SnO₂ for the initial rate of 91.35 mg/L·h⁻¹.

4. Conclusion

Photocatalysts of SnO₂/montmorillonite nanocomposites were successfully prepared. The characterization data indicated that the Sn molar-to-clay mass ratio directly affects the physicochemical characteristics, mainly the SnO₂ particle size, band gap energy, and specific surface area of the material. The materials demonstrated excellent photocatalytic activity, as shown by the higher turnover number than those of SnO₂ and other related materials, as also indicated by the
Fig. 13. (a) XPS survey scan of Sn7.5/Mt. before use and after use for 10 cycles (b) Sn 3d spectrum of Sn7.5/Mt. before use and after use for 10 cycles (c) Deconvolution of the 0 1s spectra before use and after use for 10 cycles (d) Deconvolution of the Sn 3d5/2 spectra of Sn7.5/Mt. after use for 10 cycles.

degradation efficiency of 98% over photocatalytic oxidation. Statistical modeling on the relationship between physicochemical characteristics and photocatalytic activity suggests that SnO2 and pH are the most important factors affecting the high degradation efficiency and initial rate. It was proposed that the SnO2 content of 33.02 w% will give the maximum degradation efficiency.

Acknowledgement

The authors would like to express appreciation for the support from Research and Innovation Board, Ministry of Research and Technology, Republic of Indonesia, through the World Class Research Program in 2020.

Table 5

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Parameter description/unit</th>
<th>Values for photocatalysts</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO2</td>
<td>SnO2 content (% wt.)</td>
<td>Mt: 0; Sn1.0/Mt: 4.80; Sn2.5/Mt: 14.40; Sn5.0/Mt: 21.61; Sn7.5/Mt: 38.53; Sn10.0/Mt: 46.75</td>
</tr>
<tr>
<td>C</td>
<td>SnO2 crystallite size (nm)</td>
<td>Mt: 0; Sn1.0/Mt: 14.6; Sn2.5/Mt: 42.40; Sn5.0/Mt: 47.30; Sn7.5/Mt: 48.40; Sn10.0/Mt: 49.48</td>
</tr>
<tr>
<td>SSA</td>
<td>BET specific surface area (m²/g)</td>
<td>Mt: 68.9; Sn1.0/Mt: 114.2; Sn2.5/Mt: 134.9; Sn5.0/Mt: 147.64; Sn7.5/Mt: 94.08; Sn10.0/Mt: 88.67</td>
</tr>
<tr>
<td>E_g</td>
<td>Band gap energy (eV)</td>
<td>Mt: 2.16; Sn1.0/Mt: 2.19; Sn2.5/Mt: 2.95; Sn5.0/Mt: 3.20; Sn7.5/Mt: 3.18; Sn10.0/Mt: 3.18</td>
</tr>
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Various reaction conditions:

<table>
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<th>pH</th>
<th>pH of treatment system</th>
<th>Mt: 4; 7; 10</th>
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<tr>
<td>m</td>
<td>Photocatalyst dose (g/L)</td>
<td>Mt: 0.10; 0.25; 0.40; 0.5</td>
</tr>
</tbody>
</table>


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