SYNTHESIZE METAL-ORGANIC FRAMEWORKS FROM CHROMIUM METAL IONS AND PTCDA LIGANDS FOR METHYLENE BLUE PHOTODEGRADATION

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ABSTRACT
A new photocatalyst-based metal-organic framework (MOFs) Cr-PTC was synthesized from chromium ion and sodium perylene-3,4,9,10-tetracarboxylate by the solvothermal method. This study aims to construct MOFs Cr-PTC and analyze their degradation photocatalytic activity against methylene blue under mercury lamp irradiation as the visible light source. XRD Spectrum exhibited MOFs Cr-PTC has intensity at a value of 2θ = 9.17°; 12.865°; 25.621°; and 27.85°. MOFs Cr-PTC has a narrow bandgap energy of 2.01 eV. MOFs Cr-PTC has good photocatalytic activity in methylene blue degradation under visible light irradiation at neutral pH with 87.22 mg/gram degradation capacity for 180 minutes. Species that play a dominant role in photocatalytic methylene blue degradation are hydroxyl radicals (•OH) and holes (h⁺) and are assisted by other species such as excited electrons (e⁻) and superoxide radicals (•O₂⁻).

Keywords: Methylene Blue, MOFs Cr-PTC, Photocatalyst, Solvothermal.

INTRODUCTION
Metal-organic frameworks (MOFs) materials are widely developed in photocatalysis, including the photodegradation of dyes. MOFs have advantages compared to other photocatalyst materials, such as having a large surface area with abundant active sites and bandgap energy that can be adjusted by modifying the organic ligands and the metal center ion.¹ La-MOF has synthesized based on organic linker Benzene-1,4-dicarboxylic Acid (BDC) with band gap energy of 3.61 eV for degrading rhodamine B under UV light.² According to references, MOF based on organic ligand perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) has visible light responsiveness.³ La-MOF organic linker-based 2,6-naphthalene dicarboxylic acid which produces bandgap energy of 3.1 eV.¹ Among these three organic linkers, PTCDA is an organic linker that can be employed to manufacture MOFs with high visible light sensitivity. In previous research, MOFs have been synthesized from chromium metal ions and organic linkers.⁴ BDC has photocatalytic activity in Remazol Black B dye degradation under UV light.⁵ Then, Cr-MOF based on organic linker NDC (2,6-naphthalene dicarboxylic acid) had large structural pores and better stability at high temperatures compared to Cr-MOFs based on BDC.⁶ Therefore, this study aims to construct MOFs from chromium metal

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ions and PTCDA using the solvothermal method for methylene blue degradation under mercury lamp irradiation as the visible light source.

**EXPERIMENTAL**

**Conversion of PTCDA into Na$_4$PTC**

500 mg (1.27 mmol) of PTCDA was dissolved into 50 ml of distilled water, and 356 mg of NaOH (8.9 mmol) was added. The mixtures were magnetically stirred for 1 hour at 300 rpm. Excess ethanol was added to the mixture to form a yellow Na$_4$PTC precipitate. The solid Na$_4$PTC was filtered and washed with ethanol excess until the pH was neutral. After that, the Na$_4$PTC product was dried at room temperature overnight.

**Synthesize and Characterization MOFs Cr-PTC**

MOFs Cr-PTC was synthesized by dissolving the chromium(III) chloride hexahydrate (CrCl$_3$.6H$_2$O) and Na$_4$PTC with a molar ratio of 2:1; 4:1; and 8:1 mmol in N,N-dimethyl formamide (DMF) and distilled water mixture (5:25 v/v). The mixture was stirred and transferred into a Teflon tube, then put into an autoclave, at 170 °C for 24 hours. The mixture was cooled for 24 h at room temperature. The solid Cr-PTC formed was filtered and washed until the pH was neutral. Finally, the brown crystal Cr-PTC was dried for 24 hours at 70 °C. The final products were designated as MOFs Cr-PTC-1, Cr-PTC-2, and Cr-PTC-3, corresponding to the ratio molar of metal ion and Na$_4$PTC (2:1; 4:1; and 8:1). The Cr-PTC MOFs were characterized by the Prestige 21 Shimadzu FTIR, XRD (7000 Maxima-X), UV-Vis DRS (Agilent Carry 60) carried at a 200-800 nm wavelength with BaSO$_4$ powder was used as a blank, SEM (FEI Quanta 650 with a voltage of 25 kV).

**Photocatalytic Activity of MOFs Cr-PTC Analysis**

25 mg of MOFs Cr-PTC (2:1; 4:1 and 8:1) was dispersed into 50 mL of methylene blue (25 ppm). The mixture was stirred at 300 rpm at room temperature for 3 h in the dark and under a visible light source (250-watt mercury lamp). Then 2 mL of the suspension was taken every 30 minutes for 3 hours and then centrifuged at 6000 rpm for 10 minutes. Furthermore, methylene blue concentration was measured using a UV-Vis spectrophotometer at 665 nm. The degradation capacity (DC) of methylene blue degradation is calculated using equation 1.

$$DC (\text{mg/gram}) = \frac{(A_0 - A_t)}{A_0} \times \frac{Vs}{\text{MOFs mass}} \times C_{MB} \times 100$$

Where $A_0$ is initial absorbance, $A_t$ is the absorbance at a certain reaction time, $V_s$ is the volume of solution, and $C_{MB}$ is methylene blue concentration. This experiment also determined the optimum conditions for methylene blue degradation by MOFs Cr-PTC. The variable in the experiment is the concentration of methylene blue solution (25; 50; and 75 ppm), the mass of the photocatalyst used (15, 25; 35; and 45 mg), and the pH of the solution (2; 5; 7; 9; and 11). Furthermore, adding sacrificial agents, like H$_2$O$_2$, CH$_3$OH, and tert-butanol, to determine the dominant species in the methylene blue degradation.

**RESULTS AND DISCUSSION**

**Photocatalytic Activity of MOFs Cr-PTC**

Figure-1 shows that Cr-PTC MOFs with a 2:1 ratio (Cr-PTC-1) have the highest photocatalytic activity as indicated by an increase in the degradation capacity of 17.39 mg/g in the light than dark experiments. Meanwhile, MOFs Cr-PTC at a ratio of 4:1 (Cr-PTC-2) and 8:1 (Cr-PTC-3) had lower photocatalytic activity, 4.96 mg/gram, and 14.41 mg/gram, respectively (Fig.-1). Cr-PTC MOFs degrade methylene blue dye in light conditions through a photocatalytic mechanism. When light is exposed to a photocatalyst with energy equal to or higher than the band gap, the electrons in the valence band are excited to the conduction band to form excited electrons ($e^-$) and leave holes ($h^+$) in the valence band. This process is known as photocatalytic degradation. The holes ($h^+$) will continue to react with the water to form hydroxyl radicals (•OH), which are powerful oxidizers of the dyes. Meanwhile, superoxide radicals (•O$_2^-$) are created when excited electrons ($e^-$) combine with oxygen and then oxidize the methylene blue. The other mechanism is through a direct reaction to the dye. The excited electrons ($e^-$) and electron holes ($h^+$) formed will react directly with the dye to create reactive cationic and anionic dye radicals, which in turn will attack other dye molecules so that they are further degraded to produce CO$_2$ and H$_2$O. This mechanism occurs when the
dye molecule has a LUMO energy value that is more negative than the conduction band energy level of the MOFs so that it will create cationic dye radicals. Then, the HOMO energy value of the dye is more favorable than the valence band energy of the MOFs to produce cationic dye radicals.\textsuperscript{10}

**Functional Group of MOFs Cr-PTC**

The absorption peak at 3118 cm\(^{-1}\) in the MOF Cr-PTC spectrum (Fig.-2) correlates to the stretching vibration of the OH group caused by the existence of water molecules adsorbed on the surface of the MOFs Cr-PTC. Due to water molecules adhering to the MOFs' surface, this absorption peak was also seen in other chromium metal ion-based MOFs.\textsuperscript{4,11} The absorptions at 1754 cm\(^{-1}\) and 1741 cm\(^{-1}\) were related to the C=O group's symmetric and asymmetric stretching vibrations, respectively. In addition, the absorption at 544 cm\(^{-1}\) was attributed to Cr-O strain vibration. Previous research, also found a similar absorption, namely the strain vibration of the Cr-O at 570 cm\(^{-1}\), which indicates a bond of Cr and O atoms in the carboxylate group.\textsuperscript{12} Afterward, in prior studies, absorption at 674 cm\(^{-1}\) was found to be derived from the Cr-O group, where the strain vibration between metal and oxygen is usually observed at around 400-800 cm\(^{-1}\).\textsuperscript{13}

**Crystallinity and Crystal Size of MOFs Cr-PTC**

Figure-3 shows four peaks with the highest intensity at 2θ = 9.17\(^{\circ}\); 12.865\(^{\circ}\); 25.621\(^{\circ}\); and 27.85\(^{\circ}\). The presence of sharp peaks resulting from the diffraction pattern indicated that the crystallinity of the MOFs Cr-PTC was quite good. The crystal size of the MOFs Cr-PTC is 17.50 nm from the Debye Scherrer calculation. The good crystallinity of Cr-PTC MOFs was obtained due to the solvothermal synthesis method. According to references, this solvothermal method is suitable because it can control crystal growth and size.\textsuperscript{14} In addition, the solvothermal method was carried out at a high temperature and pressure conditions in a closed system. Therefore, it was suitable for obtaining nanostructured crystals.\textsuperscript{15}

**Bandgap Energy of MOFs Cr-PTC**

Figure-4 exhibits that the bandgap energy of MOFs Cr-PTC is 2.01 eV. It indicated that MOFs Cr-PTC is a semiconductor material responsive to visible light. The bandgap energy of Cr-PTC is smaller than Cr-BDC because the conjugated bonds in PTC are higher than in BDC. Higher the number of conjugated bonds turn down bandgap energy because the orbitals overlap, decreasing the bandgap energy between neighboring orbitals, and causing an increase in light absorption intensity. In addition, the metal ions also
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affect the MOF’s band gap energy value. The MOFs based on yttrium metal ion (Y) with a PTC organic ligand have been successfully synthesized with a higher bandgap energy of 2.20 eV. It shows the effect of the metal ion used on the bandgap energy of MOFs. The bandgap energy in a material could be influenced by ligands that have conjugated phi (\(\pi\)) bonds and metal atoms by looking at the size of the Secondary Building Unit (SBU).

MOFs Cr-PTC Morphology

Figure-5 shows that the morphology of MOFs Cr-PTC has a cylindrical rod-like. However, it can also be seen that there are many impurities in the morphological appearance of MOFs Cr-PTC due to the inadequate washing process during synthesis. The particle size of MOFs Cr-PTC was measured using Image J application software and then processed further with Origin Lab. The data analysis shows that the particle size distribution of the Cr-PTC MOFs is 300-350 nm, with an average size of 337 nm.

Effect of Methylene Blue Concentration, MOFs Cr-PTC Mass, and pH

Figure-6a showed an adsorption reaction at an initial concentration of 75 ppm because the graph trendline is up and down. Meanwhile, at concentrations of 25 ppm and 50 ppm, the reaction is photocatalytic because the trendline significantly increases the degradation percentage. In reference, the degradation percentage would decrease along with the increase in dye concentration. The dye acts as a filter for the incident light, hindering light from reaching the semiconductor particles. Methylene blue is a compound that has the

Fig.-3: Diffraction Pattern of MOFs Cr-PTC

Fig.-4: Bandgap Energy of MOFs Cr-PTC

Fig.-5: Morphology of MOFs Cr-PTC with Magnificent (a) 1000x, (b) 5000x dan (c) 10000x
character of a light absorber. The increase in the concentration of methylene blue also causes more methylene blue to be adsorbed on the photocatalyst surface. It inhibits the penetrating light energy to the solution system so that the photocatalyst is not exposed to light, and the electron excitation process is not formed. According to the reference, that described crystal violet degradation using Zn-MOFs. At a dye concentration of 5 ppm, 70% degradation occurred, while at a concentration of 20 ppm, only 22% degradation occurred.

Figure-6b showed that 25 mg of MOFs Cr-PTC had the largest degradation capacity of 87.22 mg/gram. While 15 mg MOFs has degradation capacity of 80.64 mg/gram, 35 mg MOFs is 61.81 mg/gram, and 45 mg MOFs is 52.69 mg/gram. The more amount of the photocatalyst, the greater degradation of the dyes. The degradation capacity was increased due to more dye being adsorbed at the active site of the photocatalyst. However, the trendline of the graph increased every 30 minutes (Fig.-6b), suggesting that 45 mg Cr-PTC had an insignificant upward trendline. The number of MOFs was abundant and generated low photocatalytic activity because the solution was cloudy and blocked the penetrating light to the photocatalyst surface. Therefore, it reduced the degradation efficiency of dyes.

Figure-6c showed that under acidic conditions pH 2 and 5, MOFs Cr-PTC degrade 26.34 mg/gram and 20.74 mg/gram of methylene blue after 3 hours of reaction. At neutral (pH 7), MOFs Cr-PTC revealed a high degradation capacity of 87.22 mg/gram during the same reaction time. Meanwhile, in alkaline conditions, pH 9 and 11, the degradation capacity was very high in just 30 minutes, 88.24 mg/gram and 91.29 mg/gram, respectively. When viewed from the trendline of increasing the degradation capacity, under acidic conditions, there is no photocatalytic activity because there is no significant increase in the degradation but a downward trendline. Under acidic conditions, the surface charge of the photocatalyst becomes positively charged. In contrast, under alkaline conditions, the surface charge of the photocatalyst becomes negatively charged. It facilitated the powerful adsorption of cationic dyes like methylene blue due to electrostatic attraction and enhanced the reaction rate. In an acidic environment, there is an interaction between H⁺ ions and carboxylate, which causes the surface to become positively charged, while in an alkaline environment, there is an interaction between OH⁻ ions and H atoms in organic ligands which then causes the surface to become negatively charged. It is known that the repulsion between MOFs and methylene blue occurs in acidic conditions if there are excess H⁺ ions (low pH conditions). Meanwhile, under alkaline conditions, the surface of the Cr-PTC MOFs will be negatively charged, resulting in an attractive force with the cationic methylene blue molecule. It causes the adsorption of methylene blue on the surface of the MOFs, and the degradation percentage also increases under alkaline conditions.

**Methylene Blue Photocatalytic Degradation Mechanism of MOFs Cr-PTC**

Figure-7 exhibited that when H₂O₂ was added, the degradation capacity was 97.00 mg/gram for 180 minutes. Then, adding H₂O₂ and tert-butanol resulted in a degradation capacity of 98.25 mg/gram. Meanwhile, the degradation capacity was 87.22 mg/gram without adding a sacrificial agent. The increasing methylene blue degradation when adding H₂O₂ compared to without the addition of H₂O₂ indicates that the hydroxyl radical (•OH) is the species that plays a dominant role in the photocatalytic reaction. However,
when tert-butanol molecules are added, the number of hydroxyl radical species (•OH) is enhanced. Adding H$_2$O$_2$ will produce a hydroperoxyl radical (•HO$_2$) and react with hydroxyl radical (•OH) to form water and oxygen. Therefore, adding tert-butanol will capture the hydroxyl radical and inhibit oxygen and water formation.

The reduced degradation capacity when adding methanol can be explained by the capture of holes (H$^+$) by methanol so that hydroxyl radicals (•OH) are not formed, and only superoxide radicals (•O$_2^-$) degrade methylene blue. Holes (H$^+$) will oxidize methanol to hydroxyalkyl radicals (•CH$_2$OH) and further oxidize to formaldehyde (CH$_2$O). Therefore, the formation of hydroxyl radicals (•OH) which play an essential role in the degradation process of methylene blue, does not occur. Furthermore, the superoxide radical (•O$_2^-$) has a lower strength than the hydroxyl radical (•OH), so the degradation percentage of methylene blue with the addition of methanol is lower than the addition of H$_2$O$_2$.

**CONCLUSION**

MOFs Cr-PTC has a 25.7 nm crystal size and 337 nm particle size with a cylindrical rod-shaped morphology. MOFs Cr-PTC has narrow 2.01 eV bandgap energy. MOFs Cr-PTC has good photocatalytic activity in degrading methylene blue under visible light irradiation. The optimum reaction condition is 50 ppm methylene blue, 25 mg MOFs and carried out at pH 7 resulting methylene blue degradation of 87.22 mg/gram.

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