Interleaving of 2,4-Dichlorophenoxyacetate Acid into Calcium-Aluminium-Layered Double Hydroxide by Comparison of Co-Precipitation and Ion Exchange Methods

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Herbicide 2,4-dichlorophenoxyacetic acid, or also known as 2,4-D, was studied for the comparison between two methods, namely ion exchange and co-precipitation methods, for intercalating with the Ca-Al-Layered Double Hydroxide (LDH) host in this research. Based on PXRD results, 2,4-D anions were successfully intercalated into the interlayer of Calcium-Aluminium-Layered Double Hydroxide (Ca-Al-LDH) with the co-precipitation method compared to the ion-exchange method. The interleaving of the former occurred with the optimum concentration at 0.05 M and with basal spacing increased from 8.67 to 17.59 Å, compared with the latter. From the attenuated total resonance fourier transform infrared (ATR-FTIR) observation, the nitrate peak at 1350.01 cm^{-1} disappeared and a new peak which represents the carboxylic ion at 1726.41 cm^{-1} was observed, with Carbon, Hydrogen, Nitrogen, and Sulphur analysis (CHNS) showed a percentage of loading of 92.78% (w/w) estimated from the percentage of carbon. The Barret, Joyner and Halenda (BJH) average pore diameter of the synthesized nanocomposite was 136.1 Å, which shows a mesoporous-type material that was confirmed with Brunauer-Emmett-Teller surface area analysis (BET). This research demonstrated that the 2,4-D-Ca-Al-LDH nanocomposite was suitable using direct co-precipitation method compared to ion-exchange method.

Key words: 2,4-dichlorophenoxyacetic acid; interleave; intercalation; co-precipitation; ion-exchange; LDH-Calcium-Aluminium

Layered material is a material that is built up by stacking 2D units associated to each other by weak forces. This material can be classified as synthetic or natural and positive, neutral or negative, depending on its layer charges and the layer thickness based on materials used that may be one-, three- or seven-atom-thick [3-6]. LDH has unique properties where the atomic layer thickness, which (i) the cation layers can be tuned easily, (ii) can host a variety of anions by intercalation, and (iii) has a distinctive memory effect [12]. This material is widely applied in the synthesis of novel organic/inorganic nanocomposite materials in agriculture, drug delivery, catalysis, etc. [1–3]. The general formula for LDH is $M^{2+}_{1-x}M_x^{3+}(OH)_2(A^{n-})_{x/n} \cdot yH_2O$, where M^{2+} and M^{3+} are metal cations and x = $M^{3+}/(M^{2+} + M^{3+})$, which represents the interlayer anions. The combination of M^{2+}/M^{3+} could be any metals, for instance, Zn-Al, Mg-Al, Fe-Al, Ca-Al, etc. In most of the studies, the synthesis of these materials is depending on the type of material to be resulted, and different approaches have been used to synthesize LDH nanocomposites, such as ion exchange [8, 13], co-precipitation [11, 12], electron beam irradiation technique [14], pH control method [15], and urea

hydrolysis [9]. Above all, ion exchange is frequently used due to its ease of substitution of initial and incoming anions within the interlayer region [13]. This method is useful when the co-precipitation method is inapplicable, such as when the divalent or trivalent metal cations or the anions involved are unstable in alkaline solution, and when intercalated with bigger sized anions [12]. The co-precipitation method is well known as a facile method of synthesizing nanocomposites, especially for the preparation of LDH nanocomposites especially in LDH-Ca-Al is not being prepared in advance, as previously reported by Arizaga *et al*. [10] and Liu *et al*. [9]. 2,4-D is the agrochemical that kills broadleaf weeds by causing the cells in the plant tissues that carry water and nutrients to divide and grow without stopping. Herbicides that act this way are called auxin-type herbicides. In previous studies, 2,4-D was intercalated into zinc-layered hydroxide [18] and Zn-Al-layered double hydroxide (Zn-Al-LDH) [19] via the direct and ion-exchange methods, respectively. However, to the best of our knowledge, there are a few reports on the intercalation of herbicides, namely 2,4-D into layered LDH Ca-Al for comparison using the

ion exchange and co-precipitation methods. In this research, the anionic herbicide 2,4-D had been successfully interleaved with Ca-Al host by using the co-precipitation method compared to indirect synthesis, which was the ion-exchange method [7]. The physicochemical properties of the resulting nanocomposite, such as surface area and pore size distribution, as well as the percentage of loading will also be discussed.

METHODOLOGY

1. Chemicals and Reagents

2,4-dichlorophenoxyacetic acid (Sigma Aldrich, 98%), aluminum nitrate nonahydrate (R&M, 99%), calcium nitrate hexahydrate (R&M, 99.9%), and deionized water were used without further purification.

2. Synthesis of 2,4-D-Ca-Al-LDH by Co-Precipitation Method

2,4-D-Ca-Al-LDH were prepared through the co-precipitation method. The nanocomposites were obtained by slow addition of 2,4-D solutions with concentration ranging from 0.05 M to 0.5 M into 0.05 M of calcium nitrate, $Ca(NO_3)_2.6H_2O$ and 0.1 M of aluminum nitrate, $Al(NO_3)_3.9H_2O$ under the purge of nitrogen gas. The pH of the solutions was adjusted to pH 13.0 ± 0.02 by dropwise addition of sodium hydroxide (2.0 M). The precipitates were aged at 70°C in an oil bath shaker for 18 h. The synthesized materials were then centrifuged, thoroughly washed with deionized water, and dried in an oven at 70°C [11]. The resulting nanocomposites were then ground into fine powders and stored in sample bottles for further use and characterizations.

3. Synthesis of 2,4-D-Ca-Al-LDH by Ion-Exchange Method

Layered Ca-Al-LDH were prepared beforehand using the following procedure. In brief, 0.5 M of calcium nitrate, $Ca(NO_3)_2.6H_2O$ and 0.1 M of aluminum nitrate, $Al(NO_3)_3.9H_2O$ were mixed with 125 mL of deionized water in a conical flask where the final pH was adjusted to pH 13.0 ± 0.02 by dropwise addition of aqueous NaOH (2.0 M) [11]. The solution was placed in an oil bath shaker for 18 h at 70°C. The mixture was cooled, centrifuged, and washed four times with deionized water. Later, 0.350 g of host Ca-Al-LDH was mixed with 2,4-D (0.05 M, 0.5 M). The mixture was stirred for 3 h under titration with of sodium hydroxide (2.0 M) to reach pH 13 ± 0.05. The mixture was aged for 18 h at 70°C. The sample was then filtered using a vacuum filter, washed with deionized water, dried in an oven at 70°C, ground,

and kept in a sample bottle for further use and characterizations.

4. Characterization Technique

X-ray powder diffraction (PXRD) patterns were recorded in the 2θ range of 10° to 70° with Panalyticalmodel Empyrean (Panalytical, Almelo, Netherlands), operating at 40 kV and 35 mA using Cu Kα radiation (λ = 1.54059 Å) at 30 mA and 40 kV with a scanning speed of 2° min^{-1}. The Fourier Transformed Infrared spectroscopy (FTIR) spectra were recorded on Perkin-Elmer infrared spectrophotometer using ATR mode with resolution of 4 cm^{-1} in the range of 4000-650 cm^{-1} and elemental analysis was performed using CHNS-932 (LECO). The surface characterization of the nanocomposites was determined by Micromeritics surface area and pore size analyzer (ASAP2000) using nitrogen gas adsorption desorption technique at 77 K together with the BET equation and degassed in an evacuated heated chamber at 120°C, overnight.

RESULTS AND DISCUSSION

1. Co-precipitation Method

Figure 3.1 shows the PXRD patterns for Ca-Al-LDH, 2,4-D anion, and the intercalated nanocomposites by using the co-precipitation method. The PXRD pattern of Ca-Al-LDH (Figure 3.1(b)) showed a basal spacing at 8.67 Å, which was in the range between 8.00 Å to 9.00 Å for nitrate peak, as stated by Ghazali *et al*. [10]. The PXRD pattern in Figure 3.1(c) shows the presence of the narrowly sharp and intense peak at a lower angle of 2θ with basal spacing of 17.59 Å that indicates the intercalation had been successfully obtained at 0.05 M by using the co-precipitation method. The increase of basal spacing from 8.67 Å to 17.59Å demonstrated that 2,4-D anions were intercalated in between the Ca-Al-LDH layered structures where the anions were in vertical positions and in bilayer manner in the interlayer region. Furthermore, the absence of nitrate peak, which was at 8.67 Å in 0.05 M 2,4-D-Ca-Al-LDH, shows that nitrate was being completely replaced by 2,4-D in between the interlayer spaces. Although the intercalation of 2,4-D into host Ca-Al-LDH occurred as shown in Figure 3.1(d), it was in saturated phase where the interleave guest anion, 2,4-D happened at the interlayer and intralayer regions of Ca-Al-LDH. This was due to the supersaturation properties where its homogeneous nucleation and growth processes compete to reduce the supersaturation. A supersaturation phase leads to lower the precipitates of high crystallinity that makes the rate of nucleation higher than the growth rate of the crystal, which then results in the nanocomposites to contain impurities [5].
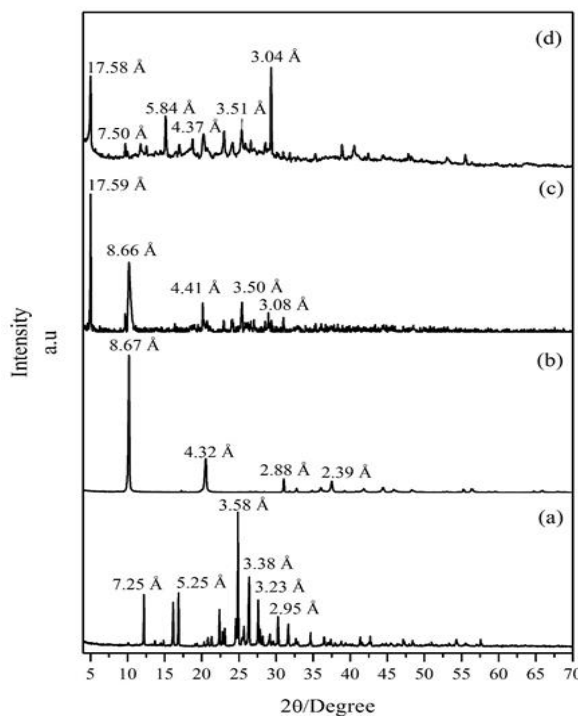
105   Fatin Haizira Mohd Hayazi, Nurain Adam, Nur Nadia
Dzulkifli, Muhammad Alinsan Kamil Mukamil
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Figure 3.1. PXRD patterns for (a) pure anion, 2,4-D; (b) host, Ca-Al LDH; (c) 0.05 M of 2,4-D-Ca-Al-LDH; and (d) 0.5 M of 2,4-D-Ca-Al-LDH (co-precipitation method)
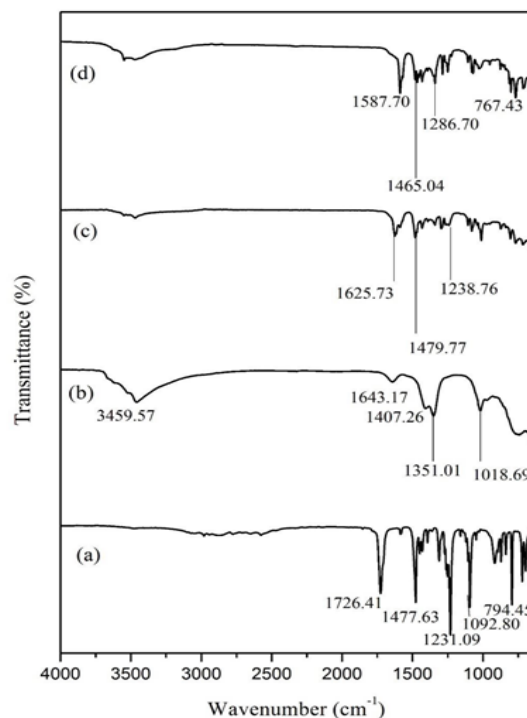

Figure 3.2. ATR-FTIR spectra for (a) pure anion, 2,4-D; (b) host, Ca-Al LDH; (c) 0.05 M of 2,4-D-Ca-Al-LDH; and (d) 0.5 M of 2,4-D-Ca-Al-LDH (co-precipitation method)

Further proof with supported results for successful host Ca-Al-LDH interleaved with 2,4-D from FTIR spectra are shown in Figure 3.2 and Table 1. The ATR-FTIR technique was used to support the results from PXRD and confirmed the intercalation occurred in between the interlayer spaces of the Ca-Al-LDH nanocomposites. In the ATR-FTIR spectrum of 2,4-D, as shown in Figure 3.2(a), the absorption band at 1726.41 cm^{-1} indicated the presence of carbonyl compound, C=O stretching. Asymmetrical stretchings of C-O and C=C were assigned at 1231.09 cm^{-1} and 1583.70 cm^{-1}, respectively. Furthermore, C=C (aromatic) asymmetrical stretching was assigned at 1477.63 cm^{-1}. The C-Cl stretching bond could be detected at 794.45 cm^{-1} due to the electronegative element. Figure 3.2(b) shows the ATR-FTIR spectrum of Ca-Al-LDH where the nitrate peak was observed at 1351.01 cm^{-1}, which corresponded to the data stated by Ghazali *et al*. [10]. The presence of the broad peak at 3459.57 cm^{-1} (Figure 3.2 (b)) corresponded to O-H stretching due to the presence of hydroxyl functional group. Once the intercalation occurred, the peak at 1351.01 cm^{-1} was observed to decrease and disappeared. The absence of nitrate ions indicated that the intercalation has been successful, thus ATR-FTIR was used to confirm the presence of nitrate peak in the IR spectra of the nanocomposites in the range of 1352 cm^{-1} to 1400 cm^{-1} [10].

2. Ion-exchange Method

Figure 3.3 shows the PXRD patterns for 2,4-D, Ca-Al-LDH, and the intercalated nanocomposites by using ion-exchange reaction. The increase in the basal spacing from 8.67 to 15.46 Å indicated that intercalation had occurred. Referring to the PXRD pattern for ion-exchange method in Figure 3.3(c), although the interleaving process of 2,4-D into host Ca-Al-LDH occurred, it was not complete. Thus, increasing the concentration to 0.5 M (Figure 3.3(d)) caused the presence of nitrate and carbonate ions in between the interlayer spaces of Ca-Al-LDH to be observed. The co-existence of nitrate and carbonate ions is known as dual phase. This showed that the intercalation of the anion into the interlayer spaces of Ca-Al-LDH was unsuccessful due to the contamination of carbon dioxide that converted into carbonate ions. X-ray scattering in amorphous solids was unable to obtain high definition peaks in the analysis [11]. This could be proven with the non-distinguished and less intense peak, resulting in the incapability of the nanocomposites to perform ion-exchange reactions. Significantly, the ion-exchange method broadened peaks of low intensities, while the co-precipitation synthesis showed well distinguished peaks of higher intensities [4].
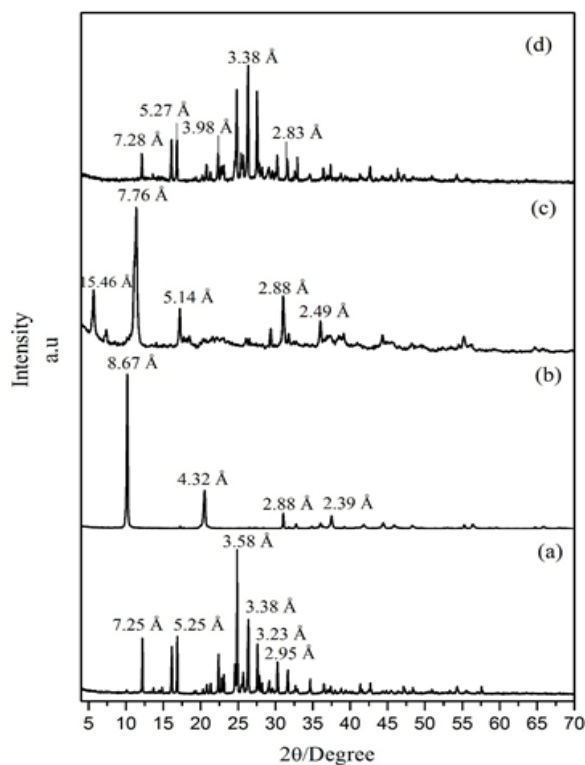
Figure 3.3. PXRD patterns for (a) pure anion, 2,4-D;
(b) host Ca-Al LDH; (c) 0.05 M of 2,4-D-Ca-Al-
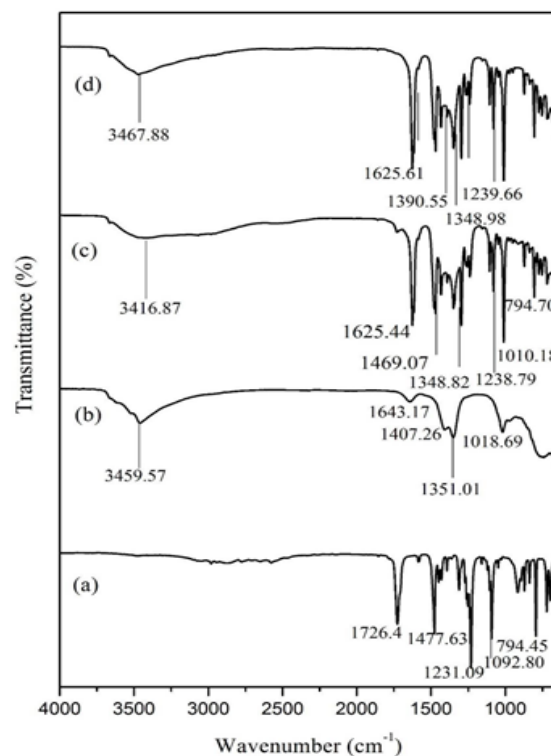LDH; and (d) 0.5 M of 2,4-D-Ca-Al-LDH (ion-
exchange method)

Figure 3.4. ATR-FTIR spectra for (a) pure anion, 2,4-
D; (b) host Ca-Al LDH; (c) 0.05 M of 2,4-D-Ca-Al-
LDH; and (d) 0.5 M of 2,4-D-Ca-Al-LDH (ion-
exchange method)

Referring to parts (c) and (d) in Figure 3.4, nitrate peaks were still observed at 1348.82 cm^{-1} and 1348.98 cm^{-1}, respectively, which confirmed that the nanocomposites were not fully intercalated or unsuccessful intercalated. The broadness of the nitrate peaks indicated the presence of carbonate ions that may be overlapping within the nitrate peaks, and carbonate peaks that are normally observed at 1340 cm^{-1} to 1460 cm^{-1}. The carbonate ions were able to interfere with the interleaving process of the anion into the host [10]. The presence of carbonate ions, which mainly come from the atmospheric carbon dioxide, with higher electron affinity compared to the nitrate ions and the anion caused it to become trapped strongly in-between the positively charged interlayer spaces of Ca-Al-LDH. Thus, it was hard and impossible to remove the carbonate ions in the interlayer spaces, resulting in intercalation to poorly happened or did not happen completely [11].

In addition, the ion-exchange method was not suitable for the intercalation of 2,4-D due to indirect synthesis, where the host were synthesized first before the addition of the anion and the purging of nitrogen gas was not applied, making it more vulnerable for contamination with carbon dioxide that converted to carbonate ions [9]. The presence of hydroxyl group, as shown in parts (c) and (d) in Figure 3.4, was from the pure anion, 2,4-D that has the carboxylic acid

functional group, COOH and thus the presence of OH group at 3416.87 cm^{-1} and 3467.88 cm^{-1}, respectively. This was due to dehydroxylation of the framework that enabled the insertion of 2,4-D into host Ca-Al-LDH. The phenomenon was due to the hydrogen bond complex between the pure anion, 2,4-D that has the carboxylic acid functional group and host Ca-Al-LDH with the presence of hydrate in the chemical compound. This led to the high degree of dipole moment changes without polarization that resulted in deintercalation, making intensity of water peak to be increased [9].

3. CHNS Analysis

Table 1 shows the carbon, hydrogen, nitrogen, and sulfur analysis (CHNS) results of host Ca–Al-LDH, nanocomposite Ca-Al-2,4-D (co-precipitation method), and Ca-Al-2,4-D (the ion exchange method), including the surface properties of the host, Ca-Al-LDH and the nanocomposite, Ca-Al-2,4-D. As shown in Table 1, Ca–Al-LDH contained 7.24% nitrogen that agreed to the presence of a strong band at 1345 cm^{-1} in the FTIR spectrum of Ca–Al-LDH, which corresponded to the nitrate group, as shown in Figures 3.2 and 3.4. Compared to Ca-Al (the ion-exchange method), which still having ion nitrate (33.56%) which agree with FTIR spectra which contains a functional group of nitrate peak at 1348-1350 cm^{-1}.

Table 1 Elemental and surface properties of Ca–Al-LDH and its intercalated compound, Ca–Al-2,4-D

Material	Basal spacing (Å)	% C	% N	2,4-D (% w/w)	BET surface area ($m^2 g^{-1}$)	BJH desorption pore volume ($cm^3 g^{-1}$)	BET average pore diameter (Å)	BJH average pore diameter (Å)
Ca–Al-LDH	8.67	12.65	7.24	0.00	4.5930	197.355	112.4	204.1
Ca–Al-2,4-D (co-precipitation-method)	17.59	40.49	0.00	92.78	16.8393	194.235	144.9	136.1
Ca-Al-2,4-D (ion-exchange method)	15.49	23.65	33.56	-	-	-	-	-

Hence, the CHNS analysis for the co-precipitation method of nanocomposite Ca–Al-2,4-D showed no nitrogen, which indicated the absence of this element in nanocomposite Ca–Al-2,4-D, resulting the intercalation of 2,4-D and the negation of nitrate anions into the interlayer. This was in line with the high content of carbon in host Ca-Al-LDH due to the presence of carbon in 2,4-D herbicide [8]. The percentage of 2,4-D content was 92.78% (w/w) using a CHNS analyzer. The CHNS analysis also showed that 2,4-D contained around 40.49% of carbon, while 2,4-D was intercalated into the interlayer lamella of LDH at 12.65%, regardless of the method of preparation.

4. Surface Area Analysis by BET

Figures 3.5 to 3.10 show the adsorption–desorption isotherm for host Ca–Al-LDH and nanocomposite Ca–Al-2,4-D (ion-exchange and co-precipitation methods). As shown in Figure 3.5, the adsorption–desorption for nanocomposite Ca–Al-2,4-D was a Type IV, indicating a mesoporous-type material, with adsorption increased rapidly at a low relative pressure in the range of 0.05–0.5, followed by a slow uptake of the adsorbent at a higher relative pressure of 0.5–0.8. Further increase of the relative pressure resulted in a rapid adsorption of the adsorbent, reaching an optimum at more than 200 $cm^3 g^{-1}$ at STP [8]. A general shape of the isotherm for nanocomposite Ca–Al-2,4-D seemed almost similar to host Ca–Al-LDH, hence it was a mesoporous-type material. An optimum uptake was about 8 $cm^3 g^{-1}$ at STP, indicating the slow uptake of nitrogen gas. Desorption branch of the hysteresis loop for nanocomposite Ca–Al-2,4-D was much narrower compared to host Ca–Al-LDH, showing a different pore texture of the resulting material. This could be related to the different pore structure when nitrate was replaced by 2,4-D during the formation of nanocomposite Ca–Al-2,4-D,

together with the formation of interstitial pores between the crystallite, and different particle size and morphology. The surface properties of host Ca–Al-LDH and nanocomposite Ca–Al-2,4-D are summarized in Table 1. The intercalation of 2,4-D had increased the BET specific surface area from 4.5930 $m^2 g^{-1}$ for host Ca–Al-LDH to 16.8393 $m^2 g^{-1}$ for nanocomposite Ca–Al-2,4-D, which was due to the inclusion of the bigger guest anion than the counter anion, nitrate. The intercalation of the bigger anion of 2,4-D resulted in the expansion of basal spacing of the resulting Ca–Al-2,4-D nanocomposite and created more pores in the crystallites, hence the surface area increased significantly [8]. Table 1 also shows that the BET average pore diameter for nanocomposite Ca–Al-2,4-D was lower than that of host Ca–Al-LDH, amounting from 112.4 to 144.9 Å, respectively. On the other hand, the BJH desorption pore volume of nanocomposite Ca–Al-2,4-D was higher than that of host Ca–Al-LDH. The BJH pore size distribution for host Ca–Al-LDH and nanocomposite Ca–Al-2,4-D are indicated in Figure 3.6. Both materials showed mesoporous-type materials. The BJH pore size distribution for host Ca–Al-LDH showed a broad peak at around 204.1 Å, while for nanocomposite Ca–Al-2,4-D an intense peak at 136.1 Å. This indicated the modification of pore texture in agreement with the formation of a new intercalated compound, Ca–Al-2,4-D with basal spacing of 17.59 Å.

CONCLUSION

In conclusion, the synthesis between the layered double hydroxide and anion, 2,4-D herbicide managed to form a new organic-inorganic nanocomposite called 2,4-D-Ca-Al-LDH. Two different methods, which were ion-exchange and co-precipitation methods using different concentrations of 0.05 M and 0.5 M for each method. The molar ratio for these methods was 1:2, where R=2 at constant pH 13 ± 0.02. Based on the
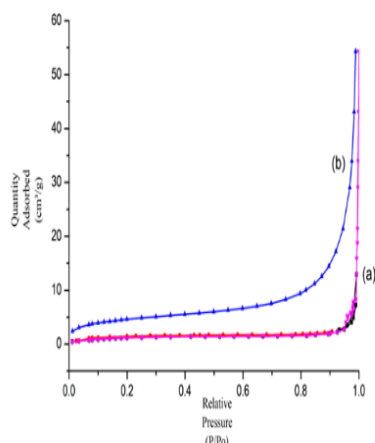
108 Fatin Haizira Mohd Hayazi, Nurain Adam, Nur Nadia Dzulkifli, Muhammad Alinsan Kamil Mukamil Hamzah, Monica Limau Jadam, Siti Halimah Sarijo and Sheikh Ahmad Izaddin Sheikh Mohd Ghazali

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Figure 3.5. Adsorption–desorption isotherms for (a) Ca–Al-LDH and (b) Ca–Al-2,4-D
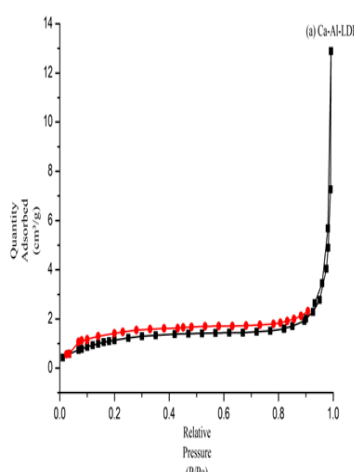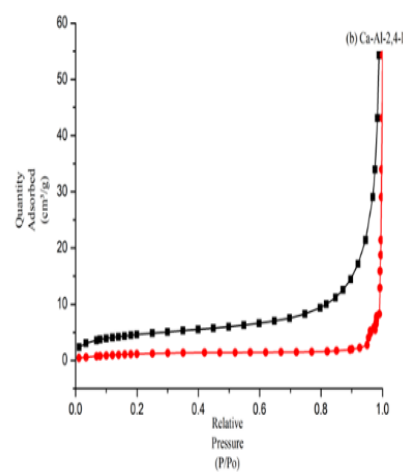

Figure 3.6. Adsorption–desorption isotherms for Ca–Al-LDH

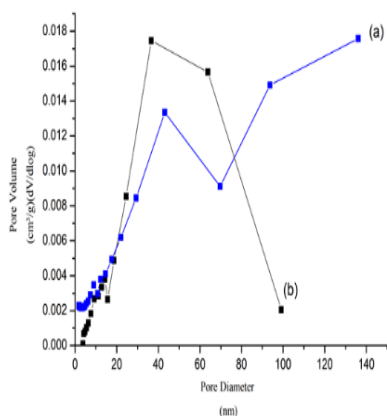**Figure 3.7.** Adsorption–desorption isotherms for Ca-Al-2,4-D

Figure 3.8. BJH pore size distribution for (a) Ca–Al-LDH and (b) Ca–Al-2,4-D
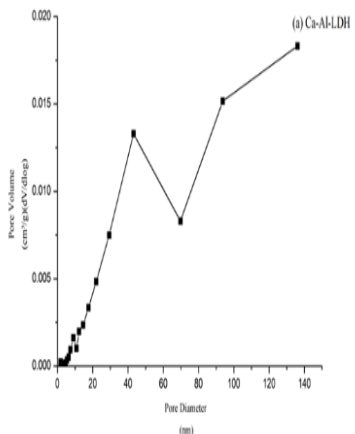

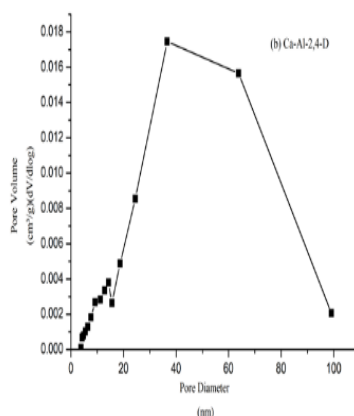**Figure 3.9.** BJH pore size distribution for Ca–Al-LDH

Figure 3.10. BJH pore size distribution for Ca-Al-2,4-D

main PXRD results, it was shown that the number of basal spacing of host Ca-Al-LDH was increased from 8.67 Å to 17.59 Å for the co-precipitation method compared to the ion-exchange method which was from 8.67 Å to 15.46 Å. The peaks were sharp and intense for the co-precipitation method, whereas for the ion-exchange method the peaks were less intense. The results were further supported with the ATR-FTIR results, where the nitrate peak completely disappeared at 1351.01 cm^{-1}. This was confirmed and supported by the CHNS results, which showed 0.00% of nitrogen. Percentage loading of 2,4-D in the interlayer of the nanohybrid was 92.78% (w/w). The BET surface area increased from 4.59 m^2 g^{-1} for Ca–Al-LDH to 16.84 m^2 g^{-1} for its intercalated compound, Ca–Al-2,4-D, confirming it as a mesoporous-type composite material. Based on the data collection obtained above, it was indicated that the 2,4-D anion was successfully intercalated by using the co-precipitation method compared to the ion-exchange reaction.

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Interleaving of 2,4-Dichlorophenoxyacetate Acid into Calcium-Aluminium-Layered Double Hydroxide by Comparison of Co-Precipitation and Ion Exchange Methods

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