Synthesis and characterization of metal organic framework using succinic acid ligand with cobalt and iron metals as methylene blue dye adsorbent

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Abstract. Metal-organic Framework (MOF) as a porous material has a potency for an organic dye adsorbent due to its tunable pore size. It can be a good candidate for selective separation of organic dye waste because of its organic functionality, high thermal and stability. In this study, MOF based on cobalt (Co) and iron (Fe) cations with succinic acid ligand was utilized for Methylene Blue (MB) removal from aqueous solution. Co-MOF and Fe-MOF were synthesized using solvothermal method at 120 °C for 20 h and characterized by using infrared spectroscopy, X-Ray diffraction technique, thermogravimetric analyses, N₂ adsorption-desorption isotherm, and scanning electron microscope. The adsorption of MB from aqueous solution by Co-MOF and Fe-MOF were carried out and their adsorption properties were investigated in various parameters such as pH solution, contact time, MOF loading. Moreover, their adsorption isotherm and reusable capacity were explored. As the results, the optimal adsorption was achieved at pH 9 for both MOFs, 5 mg of MOFs loading in 5 mL MB and 180 min for Co-MOF and 150 min for Fe-MOF. Both MOFs could be reused as a good adsorbent with the ratio of ethanol and H₂O (70:30) as an eluent. This adsorption activity followed the Langmuir isotherm with the maximum adsorption capacity (Qm) of 3.9494 mg/g and 4.6685 mg/g for Co-MOF and Fe-MOF respectively.

Keywords: Metal-organic framework, adsorption, methylene blue

1. Introduction
Along with the increasing necessity in life, the world’s industrial has also increased. One of the very rapid industrial developments is textile industry that contains organic dyes, which have complex and stable structure and difficult to decompose under natural condition [1]. The most commonly used cationic dyes in industry is methylene blue (MB) which is easily dissolved in water, relatively easy to produce, have bright colors and are easier to use in fabrics. MB can be toxic to the environment and health. The existence of concentrated MB in the waters can prevent the penetration of sunlight into the water so that it can automatically disrupt the life of the aquatic ecosystem. Meanwhile, the impact on health, MB content can cause burning eyes which can be a permanent injury to humans or animals, difficult breathing, digestive system disorders, and can also cause nausea, vomiting, excessive sweating, and methemoglobinemia or abnormalities in the blood [2].

Many methods have been developed to eliminate dyes pollutant in industrial wastewater such as membrane filtration, photocatalysis, coagulation and adsorption [3-5]. Adsorption is considered
method due to simplicity, efficiency, and low consumption to reduce dyes pollutant. The common adsorbents used in the treatment of organic dyes carbon active, zeolites, graphene, and polymeric resins [6-7] whereas some of them are lacking of selectivity and have small diameter porous.

Metal-Organic Framework (MOF) is a porous coordination polymer composed of organic compounds (can be bidentate or polydentate ligands) bound to inorganic compounds (can be metal-oxide clusters or metal cations) as secondary building units (SBUs) form an unlimited network. MOF can be used as an adsorbent because it has the properties of organic substances which are expected to be able to interact with organic dyes and have a large surface area and pore volume so that they can be used as good adsorbents [8-9]. The removing of cationic dyes (MB) using Ti-MIL has been reported by Oveisi et al which has high adsorption capacity and stability over three cycles [10]. The 1,4-benzenedicarboxylate (BDC) and 2-amino-1,4-benzenedicarboxylate (NH2-BDC) were used as linker. The transition metal used in synthesis of MIL-101 (Fe) has high adsorption capacity 472.7 mg·g⁻¹ and has a good reusability [11]. In previous research, Yt-MOF has been synthesized using succinic acid as linker. The synthesized material exhibits high capacity over Rhodamine B adsorption. In this study, the transition metal (Fe and Co) and succinic acid linker based MOFs have been investigated to MB removal in aquatic system. The combination of low cost and non-toxic material (transition metal and succinic acid) could improve the surface area and increase the adsorption ability for cationic dyes. The reusability of the adsorbent is also studied for three cycle experiments.

2. Materials and method

2.1. Materials

The materials used in this study were Fe(NO₃)₃.9H₂O, Co(NO₃)₂.6H₂O 99 %, succinic acid 99.5 %, N,N-dimethylformamide 99.5 %, NaOH 99 %, acetic acid 100 % obtained from Merck, and distilled water.

2.2. Method

2.2.1. MOF synthesis. The synthesis of Co-MOF and Fe-MOF was carried out using the solvothermal method (Wu et al. with modification) [12]. Approximately, 1.5 mmol of succinic acid ligand (0.1771 g) was dissolved into a mixture of 5 mL DMF and 0.25 mL H₂O solvents. The mixture was stirred for 10 min. Then, 1 mmol of each Fe(NO₃)₃ and Co(NO₃)₂ were added into the mixture and stirred for 30 min. The mixture was heated at 120 °C for 20 h. The resulting of brown crystal for Fe-MOF and purple crystal for Co-MOF were isolated and washed with the mixture of DMF and H₂O with ratio of 5:0.25 for several times. The obtained of products were dried in the oven at 60 °C overnight.

2.2.2. MOF characterization. The Co-MOF dan Fe-MOF were characterized by XRD, TGA, N₂ adsorption-desorption isotherm, FTIR, and SEM. X-Ray Diffraction (XRD) was used to determine the crystallinity of MOFs, which used CuKα ray radiation, λ = 1.5406 Å and continuous scan type with a Shimadzu 6000. Thermogravimetric analysis (TGA) was used to know the thermostability of MOFs and performed with a heating rate 10 °C/min and temperature ranging from 30–600 °C in a flowing atmosphere of N₂. Surface area and pore size of MOFs samples were analyzed using the BET and BJH methods. The determinations of surface area and pore size were based on the isotherm of adsorption and desorption of nitrogen at 300 °C with SAA NOVA 2200e instrumentation. The functional groups of MOFs samples were analyzed by a FTIR Prestige 21 within the wave range 400–4000 cm⁻¹. The morphological and surface characteristic of MOFs was obtained from field emission scanning electron microscope (FESEM) using FESEM JEOL JESM-6700F.333. For application, UV-Vis spectrophotometer was used to measure the concentration of MB before and after adsorption process.
2.2.3. Methylene blue adsorption. The adsorption process was carried out by dispersing 10 mg MOF into 5 mL of 5 ppm methylene blue solution, then put in a closed beaker glass and stirred using a magnetic stirrer with a pH variation of 3, 5, 7, 9 and 12 with a speed of 120 rpm for 2 h at room temperature. After that, the variation of contact time was conducted for 120, 150, 180, 240, 300 and 360 min at the optimum pH. The optimum adsorbent mass was also determined with variations of 2, 5, 10, 15, 20, 25 mg under optimum pH and contact time conditions. Langmuir and Freundlich isotherm models were explored to study the type of adsorption mechanism and to obtain the theoretical maximum adsorption capacity. The reusability of synthesized adsorbent was determined for three cycle experiments.

3. Results and discussion

3.1. Characterization of MOFs

3.1.1. FTIR characterization of MOFs. The result of the FTIR of all MOF samples can be seen in figure 1. The spectra show the absorption peak at 1700 cm\(^{-1}\) of succinic acid is shifting to the lower wavenumber and getting the smaller intensity of both Fe-MOF and Co-MOF. Peak around 1700 cm\(^{-1}\) indicates the presence of C=O. This shifting might be an indication that C=O in succinic acid ligand form coordination with metal so the bonding is getting weak. The spectra of both MOFs show a shifting of absorption peak to a higher wavenumber around 3000–3500 cm\(^{-1}\) that indicates a stronger bond of a presence O-H group from H\(_2\)O as a solvent. All MOF spectra also exhibit absorption peak at around 1490 cm\(^{-1}\) and 1220 cm\(^{-1}\), as in the spectrum of succinic acid ligand, which shows asymmetrical and symmetrical vibration of COO\(^-\) group [13]. Therefore, all of the spectra show that the cobalt and iron metals have successfully formed a coordination with ligand.

3.1.2. XRD characterization of MOFs. The XRD patterns of Co-MOF and Fe-MOF are shown in figure 2. The diffraction peaks in 2\(\theta\) area of Co-MOF matched with the previous report that has synthesized Cd-Succinate MOF [14], indicating that Co-MOF sample was well crystallized and the crystallinity of MOF is similar to the Cd-MOF reference. The diffraction peak of Fe-MOF is also nearly matched with the previous report that has synthesized Y-Succinate MOF, indicating that

![Figure 1. FT-IR spectra of Fe-succinate MOF, Co-succinate MOF and succinic acid ligand.](image-url)
Fe-MOF was well crystallized and has a similar crystal structure compared with Y-MOF reference [15]. Furthermore, the synthesized MOFs are insoluble in some solvents i.e. H₂O, DMF, and ethanol, indicating the high crystallinity.

3.1.3. TGA characterization of MOFs. Figure 3 shows that the main weight loss of Co-MOF is produced in the temperature range of 322–428 °C of 47.97 % weight. Fe-MOF also shows the main weight loss of 9.06 % in the range temperature of 249–380 °C. These weight losses indicate the organic linker decomposition, which is succinic acid. It was also known that the pyrolysis temperature of the succinate group is 320 °C [16]. The result shows the synthesized Co-MOF is having a higher thermal stability compared with Fe-MOF sample. The TGA curves also show that Co-MOF is more hydrophilic than Fe-MOF because it has more water content with comparison 2.6 to 2.2 %.

![Figure 2. XRD pattern of (a) Co-MOF and (b) Fe-MOF.](image)

![Figure 3. TGA curves of (a) Co-succinate MOF and (b) Fe-succinate MOF.](image)
3.1.4. Surface area and pore analysis of MOFs. The surface area and pore of both MOFs were characterized by nitrogen adsorption-desorption experiments at 300 °C (figure 4). From figure 4, the synthesized Co-MOF shows type I adsorption-desorption isotherm indicating only microporous in the network. Whereas, Fe-MOF is similar to type IV isotherm of adsorption-desorption, which is the typical microporous and mesoporous network [17]. Mean pore size of Co-MOF is 1.5806 nm and Fe-MOF is 1.5816. The data of the surface area, pore-volume, and radius pore are listed in table 1.

3.1.5. FESEM characterization of MOFs. Figure 5 shows the SEM images of both Co-MOF (a) and Fe-MOF (b). Co-MOF shows spherical crystal structure as reported by Zhang et al. [18] with range crystal size 15–20 μm. Fe-MOF shows a clear cuboid shape crystal that is in good agreement with the report by Zhu et al. [11]. Fe-MOF has a crystal size in the range of 2–5 μm.

3.2. Methylene blue adsorption

3.2.1. Determination of optimum pH. pH is one of the important parameters which controls the MB adsorption [1]. Figure 6 shows that adsorption capacity increase at pH range 3 to 9 and decrease at pH 12 of both MOFs. As the increasing of pH, the negative charges in adsorbent also increase. The carboxylic group in ligand turns into anion carboxylate and can be reacted with methylene blue dyes which have a positive charge. However, a significant increase of pH exhibited the competition of adsorbent and hydroxyl ions [OH⁻] [1]. Due to its optimum adsorption capacity, pH of 9 was selected for further experiments.

Figure 4. N₂ adsorption-desorption isotherm of (a) Co-succinate MOF and (b) Fe-succinate-MOF.
Table 1. Some properties of Co-MOF and Fe-MOF for nitrogen adsorption experiments at 300 °C.

| Parameter       | Co-succinate MOF | Fe-succinate MOF |
|-----------------|------------------|------------------|
| Pore volume     | 0.013 cc/g       | 0.283 cc/g       |
| Pore radius     | 1.5806 nm        | 1.5816 nm        |
| Surface area    | 15.115 m²/g      | 61.326 m²/g      |

Figure 5. FESEM images of (a) Co-succinate MOF and (b) Fe-succinate MOF.

Figure 6. (a) Determination of optimum pH and (b) contact time in MB adsorption by Co- and Fe-MOFs.

As seen in figure 6b, MB adsorption increased with the increase of contact time (from 120 to 180 min) and remained unchanged at higher contact time due to the electrostatic interaction between MOFs and MB. The optimum contact time of Fe-MOF was 150 and Co-MOF adsorbed MB optimally at 180 min. As the contact time increased, the MOFs adsorbent can adsorb more MB (adsorbates) and
interact with each other to reach the equilibrium point. There were two possibilities that could occur during the adsorption process: (1) the second adsorption layer occurs and forms the next layer, (2) the second layer does not form the next layer of adsorption and the adsorbate diffuses out of the pore and returns to the fluid that carries it [1].

3.2.2. Determination of adsorbent mass. It can be seen in figure 7 that the optimum adsorbent mass of both Co-MOF and Fe-MOF was 5 mg. The increasing mass of adsorbent at range of 10–25 mg caused the decreasing of adsorption capacity. It is caused by the aggregation particle due to the excessive amount of adsorbent which reduced the surface area.

3.2.3. Isotherm adsorption. Adsorption isotherm was widely used to describe the adsorption progress and investigate the mechanisms of adsorption [19]. Langmuir isotherm assumes that adsorption process forms a monolayer and homogeneous surface while Freundlich isotherm shows a multilayer adsorbent and the adsorption takes place on heterogeneous surface [1]. The Langmuir and Freundlich equations are presented in equation 1 and equation 2, respectively.

\[
\frac{C_e}{Q_e} = \frac{1}{Q_m} \times C_e + \frac{1}{b \times Q_m}
\]

\[
\log Q_e = \log K_f + \frac{1}{n} \log C_e
\]

Ce is equilibrium concentration (ppm), Qe is equilibrium concentration (mg/g), b is Langmuir Constant, Qm is optimum adsorption capacity, Kf is Freundlich Constant, and n is the intensity of adsorption [19].

As shown in figure 8 and table 2, MB adsorption on both as-synthesized MOFs were fitted to the Langmuir isotherm model based on high linear coefficient (R²). This indicates that monolayer and homogeneous surface covers the adsorbate molecules [11]. The adsorption of MB takes place on the specific sites of MOFs with the maximum capacities Qm are 3.95 for Co-MOF and 4.67 mg g⁻¹ for Fe-MOF.

3.2.4. Reusability of MOFs. Reusability is an important parameter in dyes removal application due to the ability of desorption process of adsorbent. As can be seen in figure 9, the adsorption capacity decreases slightly in two cycle experiments while it decreases significantly in three cycle experiments.

Figure 7. Determination of optimum adsorbent mass in MB adsorption by Co- and Fe- MOFs.
Figure 8. Comparison of Langmuir (a, c) and Freundlich (b, d) isotherm model for MB adsorption by Co-MOF (a, b) and Fe-MOF (c, d).

Table 2. Langmuir and Freundlich isotherm constants of Co-MOF and Fe-MOF.

| MOF   | Langmuir Isotherm | Freundlich Isotherm |
|-------|-------------------|---------------------|
|       | Qm (mg/g) | B     | R²      | n    | Kf    | R²   |
| Co-MOF|         3.95     | 0.2504 | 0.995   | 2.2894 | 0.7595 | 0.9542 |
| Fe-MOF|         4.67     | 0.1941 | 0.979   | 1.9928 | 0.7340 | 0.8916 |

Figure 9. Reusability MOFs on the MB adsorption capacity.
This could be attributed to the desorption process where MB has high affinity to MOFs and it was hardly removed from the adsorbent [1]. The RSD of three repetition experiments was 49.9 % for Co-MOF and 52.9 % for Fe-MOF. The results show that the mixture of ethanol: water (7:3 v / v) is able to remove MB from a single dye solution whereas the desorption time and the effect of washing process to the MOFs structure should be studied further.

4. Conclusion
Synthesis of Co-MOF and Fe-MOF has been successfully carried out using the solvothermal method, based on the characterization results. MOFs also have high thermal stability with the decomposition temperature was above 200 °C. According to the best linear coefficient, the adsorption followed the Langmuir adsorption where the MOFs structure has monolayer and homogeneous surface. MOFs are also able to be reused for 2nd cycle in MB adsorption application.

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