SYNTHESIS AND CHARACTERIZATION OF PHOTOCATALYST Fe$_2$O$_3$ PILLARED MONTMORILLONITE DOPED TiO$_2$ AND ITS APPLICATION FOR RHODAMINE B PHOTODEGRADATION USING VISIBLE LIGHT IRRADIATION

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ABSTRACT

A montmorillonite clay modified with semiconductor metal can act as a photocatalyst material. Montmorillonite clays were chosen because of their natural characteristics which are easily to be modified and have high specific surface area. This research aims to modify montmorillonite clay into photocatalyst material for rhodamine B degradation. The montmorillonite clay was intercalated using Fe$_2$O$_3$ to produce Fe$_2$O$_3$-pillared montmorillonite clay, then doped with TiO$_2$ to form a photocatalyst material Fe$_2$O$_3$-PILC/TiO$_2$. Modifications were intended to increase the specific surface area and number of active photocatalyst sites and thus increase the ability of photodegradation. The characterization carried out included characterizing the pillared structure using X-ray Diffraction (XRD), specific surface area by the BET method, and the number of surface acid-base sites by the titration method. Photocatalyst with the best character was Fe$_2$O$_3$-PILC/TiO$_2$ 1:3 with specific surface area, number of acid and base sites respectively 45,947 m$^2$/g, 20,1736 x 10$^{23}$ sites/g and 19,0044 x 10$^{23}$ sites/g. The result of photodegradation at optimum condition with visible light at pH 3 using 400 mg photocatalyst was 99.84%.

Keywords: photocatalyst, Fe$_2$O$_3$, montmorillonite clay, TiO$_2$, rhodamine B

INTRODUCTION

The montmorillonite clay is a material that has been used as adsorbent. The popularity of montmorillonite material increases along the development of photodegradation methods in sewage treatment systems. Clay material is used as supported material for semiconductor photocatalysts. Montmorillonite clay was selected because of its natural characteristics which are easily modified and has high specific surface area. The structure of montmorillonite clay material consists of two layers, the alumina silicate layer and the interlayer with non-strongly attached cations such as Na$^+$, K$^+$, and Ca$^{2+}$ (Wijaya et al., 2002). The montmorillonite clay-layered structure allows the material to have cation
exchangeable property and has swelling ability. As result, montmorillonite clay is able to provide a place for certain molecular ions in the interlayer that can be used for clay pillaring (Utracki, 2004). Pillarization of montmorillonite clay is carried out by exchanging cations in its inter-layer with larger inorganic polycation. The presence of pillars will increase the basal spacing as well as the specific surface area of the clay. The pillarization process can be possibly done using intercalation method, followed by calcination process to form metal oxides which will take the roles as pillars (Gill et al., 2007).

Pillarization of montmorillonite clay with iron (III) oxide has been done by Widihati et al. (2004) which shown an increase in specific surface area from 95.0587 m²/g to 170.5416 m²/g at an optimum calcination temperature of 200°C. Iron (III) oxide is a semiconductor material that is widely used as photocatalyst because of its magnetic properties that not only guarantee an efficient process but also reusable (Bharati et al., 2009). Pillarization of montmorillonite clay using Fe₂O₃ can be carried out through an intercalation method using FeCl₃ or Fe(NO₃)₃. The iron oxide (Fe₂O₃) is formed after thermal decomposition process or calcination (Greedon, 1994). The performance of the pillared clay photocatalyst can be optimized by doping another semiconductor material. Titanium dioxide (TiO₂) in anatase phase is the most popular semiconductor material used as a photocatalyst. The presence of titanium oxide which doped into the Fe₂O₃ pillared clay is expected to increase the number of active sites along with the enhancement of the photodegradation performance.

Photodegradation methods are recently used in sewage treatment system, especially for textile wastewater. Textile wastewater treatment received a lot of attention due to its significant impact on environmental health, mainly related to the presence of synthetics dyes such as rhodamine B. Rhodamine B as a toxic non-biodegradable organic substance can be a threat to the aquatic biota and human health if being presence in water bodies (Forgacs et al., 2004). Photodegradation method which provides the alteration of pollutants by light into simpler and less harmful component is expected to be an alternative solution in overcoming the problem of textile wastewater treatment (Fatimah et al., 2009).

**MATERIALS AND METHODS**

**Materials**

Montmorillonite clay, rhodamine B (C₃₅H₇₇N₂O₀Cl), FeCl₃, NaOH, TiO₂ anatase, NaCl, AgNO₃, HCl, H₂C₂O₄, phenolphthalein, ethanol 96%, aqua distillate, and aqua deionized.

**Instruments**


**Sample Preparation**

The montmorillonite clay was saturated in 1M NaCl solution for 12 hours then washed until it was free of Cl ions (shown by negative test using 0.1 M AgNO₃ solution). The saturated clay then dried at 110°C and sifted using a 100-mesh sieve.

**Material Synthesis**

The pillar solution consisting 0.1 M FeCl₃ solution and 0.2 M NaOH solution using molar ratio of OH/Fe ≤ 2.0. The aging process was carried out at pH 1.8 for 24 hours. Solution obtained was mixed with clay samples (1 g clay: 45 mL solution) and stirred for 26 hours at room temperature. The suspension then filtered. Clay solids are washed using deionized water until free of Cl ions (shown by negative test against AgNO₃ 0.1M). The clay was dried at 110°C for 12 hours followed by calcination at 400°C for 4 hours (Hristodor et al., 2013). The calcinated montmorillonite then sifted using a 100-mesh sieve. The pillar formation was characterized using X-Ray diffraction (XRD) by analysing the 20 shifting.

Solis state method was used to dope TiO₂ into Fe₂O₃ pillared montmorillonite. Fe₂O₃ pillared montmorillonite mixed with TiO₂ using several ratios which are 1:0; 1:1; 1:3; and 3:1. Each composition was added with 10 mL ethanol 96% then stirred with magnetic stirrer for 5 hours. The mixture was dried in an oven at 120°C for 5 hours, then sifted using 100-mesh sieve followed by calcination at 500°C for 5 hours. The specific surface area of each composition was analysed using the Bruneau-
Emmet-Teller (BET) method. The acid-base active sites were analysed using titration method.

Acid-Base Active Sites Characterization

Characterization of the acid-base active sites of photocatalyst Fe$_2$O$_3$ pillared montmorillonite/TiO$_2$ was carried out quantitatively using the acid-base titration method. The characterization of base site is done by adding 10.0 mL of 0.5M HCl solution into 500 mg photocatalyst. The suspension is stirred for 15 minutes then filtered. The filtrate was added 2-3 drops of phenolphthalein and titrated with 0.5M NaOH solution until the solution turn from colourless to pale pink. The volume of NaOH used in the titration was used to calculate the basicity of the photocatalyst surface using the following equation:

$$\text{Basicity} = \frac{\text{mmol HCl}}{\text{photocatalyst mass}}$$ (Kumar, et al., 1995)

Acidity = \frac{\text{mmol NaOH}}{\text{photocatalyst mass}} (2)

(Kumar, et al., 1995)

According to the acid-base sites characterization and specific surface area analysis results, an optimum composition will be obtained. The optimum composition would be the one gives the highest number of active sites and surface area. This composition will be used to determine the optimum mass of photocatalyst to degrade rhodamine B dye solution.

Photocatalyst’s Mass Optimization

The optimum composition of photocatalyst Fe$_2$O$_3$ pillared montmorillonite/TiO$_2$ (100, 200, 300, 400, 500 mg) each added 25.0 mL of 100 mg/L rhodamine B dye solution. This mixture was irradiated under visible light (30W HPL, 445 nm) while stirred using magnetic stirrer for 2 hours. The filtrate absorbance was measure with UV-Visible spectrophotometer using wavelength of 553.5 nm. The percentage of degradation (%D) of rhodamine B is calculated using the following equation:

$$\%D = \frac{[\text{RhB}]}{[\text{RhB}_0]} \times 100\%$$ (3)

The percentage of degradation was used to determine the optimum mass of photocatalyst to degrade rhodamine B dye solution.

pH Optimization

A total 25.0 mL of 100 mg/L rhodamine B dye solution was added to the photocatalyst with optimum mass. The pH was adjusted to pH 2, 3, 4, 5, 6, 7, 8, and 9 by adding 0.5 M HCl or 0.5M NaOH to the solution. The mixture then irradiated for 120 minutes while stirred using magnetic stirrer. The absorbance of filtrate was measured with a UV-Visible spectrophotometer using wavelength of 553.5 nm. The percentage of degradation (%D) of rhodamine B is calculated using equation (3).

RESULT AND DISCUSSION

Analysis of Pillar Formation

Figure 1 shows XRD spectra of montmorillonite clay and Fe$_2$O$_3$ pillared montmorillonite
indicates the presence of quartz minerals, and peak at 2θ=26.33° (d=3.38Å) is a characteristic of illite (JCPDS, 5-0490). Figure 1 also shows that the pillariization process causes a general decrease in mineral intensity caused by the cation exchange between oligomer [Fe(OH)₂]⁺ⁿ in pillar solution with mineral cations in montmorillonite clay (Cromain and Cahyaningrum, 2016).

The form of pillars was indicated by peak shifting at 2θ = 11.88° (d=7.45Å) on the lower diffraction angel, where the peak does not reappear on the pillared montmorillonite. The peak has shifted from 2θ = 11.88° (d=7.45Å) to 2θ < 11.88° (d>7.45Å) in the d₀₀₁ because the formation of pillars has increased the basal spacing. These phenomena accordance with the Bragg’s law:

\[ 2d \sin \theta = n \lambda \] (4)

Bragg’s equation shows that if the basal spacing increased, the value of θ in the same n and λ condition will be decrease. The formation of pillar has also showed by the increased of specific surface area (Table 1).

**Specific Surface Area**

Specific surface area is one of the important characters that support the performance of photocatalysts. Specific surface area expresses the total photocatalyst surface area per photocatalyst mass (m²/g). The specific surface area of Fe₂O₃-PILC/TiO₂ analysed by the BET Method using surface area analyser are shown in the Table 1.

<table>
<thead>
<tr>
<th>Composite</th>
<th>Specific surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite clay</td>
<td>93.361</td>
</tr>
<tr>
<td>Fe₂O₃-PILC</td>
<td>140.863</td>
</tr>
<tr>
<td>Fe₂O₃-PILC/TiO₂ 1 : 1</td>
<td>71.657</td>
</tr>
<tr>
<td>Fe₂O₃-PILC/TiO₂ 1 : 3</td>
<td>45.947</td>
</tr>
<tr>
<td>Fe₂O₃-PILC/TiO₂ 3 : 1</td>
<td>89.263</td>
</tr>
</tbody>
</table>

**Source:** Sitanggang, et al., (2017)

Photocatalyst Fe₂O₃-PILC showed the highest surface area at 140.863 m²/g. The specific surface area of Fe₂O₃ pillared montmorillonite has increased compares to montmorillonite clay. This is due to the increase of basal spacing which directly impacts the specific surface area. The presence of TiO₂ material in the catalyst has cause a decrease in specific surface area. The specific surface area decreases along with the amount of TiO₂ that doped into the Fe₂O₃ pillared montmorillonite. This depression is caused by trapped TiO₂ molecules between the layers and on the surface area of pillared montmorillonite that it covers the pores (Wu et al., 2013). The lowest specific surface area is 45.947 m²/g and showed by Fe₂O₃-PILC/TiO₂ 1:3 respectively.

Specific surface area is not the only factor that support the performance of photocatalysts. The amount of acid-base active sites on photocatalyst surface also takes huge impact. Therefore, the result of active sites characterization must be considered.

**Acid-Base Active Sites**

The acidity and basicity of catalyst surface are values that represents the number of active sites of Bronsted or Lewis acid or base that is presence on the surface of the catalyst and it was expressed as the number (in millimoles) of acid or base in each g of catalyst. The number of active sites of acid and base catalyst surface can be determined by multiplying the acidity or basicity by the Avogadro’s number. The acidy-alkaline titration method was used to determine the acidity and basicity of the catalyst surface. The results of the acid-base active sites characterization are shown in the following table:

<table>
<thead>
<tr>
<th>Composites</th>
<th>Acid active sites (sites/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃-PILC</td>
<td>14.2775 x 10⁻²³</td>
</tr>
<tr>
<td>Fe₂O₃-PILC/TiO₂ 1 : 1</td>
<td>11.1199 x 10⁻²³</td>
</tr>
<tr>
<td>Fe₂O₃-PILC/TiO₂ 1 : 3</td>
<td>20.1736 x 10⁻²³</td>
</tr>
<tr>
<td>Fe₂O₃-PILC/TiO₂ 3 : 1</td>
<td>19.8456 x 10⁻²³</td>
</tr>
</tbody>
</table>
Table 3. Number of Base Active Sites of Photocatalyst Fe$_2$O$_3$-PILC/TiO$_2$

<table>
<thead>
<tr>
<th>Composites</th>
<th>Base active sites (situs/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$-PILC</td>
<td>$12.3491 \times 10^{23}$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-PILC/TiO$_2$ 1 : 1</td>
<td>$13.3847 \times 10^{23}$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-PILC/TiO$_2$ 1 : 3</td>
<td>$19.0044 \times 10^{23}$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-PILC/TiO$_2$ 3 : 1</td>
<td>$15.2657 \times 10^{23}$</td>
</tr>
</tbody>
</table>

The acid-base active sites characterization of photocatalyst Fe$_2$O$_3$ pillared montmorillonite/TiO$_2$ according to the Table 2 and Table 3 showed that Fe$_2$O$_3$ pillared montmorillonite/TiO$_2$ 1:3 is the composition with the highest acid-base sites. It has surface acidity, number of acid sites, basicity, and number of base sites of 3.3511±0.1159 mmol/g, 20.1736x10$^{23}$ sites/g, 3.1569±0.1634 mmol/g and 19.0044x10$^{23}$ sites/g respectively.

The active site plays an important role in the process of heterogeneous catalysis as well as the determination of reaction properties. The presence of active sites on the surface of the catalyst have two main functions, increasing reaction kinetics and improve product selectivity (Pan et al., 2018). The high number of active sites increased the formation of •OH radicals that play important roles in the process of photodegradation (Coleman et al., 2007). This condition means that the number of active acid-base sites on a photocatalyst are able to increase the performance of photocatalyst due to its function in degradation of rhodamine B. Therefore, the Fe$_2$O$_3$-PILC/TiO$_2$ 1:3 was chosen as the composition to be used in determining the optimum condition for rhodamine B photodegradation although its specific surface area is relatively lower than the other compositions.

**Optimum Mass Condition**

Optimum mass is the lowest photocatalyst mass needed to provide the highest percentage of degradation. The optimum mass of Fe$_2$O$_3$-PILC/TiO$_2$ 1:3 for rhodamine B photodegradation is shown by Figure 2.

**Optimum pH Condition**

The optimum pH is the pH condition of the solution needed to provide the highest %D in photodegradation of rhodamine B using Fe$_2$O$_3$-PILC/TiO$_2$ 1:3. The value of pH affect the surface charge and shifting the reaction potential which affect the degradation process. The relationship between the pH and %D in the rhodamine B photodegradation by Fe$_2$O$_3$-PILC/TiO$_2$ photocatalyst is shown in Figure 3.
Figure 3 shows that rhodamine B is relatively easier to degrade in acidic pH than alkaline pH. Percentage of degradation decrease significantly from pH 6 until pH 9. Fauzi (2018) obtained a similar result with %D of rhodamine B of 97.40% occurred at pH 4. Sibarani (2016) also obtained the highest percentage of rhodamine B degradation of 95.05% at pH 4. These phenomena can be explained using surface charge theory. Titanium dioxide can be protonated or deprotonated under acidic or basic condition. The protonation and deprotonation reactions occur according to the following reaction:

\[
\text{Ti}^+\text{OH} + \text{H}^+ \rightarrow \text{TiOH}^2+ \\
\text{Ti}^+\text{OH} + \text{OH}^- \rightarrow \text{TiO}^- + \text{H}_2\text{O}
\]

The surface of TiO\(_2\) will be positively charged on an acidic medium and negatively charged on a alkaline medium. Mozia \textit{et al.}, (2009) reported that TiO\(_2\) has higher oxidation activity at low pH, but excess H\(^+\) ions can reduce the rate of reaction. TiO\(_2\) is a Lewis acid in acidic medium, so if pollutants are Lewis bases, it will be easily interacted with the photocatalyst. Rhodamine B forms negatively charged ions in water solvents. The difference surface charge between the positively charged photocatalyst and negatively charged rhodamine B pollutant causes electrostatic interaction and produces strong adsorption. Meanwhile, in alkaline solution there would be a repulsion force (Coulombic repulsion) caused by the surface of the catalyst and pollutants that have same charged. According to this result, pH 3 was chosen as the optimum working pH for photodegradation of rhodamine B using Fe\(_2\)O\(_3\)-PILC/TiO\(_2\) 1:3 with %D of 99.84%.

**CONCLUSIONS**

The montmorillonite photocatalyst with the best character was Fe\(_2\)O\(_3\)-PILC/TiO\(_2\) 1:3 which had specific surface area, number of acid and base active sites of 45.947 m\(^2\)/g, 200.1736 x10\(^{23}\) sites/g, and 19.0044 x 10\(^{23}\) sites/g respectively. The optimum condition for photodegradation of rhodamine B was at pH 3 using 400 mg of photocatalyst with percentage of degradation of 99.84%.

**RECOMMENDATION**

Further analysis of the solution that has been degraded needs to be done using LCMS or HPLC to ensure the product of the photodegradation process.

**REFERENCES**


