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Research Article

Synthesis of Metal-Organic Framework (MOF) Cr-PTC-HIna for Heavy Metal Ion Adsorption

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Abstract

As an adsorbent material, Metal-Organic Framework (MOF) provides several advantages, such as large surface area and pore volume, as well as stability in aqueous systems both in acidic, basic, and neutral conditions. The research successfully made a metal organic framework (MOF) from chromium and perylene that was modulated by isonicotinic acid. It was done using three different methods: hydrothermal (Cr-PTC-HIna-HT), solvothermal (Cr-PTC-HIna-ST), and sonochemical (Cr-PTC-HIna-SC). The Cr-PTC-HIna-SC showed the greatest Pb^{2+} ion adsorption capacity. The optimum adsorption of Pb^{2+} ions occurred at 150 ppm Pb^{2+} ion concentration, pH of 5, 90 min of contact time, and an adsorption capacity of 149.95 mg/g at 35 °C. The dominant adsorption isotherm model is the Langmuir isotherm model with $R^2 = 0.9867$ and follows the pseudo-second-order. The selectivity test showed that Cr-PTC-HIna-SC MOF could adsorb more Cd^{2+} ions than Pb^{2+} ions, with 250 mg/g being the best amount.

Keywords: Adsorbent; Cd^{2+}; Pb^{2+}; Cr-PTC-HIna; sonochemical

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1. Introduction

Lead ion (Pb^{2+}) and cadmium ion (Cd^{2+}) are two heavy metal contaminants that pose a significant threat to human health. Lead and cadmium ions are non-biodegradable and cause serious diseases, such as digestive, circulatory, kidney, and even death, if they accumulate in the human body through the food chain [1–2]. It is worth noting that the Indonesian Minister of Health has set a maximum limit of metal content in drinking water to 0.01 mg/L for Pb and 0.003 mg/L for Cd [3].

Efforts to remediate environmental vandalism by heavy metal ion pollutants can be carried out using various methods, such as electrolysis, ion exchange, precipitation, photocatalysis, and adsorption. Heavy metal ion contaminants are thought to be most easily removed by adsorption because it has many benefits, such as low cost, low impact on the environment, high efficiency, operational flexibility, and the ability to be reversed.

The adsorption ability of an adsorbent material is highly dependent on its surface area and chemical stability in an aqueous system. It means that the larger the adsorbent material's surface area and porosity, the more effective it is

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for adsorption. Heavy metal contaminants are commonly found in acidic aqueous systems like wastewater or water. To effectively remove these contaminants, adsorbent materials with small particle sizes, high porosity, and good chemical stability, particularly in acidic conditions, are required.

Metal-organic frameworks (MOFs) are an interesting class of materials that have attracted attention in recent years due to their unique properties. The MOFs consist of metal ions and organic linkers, forming a three-dimensional crystal structure. Li *et al.* stated that MOFs represent a promising alternative nanoparticle-based adsorbent material for removing heavy metal ion contaminants [4]. The high surface area, large pore volume, and huge absorption capacity of MOFs make them an ideal material for heavy metal ion adsorption. Additionally, MOFs are stable in water and easy to fabricate on a large scale [5].

MOFs can be synthesized using several methods, like solvothermal, hydrothermal, and sonochemical. Solvothermal and hydrothermal techniques create MOF particles with high crystallinity. However, these methods require a long synthesis time of 48–96 h with a high reaction temperature of 453K [6]. The sonochemical method, on the other hand, can yield MOF in 30 to 180 min and at a lower temperature (273 to 313 K). This is because it utilizes ultrasonic energy to speed up the nucleation process and crystal growth [7]. The hydrothermal method was used by Zou *et al.* to make MIL-101(Cr). They added H_2O/HF and left it for 8 h. The surface area was 4100 $m^2.g^{-1}$ and the pore volume was 2.02 $cm^3.g^{-1}$ [8]. Zou *et al.* also used the solvothermal method with the addition of H_2O/HF for 96 h for producing MIL-101(Cr) with a surface area of 3780 $m^2.g^{-1}$ and a pore volume of 1.74 $cm^3.g^{-1}$ [6]. On the other hand, Ghoochani *et al.* synthesized MIL-101 (Cr) using sonication energy for 10 min, resulting in a surface area of 2282.9 $m^2.g^{-1}$ and a pore volume of 2.52 $cm^3.g^{-1}$ [9]. It confirmed that the three methods successfully synthesize MI-101 (Cr) with high surface area.

Adawiah and her team studied Cr-PTC-HIna for 240 min in the dark and discovered that it can effectively remove methylene blue pollutants (50 ppm) by up to 71.05% [10]. It is made up of chromium ions, an isonicotinic acid modulator, and a ligand called perylene-3,4,9,10-tetracarboxylate [10]. It demonstrated that Cr-PTC-HIna MOF employs an adsorption mechanism to remove methylene blue molecules. However, there has been no research conducted on the potential of Cr-PTC-HIna MOF for the adsorption of heavy metal ions, such as Pb^{2+} and Cd^{2+}, in water.

The main objective of this study is to synthesize Cr-PTC-HIna MOF using three methods, namely solvothermal, hydrothermal, and sonochemical. Then, the obtained MOFs were investigated for the adsorption of Pb^{2+} metal ions. Therefore, we focused on determining the best method that yielded Cr-PTC-HIna MOF with the highest Pb^{2+} adsorption capacity. Additionally, the effects of initial ion concentration, pH, contact time, and temperature on the Pb^{2+} adsorption capacity were investigated. The adsorption ability of Cd^{2+} at optimal conditions was also carried out to determine its selectivity in the absorption of heavy metal ions.

2. Materials and Methods

2.1 Materials

The materials used in this study were available commercially and used without further purification. Chromium (III) chloride hexahydrate ($CrCl_3.6H_2O$) (Merck), perylene-3,4,9,10-tetracharboxylic dianhydride (PTCDA) (Merck), isonicotinic acid (HIna) (Merck), distilled water, sodium hydroxide (NaOH) grade ensure (Merck), ethanol technical grade (Merck), and N, N-dimethyl formamide (DMF) grade ensure (Merck), lead nitrate ($Pb(NO_3)_2$) grade ensure (Merck), cadmium sulfate ($CdSO_4$) grade ensure (Merck), sodium chloride (NaCl) grade ensure (Merck), hydrogen chloride (HCl) grade ensure (Merck). Lead standard stock solution (Merck), and cadmium standard stock solution (Merck) with guaranteed of purity and grade.

2.2 Preparation of Sodium Perylene-3,4,9,10-tetracarboxylate (Na_4PTC)

PTCDA (0.5 g, 1.27 mmol) and NaOH (0.365 g, 8.9 mmol) were dissolved with 50 mL of distilled water in a beaker glass and then magnetically stirred at 300 rpm for 1 h. Then, the resulting greenish-red filtrate was added to excess ethanol to produce a yellow precipitate. The yellow precipitate was washed with ethanol until the pH was neutral, and then dried at room temperature for 24 h to produce yellow Na_4PTC powder.

2.3 Synthesis of Cr-PTC-HIna MOF

2.3.1 Solvothermal Method

A beaker glass held 25 mL of distilled water and 5 mL of DMF. This was mixed with 0.266 g of chromium(III) chloride hexahydrate ($CrCl_3.6H_2O$) (1.0 mmol), 0.258 g of Na_4PTC (0.5 mmol), and 0.0615 g of isonicotinic acid (HIna). Then, the mixture was magnetically stirred for 1 h at 300 rpm. The mixture was transferred into a Teflon line, put into an autoclave, and then heated for 24 h at 170 °C. The resulting precipitate was filtered and washed with hot, distilled water until a colorless filtrate was produced. The precipitate was dried for 24 h at 70 °C. The resulting sample was coded Cr-PTC-HIna-ST.

2.3.2 Hydrothermal Method

To dissolve $CrCl_3.6H_2O$ (0.266 g, 1.0 mmol), Na_4PTC (0.258 g, 0.5 mmol), and isonicotinic acid (HIna) (0.0615 g, 0.5 mmol), 30 mL of distilled water was added to a beaker glass. The mixture was then stirred magnetically at 300 rpm for 1 h. The mixture was transferred into a Teflon line, put into an autoclave, and then heated for 24 h at 170 °C. The resulting precipitate was filtered and washed with hot distilled water until a colorless filtrate was produced. The precipitate was dried for 24 h at 70 °C. The resulting sample was coded Cr-PTC-HIna-HT.

2.3.3 Sonochemical Method

Chromium(III) chloride hexahydrate ($CrCl_3.6H_2O$) (0.266 g, 1.0 mmol), Na_4PTC (0.258 g, 0.5 mmol), and isonicotinic acid (HIna) (0.0615 g, 0.5 mmol) were dissolved with 25 mL of distilled water and 5 mL in a beaker glass and magnetically stirred for 1 h at 300 rpm. The mixture was transferred into a sonicator with a degassing time of 90 min, a sonication time of 180 min, a temperature of 25 °C, and a frequency of 65 Hz (605 watts). The resulting precipitate was filtered and then washed with hot distilled water until a colorless filtrate was produced. The resulting precipitate was dried for 24 h at 70 °C. The resulting sample was coded Cr-PTC-HIna-SC.

2.4 pH Point Zero Change (pH_{PZC}) Analysis

40 mL of NaCl 0.1 M was added to 10 Erlenmeyer flasks. Then, the pH of the solution was adjusted from 1 to 10 as the initial pH (pHi) by adding NaOH 0.1 M or HCl 0.1 M. Next, 50 mg of Cr-PTC-HIna MOF was dispersed into each Erlenmeyer flask. The suspension was then shaken for 24 h. Finally, the final pH (pH_f) was measured. Next, the ΔpH was calculated according to Equation (1). A line equation was created between the x-axis (pH_i) and y-axis (ΔpH) to determine the pH. The pH_{pzc} is the pH value when ΔpH equals zero [11].

$$\Delta pH = pH_f - pH_i \tag{1}$$

2.5 Adsorption Procedure of Pb^{2+} Ions using Cr-PTC-HIna MOF

Adsorption experiments were performed according to standard batch procedures. The batch procedure was carried out by dispersing Cr-PTC-HIna MOF (50 mg) in 100 mL of Pb^{2+} solution with a concentration of 50–250 mg/L, and the pH was optimized from 2–5. Next, the mixture was magnetically stirred at 600 rpm for 30–120 min at room temperature. The mixture was centrifuged at 6000 rpm for 20 min. The Pb^{2+} absorbance in the solution was measured using an atomic absorption spectrophotometer (AAS) at 283.3 nm. The Pb^{2+} concentration was calculated from the linear regression equation of the Pb^{2+} standard solution obtained according to Equation (2). The Pb^{2+} amount adsorbed at equilibrium and at time per unit mass of MOF (Q_e and Q_t) is calculated according to Equations (3)–(4).

$$y = bx + a \tag{2}$$

$$Q_e = \frac{(C_0 - C_e)}{m} \times V \tag{3}$$

$$Q_t = \frac{(C_0 - C_t)}{m} \times V \tag{4}$$

where, y is the measured absorbance of Pb^{2+} solution, x is the measured concentration of Pb^{2+} ions (mg/L), Q_e is equilibrium Pb^{2+} concentration on the adsorbent (mg/g), Q_t is Pb^{2+} concentration on the adsorbent at time (mg/g), C_0 and C_e are the initial and equilibrium concentrations of Pb^{2+} ions in the solution (mg/L), V is the volume of solution (L), and m is the mass of adsorbent (MOF) (g).

2.6 Adsorption Isotherm Studies

Four isotherm models (Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich) were used to investigate the adsorption isotherm. The Langmuir isotherm can be expressed in linear Equation (5), where C_e/Q_e is assumed to be y, C_e is assumed to be x, and $1/Q_m$ is the slope [12].

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{Q_m K_L} \tag{5}$$

where, C_0 and C_e are the initial and equilibrium concentrations of Pb^{2+} ions in the solution (mg/L), Q_m is the maximum adsorption capacity of monolayer adsorbent (MOF) (mg/g), Q_e is the equilibrium Pb^{2+} concentration on the adsorbent (mg/g), and K_L is the Langmuir adsorption constant. K_L is important to calculate the dimensionless equilibrium parameters (R_L) that explain the favorability of the adsorption process. R_L is calculated using Equation (6) [12].

$$R_L = \frac{1}{1 + K_L C_0} \tag{6}$$

The Freundlich isotherm can be expressed in linear Equation (7), where log Q_e is assumed to be y, log C_e is assumed to be x, and $1/n$ is the slope [12].

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \tag{7}$$

where, C_e is the equilibrium concentration of Pb^{2+} ions in solution (mg/L), Q_e is the equilibrium Pb^{2+} concentration on the adsorbent (mg/g), and K_f and n are Freundlich constants incorporating the factors affecting the adsorption capacity and adsorption intensity, respectively [12].

The Temkin isotherm equation can be seen in linear Equation (8), where Q_e is assumed as y and ln C_e as x [13]. B and A can be calculated from the slopes (B) and intercepts (B ln$A$), respectively.

$$Q_e = B\ln A + B\ln C_e \tag{8}$$

$$B = \frac{RT}{b_T} \tag{9}$$

where, Q_e is the equilibrium Pb^{2+} concentration on the adsorbent (mg/g), A is the Temkin isotherm constant (L/g), B is the heat constant of adsorption (J/mol), and it is defined by the expression $B = RT/b_T$ (Equation (9)), b_T is the Temkin constant (J/mol), R is the ideal gas constant (8.314 J/mol^{-1}K^{-1}), and T is temperature (K) [12].

The Dubinin - Radushkevich isotherm equation can be seen in linear Equations (10)–(11), where ln Q_e is assumed to be y and ε^2 as x. The value of energy required to remove molecules from the surface (in the Dubinin-Radushkevich model) is determined from Equation (12) [14].

$$\ln Q_e = \ln Q_m - K_{dr}\varepsilon^2 \tag{10}$$

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \tag{11}$$

$$E = \frac{1}{\sqrt{2K_{dr}}} \tag{12}$$

In this equation, Q_m is the MOF's maximum adsorption capacity (mg/g), Q_e is the adsorbent's equilibrium Pb^{2+} concentration (mg/g), K_{dr} is the Dubinin-Radushkevich adsorption constant (mol^2/kJ^2), ε is the Polanyi potential, E is the energy needed to remove molecules from the surface (kJ/mol), T is the temperature (K), and R is the gas constant (8.314 J/mol.K).

2.7 Adsorption Kinetics Studies

The data on the contact time is used to study adsorption kinetics using pseudo-first-order and pseudo-second-order models. These models were fitted by the adsorption data of Pb^{2+} through the kinetics equation shown in Equations (13)–(14).

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \tag{13}$$

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{K_2 Q_e^2} \tag{14}$$

where, t is time (min), Q_e is equilibrium Pb^{2+} concentration on the adsorbent (mg/g), Q_t is Pb^{2+} concentration on the adsorbent at time (mg/g), K_1 is a pseudo-first-order constant (min^{-1}), and K_2 is a pseudo-second-order constant (g.mg^{-1}.min^{-1}).

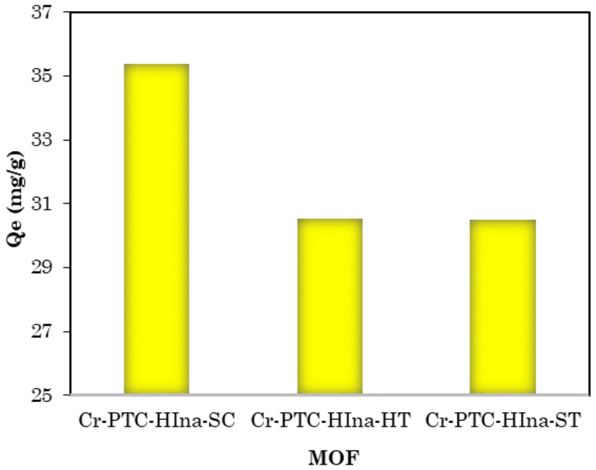

Figure 1. Adsorption capacity of various Cr-PTC-HIna MOF towards Pb^{2+} ions at concentrations of Pb^{2+} ions (m = 50 mg, pH = 5, T = 25 °C, t = 90 min).

3. Results and Discussion

3.1 Adsorption Capacity of Cr-PTC-HIna MOFs on Heavy Metal Ions Pb^{2+}

The adsorption capacity of the three MOFs (Cr-PTC-HIna-ST, Cr-PTC-HIna-HT and Cr-PTC-HIna-SC) at 50 ppm Pb^{2+} concentration is shown in Figure 1. The Figure 1 shows that sonochemical is the best way to make Cr-PTC-HIna MOF, which can hold 35.37 mg/g of Pb^{2+} metal ions. Cr-PTC-HIna-SC MOF provided a larger surface area, pore volume, and pore size than Cr-PTC-HIna-ST and Cr-PTC-HIna-HT (92.76 m^2.g^{-1}, 0.395 cm^3.g^{-1}, and 142.738 nm) [15]. The amount of Pb^{2+} ions that the Cr-PTC-HIna MOF can absorb depends on its surface area, which increases the MOF's adsorption capacity.

The ultrasound energy utilized in the sonochemical method increases the decomposition rate of precursor compounds, which enhances the MOF's particle formation with a smaller and more uniform size [16]. When MOF particles get smaller, the MOF surface area gets larger. This makes it easier for adsorbates to stick to MOF [17]. In addition, the sonochemical method produces MOF particles with a higher possibility of crystal defect formation than the solvothermal and hydrothermal methods. According to Yu *et al.* [18], crystal defect sites make MOF's surface area and pore volume bigger. It is demonstrated in the S-MOF-545 material made using the sonochemical method [18]. This material has more defect sites and produces a larger surface area and pore volume compared to the solvothermal method [18]. The crystal defect is related to the use of water solvents, which inhibit crystal formation and result in a less crystalline MOF framework. The activation energy goes up because polar solvents like water and anions like perylene-3,4,9,10-tetrakarboxylate create strong hydrogen bonds through the solvation effect [19].

3.2 Effect of Initial Pb^{2+} Concentration

Figure 2 shows that at Pb^{2+} concentrations of 50–150 mg/L, the adsorption capacity of Cr-PTC-HIna-SC continued to increase, while after exceeding 150 mg/L, the adsorption capacity decreased. It suggests that the best performance is achieved at a Pb^{2+} ion concentration of 150 mg/L with an adsorption capacity of 96.18 mg/g. The decrease in adsorption capacity at a concentration greater than 150 mg/L (200–250 mg/L) is due to the saturation of adsorption sites on the adsorbent. After reaching its maximum adsorption capacity, the adsorbate is released during stirring [20]. Liang *et al.* [21] investigated the adsorption of Pb^{2+} metal ions by ethylenediamine-modified pectins (Eps) with Pb^{2+} concentrations ranging from 20 to 250 mg/L. They reported that the Pb^{2+} sorption rate increased as the initial Pb^{2+} concentration increased (<150 mg/L) but gradually decreased at higher concentrations (150–250 mg/L) [21].

3.3 Effect of pH

Figure 3 indicates that as the pH of the solution increases, the adsorption capacity of the Cr-PTC-HIna-SC MOF also increases. The lowest adsorption capacity is observed at pH 2, which is 36.43 mg/g. At low pH, an excess of H^+ ions is present, which makes the Pb^{2+} ions and H^+ ions compete with each other to interact with the Cr-PTC-HIna-SC MOF. The extra H^+ ions in the system are easily protonate the Cr-PTC-HIna-SC MOF, making it more positively charged. It makes the MOF and Pb^{2+} ions repel each other. MOF gets charged at the nitrogen atom of isonicotinic acid and the carbon atom of the perylene aromatic ring. Besides that, protonation of MOF's functional groups leads to the unavailability of functional groups for complexation with Pb^{2+} ions. Excessive hydrogen ions (H^+) compete with Pb^{2+} on the same binding site on the MOF [22].

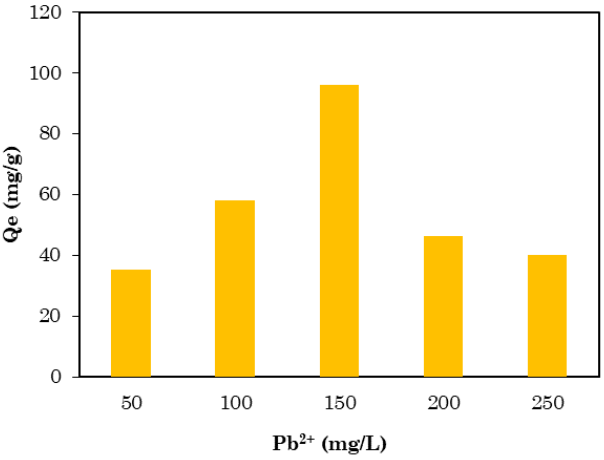

Figure 2. Effect of Pb^{2+} concentration on Pb^{2+} ions adsorption capacity of Cr-PTC-HIna-SC MOF at m = 50 mg, pH = 5, T = 25 °C, t = 90 min.

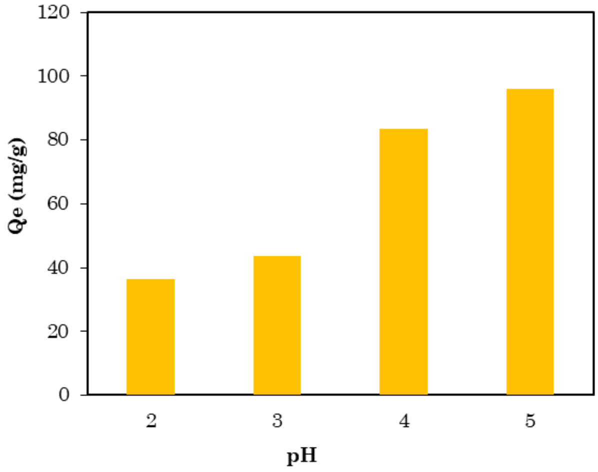

Figure 3. Effect of pH on Pb^{2+} ions adsorption capacity of Cr-PTC-HIna-SC MOF at m = 50 mg, C_0 = 150 mg/L, T = 25 °C, t = 90 min.

On the other hand, increasing the pH (from 2–5) causes the concentration of H^+ ions to decrease. The Cr-PTC-HIna MOF becomes more negatively charged due to the lower protonation effect, so there is an electrostatic interaction between the more negatively charged Cr-PTC-HIna-SC MOF and the positively charged Pb^{2+}, resulting in higher Pb^{2+} adsorption [23]. Pb^{2+} ions are adsorbed less by the Cr-PTC-HIna MOF when the pH is above 5. It is because $Pb(OH)^2$ precipitates were formed when Pb^{2+} and OH^- ions reacted at that pH. The solubility of Pb^{2+} in water tends to be high at low pH (pH <5). $Pb(OH)^+$, $Pb_2(OH)_3{}^+$, and $Pb_3(OH)_4{}^{2+}$, which are all present in very small amounts at low pH, follow Pb^{2+} as the dominant Pb^{2+} species. Conversely, at high pH (pH > 5), Pb^{2+} ions react with OH^- to form $Pb(OH)_2$ white precipitates.

The effect of pH on the adsorption capacity of MOF for heavy metal ions is closely related to the surface charge of the MOF. Therefore, it is very important to determine the pH value at which the MOF charge is zero (pH_{PZC}). The zero-charge point determines the surface charge of the adsorbent at a particular pH and provides information regarding the possible electrostatic interaction between the adsorbent and metal ions. Changes in pH can change the surface charge of the adsorbent. According to Al-Maliky *et al.* [24], pH_{PZC} (pH of point zero charge) is the pH value where the surface charge of the adsorbent is equal

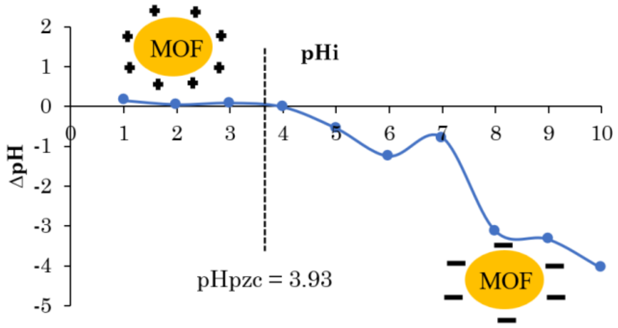

Figure 4. The correlation between initial pH (pH_i) and ΔpH.

to 0, or neutral. It implies that for pH_{PZC}, there is no charge on the surface, or there are equal amounts of negative and positive charges. The pH_{PZC} measurement results of Cr-PTC-HIna-SC MOF are shown in Figure 4.

Figure 4 showed that the pH_{PZC} of Cr-PTC-HIna-SC MOF is 3.93. The optimum pH of the Pb^{2+} adsorption in this study is at pH 5, where the pH is above the pH_{PZC} (Figure 3). Figure 4 demonstrates that the Cr-PTC-HIna-SC MOF surface has a more positive charge at $pH < pH_{PZC}$, while at $pH > pH_{PZC}$, the Cr-PTC-HIna-SC MOF surface has a more negative charge. When the pH is higher than pH_{PZC}, the positively charged Pb^{2+} cation can easily stick to the negatively charged Cr-PTC-HIna MOF anion through electrostatic attraction. When pH is less than pH_{PZC}, on the other hand, the surface of Cr-PTC-HIna MOF is positively charged. It makes the electrostatic repulsion between Cr-PTC-HIna-SC MOF and Pb^{2+} ions [25].

3.5 The Effect of Contact Time

Figure 5 illustrates that the adsorption of Pb^{2+} metal ions increased from 56.40 mg/g to 96.18 mg/g within a contact time of 30–90 min. This increase is likely due to the adsorbent surface still having many active sites that can bind with Pb^{2+} ions [26]. However, after 90 min, the adsorption capacity declined as the active sites became saturated and lost their ability to bind with Pb^{2+} ions. The lowering in adsorption capacity after reaching the optimum capacity is due to desorption of Pb^{2+} during stirring, which occurs when the MOF surface is saturated [20].

3.5 The Effect of Temperature

Figure 6 reveals that the adsorption capacity (Q_e) increased at 35 °C by 149.95 mg/g, then decreased at 45 °C by 108.65 mg/g, 55 °C by 133.51 mg/g, and 65 °C by 116.58 mg/g. It is because when temperatures are low (25–35 °C), thermal energy goes down, which also lowers the kinetic energy of molecules that want to stick to MOF. This makes it easier for Pb^{2+} to interact with MOF, which increases its ability to stick to MOF.

Meanwhile, at too high temperatures, such as 45–65 °C, too much energy causes Pb^{2+} ions to desorb from the MOF surface, leading to decreased adsorption [27]. At higher temperatures, thermal energy increases, forces faster molecular movement, and raises its kinetic energy. Aisyahlika *et al.* [28] found that when the temperature goes up, the particles in the solution have a lot more kinetic energy, which makes them move faster. It causes the adsorbate that the adsorbent had initially successfully absorbed to elute back out of its pores [28].

3.6 Isotherm Adsorption

An important factor in adsorption is the adsorption isotherm, which explains the phenomena and interactions between the adsorbent and the adsorbate. The fitting results are graphically represented in Figure 7 and Table 1. Figure 7 shows that the Langmuir model is more appropriate than the Freundlich, Temkin, and Dubinin-Raduskevich models, with a higher correlation coefficient of 0.9867, which indicates that the adsorption is monolayer. The Q_m, K_L, and R_L values were 46.9486 mg/g, 0.1109, and 0.0911-0.4702, respectively (Table 1). So, it presents a favorable sorption for the Pb^{2+} ions (favorable if $0<R_L<1$ [29,30].

We can apply the Freundlich isotherm to talk about a certain kind of physical adsorption where the adsorbate sticks to the adsorbent surface in layers. According to this isotherm model, the adsorption sites are heterogeneous. An important factor to consider in the Freundlich isotherm is

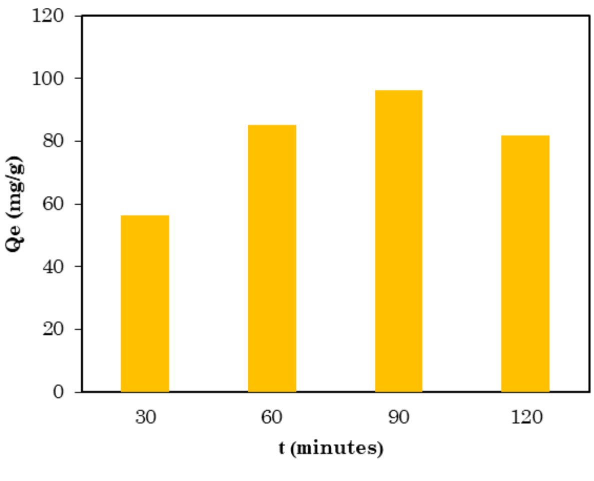

Figure 5. Effect of contact time on Pb^{2+} ions adsorption capacity of Cr-PTC-HIna-SC MOF at m = 50 mg, pH = 5, C_0 = 150 mg/L), T = 25 °C.

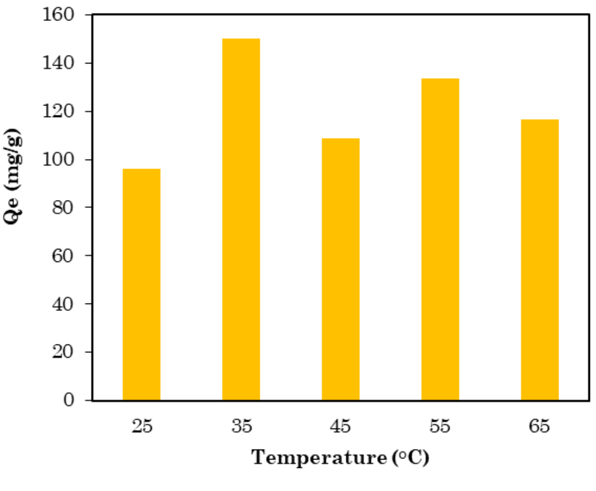

Figure 6. Effect of temperature on Pb^{2+} ions adsorption capacity of Cr-PTC-HIna-SC MOF at m = 50 mg, pH = 5, C_0 = 150 mg/L, t = 90 min.

the value of n, which represents the adsorption intensity. A value of $n < 1$ indicates that the adsorption occurs by chemical interaction, while if $n > 1$, the adsorption occurs by physical interaction [29]. From Figure 7, we see that the R^2 for the Freundlich isotherm model is 0.9305 ($R^2 >$ 0.70), which suggests multilayer adsorption. The Freundlich adsorption constant (K_f) and n value are 16.2592 and 4.5208, respectively (Table 1). Thus, it was confirmed that the adsorption process occurs due to physical interactions since n is greater than 1. Van der Waals forces or

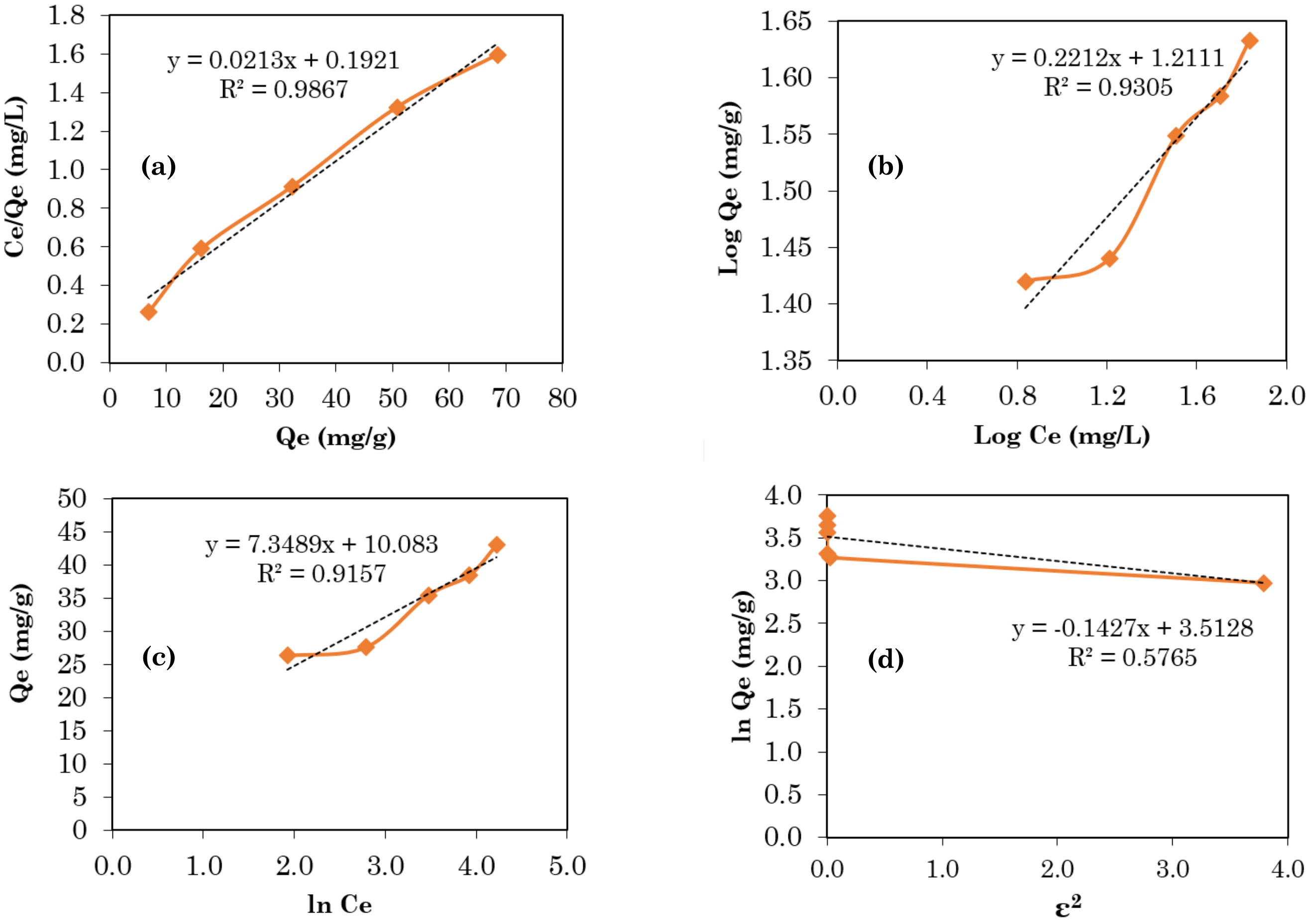

Figure 7. Linear fitting of (a) Langmuir; (b) Freundlich; (c) Temkin; (d) Dubinin-Raduskevich isotherm models.

Table 1. Adsorption isotherm constant for Pb^{2+} onto Cr-PTC-HIna-SC MOF.

Adsorption isotherm	Parameter	Value
Langmuir isotherm	Q_m (mg/g)	46.9486
	K_L (mg/L)	0.1109
	R_L	0.0911-0.4702 ($0<R_L<1$)
	R^2	0.9867
Freundlich isotherm	K_f ($mg^{1-n}g^{-1}L^n$)	16.2592
	$1/n$	0.2212
	n	4.5208
	R^2	0.9305
Temkin	A (L/g)	3.9434
	B (J/mol)	7.3489 ($B < 8$ kJ/mol)
	b_T (J/mol)	337.1351
	R^2	0.9157
Dubinin-Raduskevich	Q_m (mg/g)	33.5421
	K_{rd} (mol^2/kJ^2)	0.1427
	E (kJ/mol)	1.8719 ($E < 8$ kJ/mol)
	R^2	0.5765

electrostatic interactions with weak bonds between adsorbates and adsorbents make it possible for metal ions to stick to adsorbents [31].

The Temkin isotherm describes the adsorption process on heterogeneous media. The heterogeneous surface allows for a multilayer adsorption process on the adsorbent surface. The Temkin isotherm is based on three assumptions: the amount of heat absorbed decreases linearly as the adsorbent surface increases; the adsorbent surface has uniform binding energy; and the adsorbate and adsorbent interact during the adsorption process. An important factor in the Temkin isotherm is the B value, or adsorption heat constant. If the B value is < 8 kJ/mol, adsorption occurs physically, while if the B value is > 8 kJ/mol, adsorption occurs chemically [29].

Figure 7 displayed that the Temkin isotherm produces an R^2 of 0.9157. Ragadhita et al. stated that if $R^2 > 0.70$, then the adsorbate is uniformly distributed to the surface of the adsorbent [29]. Meanwhile, if $R^2 < 0.70$, the adsorbate is not uniformly distributed to the adsorbent surface. The resulting B value is 7.3489 kJ/mol. It indicates that the adsorption of Pb^{2+} ions by Cr-PTC-HIna-SC MOF occurs through physical adsorption [29].

The Dubinin-Raduschkevich isotherm states that the adsorption process on the adsorbent has a heterogeneous surface. The adsorption mechanism is based on the free energy of adsorption. The value of $E < 8$ kJ/mol implies physical adsorption, and $8 < E < 168$ kJ/mol is chemical adsorption [30]. The Dubinin-Raduschkevich isotherm's correlation coefficient (R^2) is less than 0.75, at 0.5765, as shown in Figure 7. It means that the Cr-PTC-HIna-SC MOF adsorbent's surface does not have micropores. The obtained E value is 1.8719 kJ/mol, is attributed to physical adsorption through electrostatic bonds or Van der Waals forces [29].

3.7 Adsorption Kinetics

We looked at the correlation coefficient (R^2) value of the first-order and second-order linear regression equations [32] to figure out how fast Pb^{2+} was adsorbed. A graph of the first-order and second-order Pb^{2+} metal ion adsorption is shown in Figure 8. Table 2 lists the parameters used to perform the calculations. Both adsorption kinetics models show the calculated Q_e ($Q_{e,cal}$) value is different from the experimental Q_e value, which possibly resulted from imprecise sampling and inaccurate testing within the error range. It is possible that equilibrium conditions have not been reached at the test time used, which is 30-120 min. The extremely low K_2 value of 2.8×10^{-5} g.mg^{-1}.min^{-1}, which indicates that the adsorption process moves very slowly, also supports this. However, the correlation coefficient (R^2) at pseudo-second order (0.9733) is higher than R^2 at pseudo-first order (0.4945). It states that the adsorption rate follows pseudo-second-order.

3.8 Adsorption Mechanism

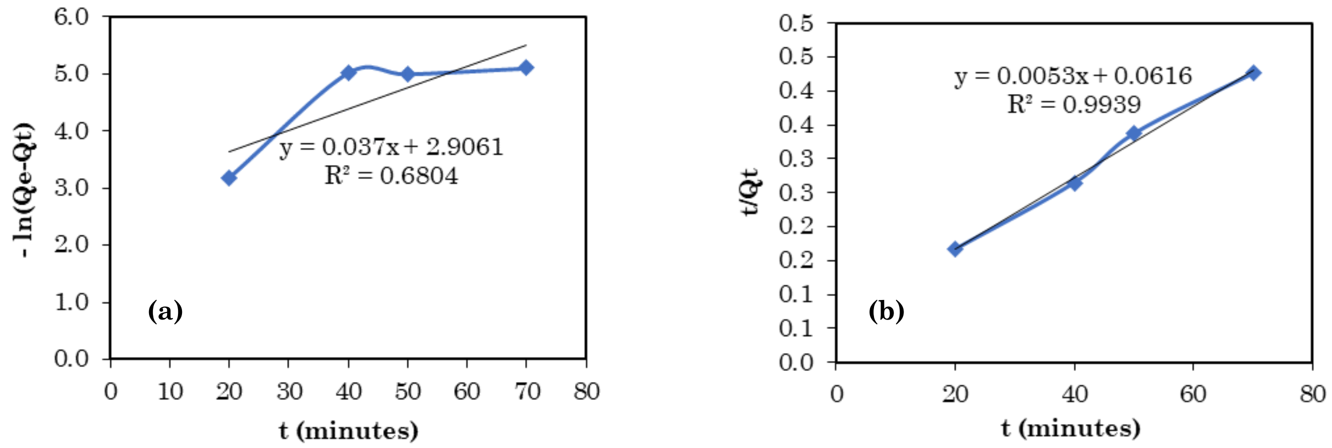

Figure 8. Pseudo-first-order (a) and pseudo-second-order (b) of Pb^{2+} ions adsorption onto Cr-PTC-HIna MOF.

Table 2. The parameter of pseudo-first-order, and pseudo-second-order model for Pb^{2+} adsorption onto Cr-PTC-HIna-SC.

Pseudo-first-order	Pseudo-second-order
Q_e experiment = 96.18 mg/g	Q_e experiment = 96.18 mg/g
Q_e calculated = 18.28 mg/g	Q_e calculated = 188.68 mg/g
K_1 = 0.037 (min^{-1})	K_2 = 2.8×10^{-5} (g mg^{-1}min^{-1})
R^2 = 0.6804	R^2 = 0.9939

Adsorption of Pb^{2+} heavy metal ions with MOF can be divided into physical adsorption and chemical adsorption based on the type of interaction between the adsorbent and adsorbate. Physical adsorption is called adsorptive adsorption, and chemical adsorption is called reactive adsorption. The adsorption mechanism of Pb^{2+} ions with Cr-PTC-HIna-SC MOF is shown in Figure 9.

Chemical adsorption is a process that involves chemical bonding. This type of adsorption occurs with only one force layer (monolayer) and is irreversible. Chemical adsorption results in the formation of new compounds through chemical reactions and chemical bonds [33]. The interactions involved in chemical adsorption include coordination interactions, acid-base interactions, and chemical bonds. Acid-base interactions are based on pair donors and electron acceptors. Acid-base interactions can be seen in the way that Pb^{2+} metal binds to N groups on Cr-PTC-HIna-SC MOF. In this case, pyridine N groups have free atoms that can donate electron pairs to the Pb^{2+} metal, while the metal acts as a proton acceptor that accepts electron pairs.

Coordination bonds are a fascinating type of chemical bond that occurs when metal ions attract electron pairs from ligands to create complexes. Oxygen in the carboxylate group gives an electron pair to Pb^{2+}, which has an empty d orbital that can take an electron pair. This study makes this clear. It leads to the formation of a coordination bond between Pb^{2+} and the carboxylate group. It's interesting to know that coordination bonds are often seen between MOFs that have been changed with functional groups such as amino groups ($-NH_2$), carboxyl groups ($-COOH$), and thiol groups ($-SH$). Furthermore, Zhang *et al.* [34] showed that thiol ($-SH$) groups, which give up an electron pair, can coordinate with Pb^{2+} and Cd^{2+} metal ions, which take an electron pair. When HS-mSi@MOF-5 binds to Pb^{2+} and Cd^{2+} metal ions, sulfhydryl ($-SH$) coordination bonds are made [34].

The FTIR spectrum of Cr-PTC-HIna-SC before and after the adsorption of Pb^{2+} reveals a shift in the peak from 534 cm^{-1} to 520 cm^{-1} (Figure 10), indicating the formation of a new chemical bond, Pb−O−Cr. This shift suggests the coordination interaction of Pb^{2+} metal with O-Cr from the Cr-PTC-HIna-SC MOF. In addition, the shape of the absorption band at 534 cm^{-1} is sharper than at 520 cm^{-1}. It may be affected by interference due to the interaction between Cr−O in Cr-PTC-HIna-SC MOF and Pb^{2+} ions. According to Abbasi *et al.* [35], a similar peak shift was observed in the interaction of TMU-5 with Cr^{3+} metal ions, indicating the metal interaction with NH (amine group) in the TMU-5 structure.

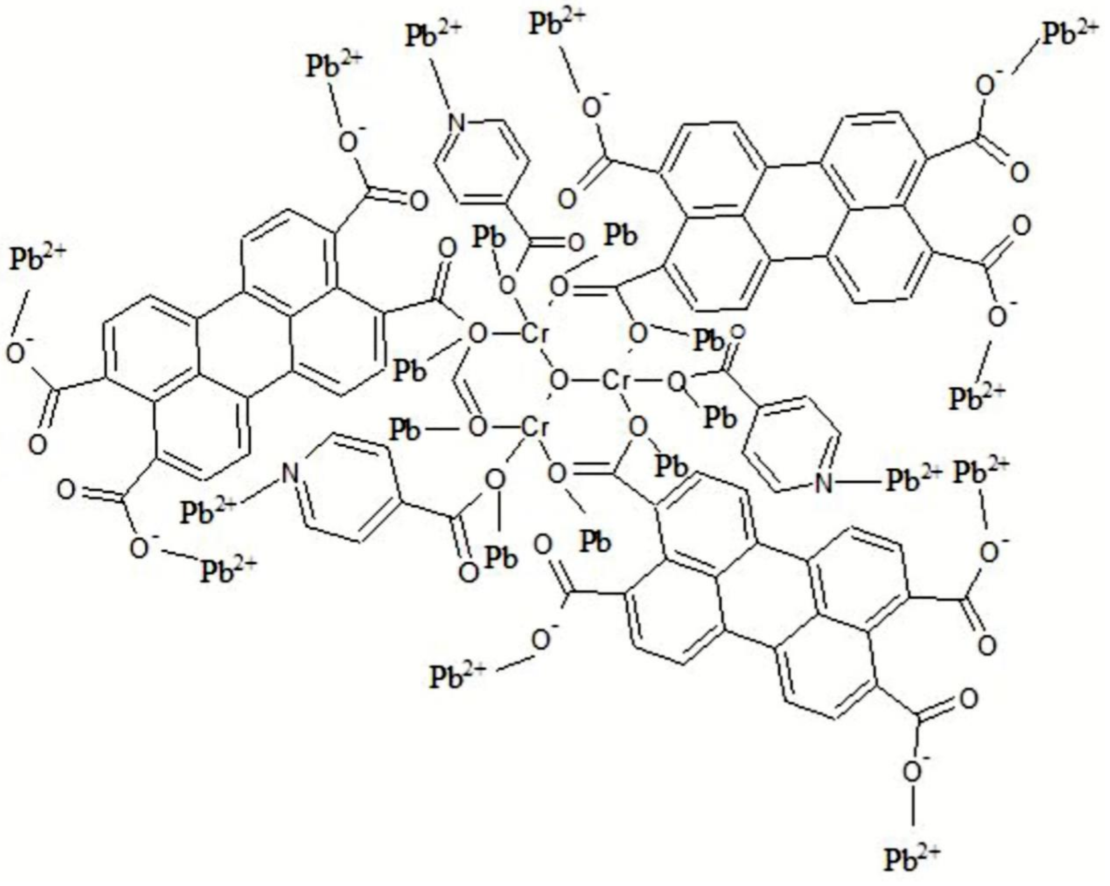

Figure 9. Adsorption mechanism of Pb^{2+} metal with Cr-PTC-Hina-SC MOF.

The XRD analysis of Cr-PTC-HIna-SC MOF before and after the adsorption process, on the other hand, shows that there is no Pb peak at intensities of 2θ: 31°, 36°, 55°, and 63° (Figure 11). It is due to its small intensity, indicating that Pb is distributed in the MOF pores. Nonetheless, there is a visible broadening of the spectrum's shape after adsorption, which suggests the presence of Pb^{2+} interacting with MOF.

Meanwhile, physical adsorption is a process that binds molecules to a surface physically without any chemical changes. These molecules are not strongly bound to the surface and are usually reversible, so they can be easily replaced with other molecules [33]. The types of interactions in physical adsorption are electrostatic interactions, and van der Waals forces. The MOF's surface charge determines the electrostatic interactions that take place during the adsorption process. The surface charge may change with a variation in pH levels. Electrostatic bonding occurs due to the electric force between electrically charged particles. The electric charge may be positive or negative, and particles with different charges attract each other while particles with the same charge repel each other [36].

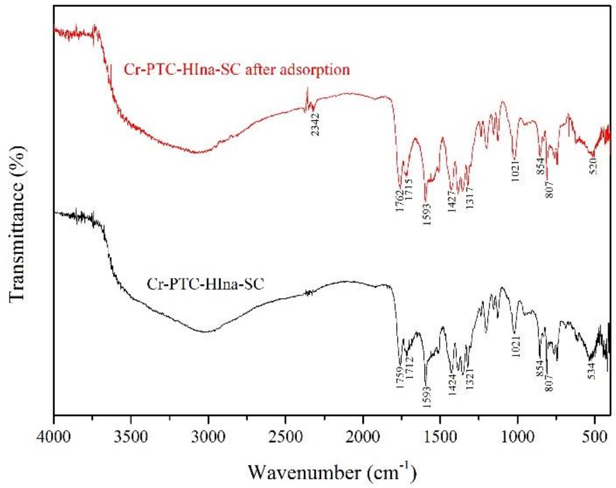

Figure 10. Fourier Transmittance Infrared (FTIR) spectrum of MOF Cr-PTC-HIna-SC before and after adsorption process.

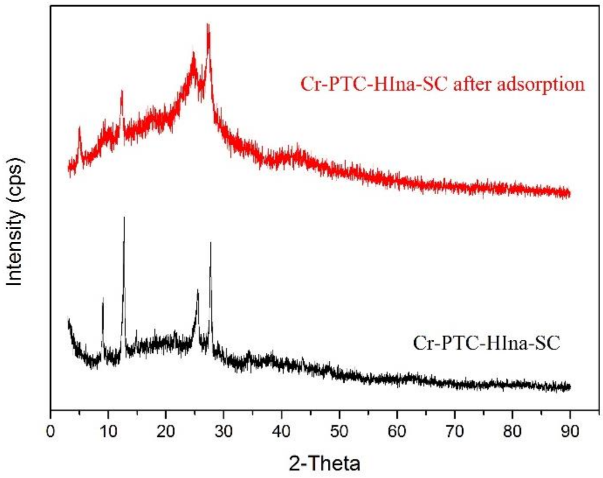

Figure 11. X-Ray Diffraction (XRD) diffractogram of Cr-PTC-HIna-SC MOF before and after adsorption process.

Meanwhile, the Van der Waals force is a temporary interaction between molecules. The Van der Waals force between Pb^{2+} and the COO- group on MOF can occur through the Van der Waals force of London dispersion. It is because of the fluctuations in electron charge on both Pb^{2+} and COO− groups. Pb^{2+} can change its electron charge, leading to the creation of temporary dipole moments. Similarly, COO-groups comprising carbon, oxygen, and hydrogen atoms may also experience fluctuations in electron charge. The temporary dipole moments on both entities interact with each other, leading to the formation of Van der Waals forces that attract Pb^{2+} and COO groups.

3.9 Adsorption Selectivity of Cr-PTC-HIna-SC MOF on Pb^{2+} and Cd^{2+} Ions

At optimum conditions, a test was conducted to determine the selectivity of Cr-PTC-HIna-SC MOF for the adsorption of Pb^{2+} and Cd^{2+} metal ions. Figure 12 demonstrates that the Cr-PTC-HIna-SC MOF has a higher affinity for Cd^{2+} than Pb^{2+}. It resulted in an adsorption capacity of 250.70 mg/g. It shows that the Cr-PTC-HIna-SC MOF is more selective towards Cd^{2+} metal ions and can effectively remove them from solutions that contain a variety of heavy metal ions.

Metal-ligand interaction can determine the selectivity factor of adsorption according to the HSAB theory. In this theory, the hard-soft acid-base properties between metal ions and ligands

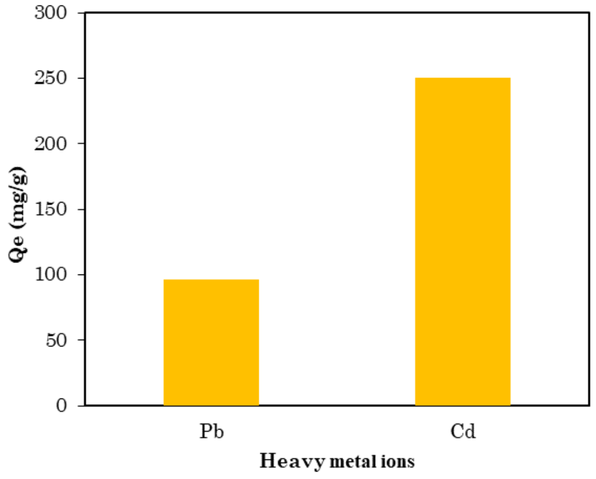

Figure 12. Adsorption capacity of Cr-PTC-HIna-SC MOF to Pb^{2+} and Cd^{2+} metal ions.

play an important role. Pb^{2+} and Cd^{2+} are two metal ions that are soft Lewis acids. They can take electron pairs from the pyridine groups in Cr-PTC-HIna-SC MOF. These groups have non-bonded electrons and aromatic groups with unsaturated bonds, which act as soft Lewis bases, donating electron pairs and their π bonds. Cd^{2+} is a soft Lewis acid, while Pb^{2+} is a border acid. Moreover, Cd^{2+} has a higher electronegativity than Pb^{2+}. It means that Cd^{2+} is easier to polarize and is therefore more likely to form covalent bonds with Cr-PTC-HIna-SC MOF than Pb^{2+}.

In addition, the ionic radius of Pb^{2+} is larger than that of Cd^{2+}. In this case, Pb^{2+} ions will have a looser electron distribution, thus making the electrostatic interaction between the ions and the adsorbent surface weak. It is possible for Pb^{2+} ions with larger ionic radii to separate from the MOF surface because of the weak interactions that happen during adsorption. In contrast to metals that have smaller ionic radii, ions will have a denser electron distribution, resulting in strong electrostatic interactions between the ions and the adsorbent surface. Therefore, ions with smaller ionic radii tend to be more quickly adsorbed [37].

4. Conclusions

This study finds that the sonochemically made Cr-PTC-HIna-SC MOF can hold more Pb^{2+} ions than Cr-PTC-HIna-ST and Cr-PTC-HIna-HT. The best conditions for adsorption were found to be 150 ppm Pb^{2+} ions, pH 5, 90 min of contact time, and 35 °C. The maximum amount of Pb^{2+} that could be absorbed was 149.95 mg/g. The Langmuir isotherm model is the main one applied to explain adsorption. The adsorption process follows pseudo-second-order kinetics. Interestingly, the Cr-PTC-HIna-SC MOF has a higher selectivity for adsorbing Cd^{2+} than Pb^{2+}. These results suggest that the Cr-PTC-HIna-SC MOF has great potential for removing heavy metal-ion pollutants especially Cd^{2+} ion in wastewter.

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CRediT Author Statement

N. Nurhasni was in responsible for supervising; *A. Adawiah* was in responsible for conceptualization, validation, resources, data curation, writing, review, and editing; *R. Hadriyani, R, Fadhillah, L. Andriyani* were in duty of formal analysis, investigation, data gathering, and draft preparation; *A. Zulys, W. Wahyudin and D. Sukandar* discussed on research, resources, and writing. All authors read the manuscript promptly approved it for future published.

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