Study of UiO-66 and UiO-66 Modulated with Acetic Acid as the Adsorbent for Eriochrome Black T Dye

M. Anugrah Rizky Pambudi, Nanda Pebri Prayogo, Ratna Ediati*, Liyana Labiba Zulfa, Muhammad Nadjib
Department of Chemistry, Faculty of Sciences and Data Analytics, Institut Teknologi Sepuluh Nopember (ITS)
Jl. Arief Rahman Hakim, Surabaya, Indonesia
*Corresponding Author: r.ediati@chem.its.ac.id

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Abstract

UiO-66, as one of the metal-organic framework (MOF) compounds, has been used to treat some anionic and cationic dye waste. In order to determine the adsorption selectivity decisively, the synthesis of UiO-66 and UiO-66 modulated with acetic acid had been carried out, along with their adsorption tests for Eriochrome Black T (EBT) dye solution. The synthesis was performed by utilizing a solvothermal method with the reaction mixtures of zirconium (IV) chloride (ZrCl4) and terephthalic acid (H2BDC) as a ligand heated at 120 °C for 24 hours. Both UiO-66 (without acetic acid) and acetic acid modulated UiO-66 were obtained as a white powder. Acetic acid as a modulator was added and being investigated for the adsorption capability compared to the normal UiO-66. This study showed that normal UiO-66 exhibited better adsorption than acetic acid modulated UiO-66 with mmol ratio of acetic acid:ligand varied from 50:1, 100:1, and 150:1. Acetic acid modulated UiO-66 with a mmol ratio of 50 exhibited the best crystallinity as observed by using x-ray diffraction. It can be concluded that the adsorption of EBT using normal and acetic acid modulated UiO-66 obeyed the pseudo-second-order reaction rate law as well as the Langmuir adsorption isotherm pattern.

Keywords: Metal-Organic Framework (MOF), UiO-66, Eriochrome Black T (EBT), Adsorption, Langmuir Isotherm.

INTRODUCTION

Synthetic dyes/coloring agents are widely utilized in many industries, such as textile, paint, and plastic industries. Most of these coloring agents are carcinogenic and considered to be harmful and threatening our health. Besides, unprocessed synthetic dyes waste will possibly pollute the environment. Therefore, it is very crucial to treat dyes waste before its disposal. Adsorption is one of the simple technique that can be used to treat dyes waste before disposal. Porous material such as Metal-Organic Frameworks (MOF) can be used as adsorbents (Rosseinsky, 2004). MOF is a porous material composed of a metal atom with empty orbitals and ligands with lone pairs. UiO-66 (1) is one of the MOF types composed of the central metal zirconium (Zr) with a benzene dicarboxylate ligand (BDC).

The adsorption test of some anionic and cationic dyes have been investigated using normal and acid modulated UiO-66 (Qiu et al., 2017). It was found out that promoting or modulating acetic acid to UiO-66 could increase the adsorption selectivity of methyl orange (MO) anionic dyes.

Although congo red (CR) dye is also an anionic dye, the adsorption ability of modulated UiO-66 towards CR is worse than MO. Supported by these previous studies, the addition of acid and the type of dye being adsorbed can exhibit different adsorption capacity. Therefore, research on the effect of acid addition against the adsorption capacity of UiO-66 should be further investigated.

Various adsorbents such as activated carbon (Indarto et al., 2019; Ni’mah et al., 2020; Santos et al., 2020; Tanasale et al., 2014, 2014), zeolite (Abbas et al., 2018; Abukhadra and Mohamed, 2019; Tumbel et al., 2015; Wang et al., 2006), and other porous
compounds (Jiao et al., 2020; Yasui et al., 2019) have been widely evaluated for their use in adsorbing dyes waste. Based on the research conducted by Khalid et al. (2018), Eriochrome Black T (EBT, 2) adsorption using graphene has an adsorption capacity of 102.04 mg/g. However, the adsorption capacity decreases to 70.42 mg/g when acid-modulated graphene (pH 2) was used (Khalid et al., 2018). In addition, the research conducted by Sonba and Ridha has tested the adsorption power of kaolin clay against EBT (2) dyes (Sonba and Ridha, 2014). To the best of our knowledge, there are still no studies that exhibited the adsorption ability of UiO-66 as an adsorbent against EBT dyes. Thus, it is necessary to investigate the adsorption test of UiO-66 against EBT and the effect of acid addition as a modulator on UiO-66.

After dissolving, the two solutions were mixed, stirred again for another 30 minutes, then kept in an oven for 24 hours at a temperature of 120°C. After 24 hours, UiO-66 was allowed to cool to room temperature, then decanted, washed sequentially using the following solution: 45 mL DMF, 30 mL chloroform, and 30 mL methanol. The obtained product was then dried by heating for 24 hours at a temperature of 120°C.

The same procedure was adopted for synthesizing UiO-66 modulated with acetic acid. The addition of acetic acid was carried out at the time of dissolving H$_2$BDC. Concentrated acetic acid was added with variations of acetic acid and H$_2$BDC ratios as followed 50:1 (12.98 mL acetic acid), 100:1 (25.97 mL acetic acid), and 150:1 (38.96 mL acetic acid).

Characterization of UiO-66 and UiO-66 Modulated with Acetic Acid

Acetic acid modulated UiO-66 and normal UiO-66 were characterized using the FT-IR (Shimadzu Type 8400) and XRD (Brand Philips X’pert MPD) instruments. Potassium bromide (KBr) pellets of the samples were scanned with infrared radiation within the wavenumber 400-4000 cm$^{-1}$. The crystallinity of the synthesized materials was characterized using XRD with Cu Kα radiation in the range of 2θ = 0-60°.

Preparation of Calibration Curves and Determination of Maximum Wavelength

A stock solution of EBT was made by dissolving 0.25 grams of EBT in 250 mL of distilled water. From the stock solution, the standard solutions of 10, 20, 30, 40, and 50 ppm were made. Then, the blank and standard solutions were tested for the absorbance with a UV-Vis Spectrophotometer at 200-700 nm. The absorbance was plotted against the concentration of the solution as a calibration curve.

Adsorption Test

Prior to the adsorption variation test was conducted, a preliminary test was carried out. UiO-66 that has been synthesized was weighed as much as 0.05 g and then added to 20 mL of 100 ppm EBT solution, then stirred with a magnetic stirrer for 60 minutes. Then, the solution was separated from its residue, and the absorbance was measured with a UV-Vis spectrophotometer. The same steps were repeated with the other acetic acid modulated UiO-66. This step aimed to determine the material with the best adsorption capacity for further adsorption test with various concentrations of EBT.

The first test to be carried out is the time variation test. Approximately 0.05 grams of normal UiO-66 (without modulator) was added to 20 mL of 100 ppm EBT solution, then stirred continuously with a
magnetic stirrer with time variations of 10-70 minutes. Furthermore, the optimal time was used to test the adsorption at different concentrations. The tests were carried out using 100, 150, 200, 250, and 300 ppm of EBT solutions.

RESULT AND DISCUSSION

Synthesis and Characterization of UiO-66 and UiO-66 Modulated with Acetic Acid

The synthesis of UiO-66 was carried out by the solvothermal method. The synthesis of UiO-66 and UiO-66 with the addition of acetic acid in mmol ratio varied from 50, 100, and 150 yielded 0.905 (% yield = 94.94%), 0.448 (46.98%), 0.742 (77.84%), and 0.941 g (98.76%), respectively.

The synthesis process of UiO-66 occurs when the lone pair of BDC ligands attack the zirconium (Zr) atom as an electrophile, which has an empty orbital, resulting in a coordination bond between the Zr central atom and the BDC ligand. BDC ligand substitution on the Zr atom occurs when the proton of terephthalic acid (H₂BDC) undergoes deprotonation (Qiu et al., 2017). In addition, the reaction conditions can be achieved if zirconium (IV) chloride (ZrCl₄) as the source of the central atom and terephthalic acid (H₂BDC) as ligand are entirely dissolved in the appropriate solvent. Dimethylformamide (DMF) is a suitable solvent used in the synthesis of MOF (Wu et al., 2014; Zhao et al., 2011).

At the time of synthesis, the dissolving and mixing process of ZrCl₄ with H₂BDC was carried out in a tightly closed container. This treatment aims to prevent the oxidation process of ZrCl₄ into zirconium (IV) oxide (ZrO₂), which can inhibit the synthesis process. Furthermore, the mixture of ZrCl₄ and H₂BDC solutions in DMF solvent was heated using an oven at 120°C to obtain UiO-66 with a regular and octahedral crystalline structure (Qiu et al., 2017).

Acetic acid as a modulator was investigated during the UiO-66 synthesis process by varying the mmol ratio of acetic acid and H₂BDC (50:1, 100:1, and 150:1). The addition of acetic acid contributes to the acidic atmosphere of the solution. Moreover, there was a coordination bond competition between acetate ligands and BDC ligands against the central atom of zirconium. Additionally, the acidic atmosphere can also inhibit the H₂BDC deprotonation process. Thus, the reaction rate of the nucleation process of Zr-BDC (UiO-66) becomes slower, and it is expected that the product of the reaction will have better crystallinity (Qiu et al., 2017). The crystallinity of those products can be studied through the diffractogram, as shown in Figure 1.

![Figure 1. Diffractogram of UiO-66 and its variations](image)

It can be interpreted from Figure 1 that there are two characteristic peaks of the UiO-66 crystal lattice at 2θ = 7.4° (x) and 25.6° (xx). It can be seen that the more acetic acid was added (variations of 50 and 100 mmol), the sharper peaks were obtained. However, a deviation showed that the UiO-66, with the acid mmol ratio of 150:1, have a broader and lower peak. In other words, UiO-66 with the acetic acid mmol ratio of 150 is less crystalline than the other variations. This phenomenon was probably due to the formation of an imperfect crystal (defect). It has been investigated that the presence of monocarboxylic acid as a modulator in synthesizing UiO-66 contributes to the missing cluster defects. The higher concentration of acid is used, the more defects will likely to occur (Atzori et al., 2017; Shearer et al., 2016).

Furthermore, the FTIR spectra of UiO-66 is showed in Figure 2. The spectra exhibited functional groups consisting of the broad peak at 3398 cm⁻¹ indicating the O-H stretching vibrational mode of carboxylic acid from H₂BDC, and O-H bending at 600-700 cm⁻¹ near Zr-O absorption peak. The intense peaks at 1656 and 1400 cm⁻¹ were confirmed to be C=O and C-O stretching modes from carboxylic acids. Distinctively, the peak at 1579 cm⁻¹ is associated with C=C in the aromatic ring of the organic linkers. Characteristic peaks at 547 and 746 cm⁻¹ pointing out the Zr-O stretching and bending modes, respectively. These peaks validated the UiO-66 was successfully synthesized according to the previous study (Jin and Yang, 2017).
Figure 2. FTIR spectra of Normal UiO-66

Preparation of Calibration Curves and Determination of Maximum Wavelength

From the experiments conducted using a UV-Vis spectrophotometer, it can be identified that the maximum wavelength of the EBT standard solution with a concentration of 10-50 ppm is 541 nm. A calibration curve was made by plotting the concentration of EBT (in ppm unit) and the absorbance data. The data were collected in duplo procedure with a standard deviation of 0.00224. The calibration curve is shown in Figure 3.

Figure 3. Calibration Curve of EBT standard solutions (\( \lambda_{\text{max}} = 541 \text{ nm} \))

Adsorption Test, Adsorption Kinetics and Adsorption Isotherm

A preliminary test to determine the optimal material and time required for the EBT adsorption process was conducted. The initial test was carried out by mixing 0.05 grams of normal UiO-66 with 20 mL of 100 ppm of EBT solution. The mixture then stirred with a magnetic stirrer for 60 minutes. Next, the solutions were filtered and separated from their residue before subjected to read the absorbance. The test was repeated using the other variations of modulated UiO-66. The preliminary test results are shown in Table 1.

Table 1. The adsorption capacity of UiO-66 and Modulated UiO-66

<table>
<thead>
<tr>
<th>No.</th>
<th>Adsorbent</th>
<th>Adsorption Capacity (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Normal UiO-66</td>
<td>37.031</td>
</tr>
<tr>
<td>2</td>
<td>UiO-66 (50)</td>
<td>34.268</td>
</tr>
<tr>
<td>3</td>
<td>UiO-66 (100)</td>
<td>14.943</td>
</tr>
<tr>
<td>4</td>
<td>UiO-66 (150)</td>
<td>14.776</td>
</tr>
</tbody>
</table>

It can be interpreted from the data in Table 1 that UiO-66 without acid modulation (normal) exhibits the best adsorption capacity. The adsorption capacity is calculated by Equation 1.

\[
Q_t = \frac{V(C_0 - C_f)}{M}
\]  

Notes:
- \( Q_t \) = adsorption capacity at time \( t \) (mg/g)
- \( C_0 \) = initial concentration (ppm)
- \( C_f \) = concentration after adsorption for \( t \) minutes (ppm)
- \( M \) = mass of adsorbent (g)
- \( V \) = total volume (L)

The previous research conducted by Qiu et al. (2017) found out that the modulation with acid can increase anionic dyes’ adsorption capacity. However, in this research, it turned out that the addition of acetic acid as a modulator in UiO-66 did not give a better adsorption capacity. In other words, this fact indicated that UiO-66 modulated with acid was not suitable for EBT adsorption. It also corresponds to the previous report that modulation of UiO-66 with acetic acid was more selective against MO. Nevertheless, it was not specific against CR, of which the adsorption capacity decreased (Qiu et al., 2017). Therefore, it can be assumed that the type of dye also influences adsorption capacity. The results of this study also correspond with other related studies proving that activation of graphene with acid reduced the adsorption capacity of EBT (Khalid et al., 2018).

Furthermore, the test of reaction kinetics was carried out by adding 0.05 grams of normal UiO-66 into 20 mL of 100 ppm EBT solution, with time variations ranged from 10-70 minutes. The results of the adsorption test can be seen in Table 2.
Determination of the adsorption kinetics is carried out using the pseudo-first-order and the pseudo-second-order kinetics law. In this research, we figured out that the adsorption process of EBT using UiO-66 tend to follow the pseudo-second-order rate law rather than the pseudo-first-order law. The pseudo-first-order equation is shown in equation (2), whereas the pseudo-second-order equation is showed in equation (3):

$$\ln \left( \frac{Q_e - Q_t}{Q_e} \right) = \ln Q_e - \frac{k_1}{2.303} t$$

$$\frac{1}{Q_t} = \frac{1}{k_2Q_e^2} + \frac{1}{Q_e}$$

where \(Q_e\) is the adsorption capacity at equilibrium (mg/g), \(Q_t\) is the adsorption at the time of \(t\) (min), \(k_1\) is a pseudo-first-order rate constant (min\(^{-1}\)), while \(k_2\) is a pseudo-second-order rate constant (g mg\(^{-1}\) min\(^{-1}\)). The pseudo-first-order and the pseudo-second-order graphs for the adsorption process were plotted, as shown in Figure 4 and Figure 5, respectively.

![Graph of ln(Qe - Qt) against time for pseudo-first-order](image)

![Graph of t/Qt against time for pseudo-second-order](image)

Based on the graphs above, it is known that the adsorption of EBT by using UiO-66 followed the pseudo-second-order kinetic law. The obtained \(k_2\) and \(Q_e\) value were of 0.0561 g mg\(^{-1}\) min\(^{-1}\) and 39.2157 mg/g, respectively. The pseudo-first-order (Figure 4) is unfavorable in this adsorption kinetic since the coefficient of determination (\(R^2\)) is very low (non-linear). Additionally, it should be noted that these data correspond to the research reported by Qiu et al. (2017) investigating the adsorption process of UiO-66 against anionic dyes via the pseudo-second-order kinetics (Qiu et al., 2017).

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>Adsorption Capacity (mg/g)</th>
<th>Adsorption Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>38.839</td>
<td>98.068</td>
</tr>
<tr>
<td>150</td>
<td>58.808</td>
<td>98.210</td>
</tr>
<tr>
<td>200</td>
<td>78.104</td>
<td>97.630</td>
</tr>
<tr>
<td>250</td>
<td>96.813</td>
<td>97.200</td>
</tr>
<tr>
<td>300</td>
<td>113.778</td>
<td>95.383</td>
</tr>
</tbody>
</table>

After knowing the optimal time for the adsorption test, concentration variation tests were carried out to determine the adsorption isotherm pattern. The concentration variation tests were carried out by adding 0.05 grams of UiO-66 (without modulation) into 20 mL of EBT solution which concentration varied from 100, 150, 200, 250, and 300 ppm and then stirred for 50 minutes. The data from the concentration variation test results are summarized in Table 3.

In Table 3, it can be seen that the value of adsorption efficiency decreased when the concentration of EBT increased. It occurred because...
the adsorbent became saturated with the increasing number of adsorbates. Thus, the additional amount of adsorbent is needed to improve its adsorption efficiency. The adsorption isotherm was identified and determined by comparing Langmuir and Freundlich adsorption isotherm patterns. Further analysis showed that the adsorption process in this research tended to follow Langmuir isotherm rather than Freundlich adsorption isotherm pattern. Langmuir adsorption isotherm is described in equation (4), whereas Freundlich adsorption isotherm is described in equation (5):

\[ \frac{C_e}{Q_e} = \frac{1}{K_L Q_{\text{max}}} + \frac{C_e}{Q_{\text{max}}} \quad (4) \]

\[ \ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5) \]

where \(C_e\) is dye concentration at equilibrium, \(K_L\) is the Langmuir adsorption isotherm constant related to the adsorption binding energy, and \(Q_{\text{max}}\) is the maximum adsorption capacity (mg/g).

The graphs of Langmuir and Freundlich adsorption isotherm were shown in Figure 6 and Figure 7, respectively. Langmuir and Freundlich coefficient of determination values (R²) can be seen in Figure 5 and Figure 6, respectively. The R² value of Langmuir isotherm (R² = 0.998) is higher than that of Freundlich isotherm (R² = 0.964). Thus, it can be concluded that the adsorption of EBT by using UiO-66 was most likely to follow the Langmuir isotherm. The Langmuir isotherm describes that adsorption occurs chemically (chemisorption), where the adsorbate forms a single layer on a homogeneous surface (Lin et al., 2015).

**Figure 6. Langmuir isotherm adsorption plot**

\[ y = 0.0068x + 0.0272 \quad R^2 = 0.998 \]

**Figure 7. Freundlich isotherm adsorption plot**

Briefly, the R² value of the Langmuir model is higher than that of the Freundlich model, representing that monolayer chemisorption is dominant. This finding agrees with other previous research reported by Mohammadi et al. (2017) that the adsorption of methylene blue dye by using UiO-66 also follows the Langmuir isotherm pattern (Mohammadi et al., 2017). However, it is essential to state that generally, depending on the thermodynamic conditions (i.e., the increase of temperature), the adsorption isotherm may change into the Freundlich isotherm (Liu et al., 2019).

Additionally, from Figure 5, the obtained value of \(K_L\) and \(Q_{\text{max}}\) are 0.202 and 156.25 mg/g, respectively. It indicates that the maximum adsorption capacity of EBT by using UiO-66 is 156.25 mg/g, with the Langmuir adsorption isotherm constant of 0.202.

**CONCLUSION**

In this study, UiO-66 and UiO-66 modulated with acetic acid have been successfully synthesized with a mmol ratio of acid:ligand as followed: 50:1, 100:1, and 150:1. The diffractogram results showed that the crystallinity increased with the addition of acetic acid. However, in this study, acid modulated UiO-66 with a mmol ratio of 150:1 showed a defect, where the crystallinity decreased. Thus, further research should be conducted to confirm the morphology. UiO-66 without modulation showed the most significant adsorption capacity towards Eriochrome Black T (EBT) with the maximum adsorption capacity value of 156.25 mg/g. EBT dyes turned out to be less suitable to be adsorbed with MOF adsorbent modified with acetic acid as a modulator. The adsorption kinetics followed the pseudo-second-order kinetics law, and the type of isotherm followed the Langmuir isotherm.

**Figure 5**
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