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Synthesis of an herbicides–inorganic nanohybrid compound by ion exchange-intercalation of 3(2-chlorophenoxy)propionate into layered double hydroxide

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A new layered organic–inorganic nanohybrid material in which an agrochemical, 3(2-chlorophenoxy)propionate (CPPA) is encapsulated into Zn/Al-layered double hydroxide (LDH) inorganic interlayers was synthesised using ion exchange method. CPPA-LDH nanohybrid yielded mesoporous-type, phase pure, well-ordered material with a basal spacing of 19.9 Å and organic loading of around 42.3%. FT-IR study confirms the presence of CPPA in the interlamellae of the LDH, while the thermal analysis shows that LDH host enhances the thermal stability of CPPA.

Keywords: nanohybrid; 3(2-chlorophenoxy)propionate; layered double hydroxide; hydrotalcite; intercalation

1. Introduction

Hydrotalcite-like compounds, also called anionic clays or layered double hydroxides (LDHs), constitute a unique class of layered solids comprised of positively charged, brucite-like layers separated by charge balancing anions. The general formula that represents this class of materials is $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{m-})_{x/m}\text{nH}_2\text{O}$, where M^{2+} is a divalent cation (Ca^{2+} , Mg^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Mn^{2+}), M^{3+} is a trivalent cation (Al^{3+} , Cr^{3+} , Fe^{3+} , Co^{3+} , Ni^{3+} , Mn^{3+}) and A^{m-} is an interlayer anion (Cl^- , NO_3^- , ClO_4^- , CO_3^- , SO_4^{2-} and many other inorganic anions). The x value is the charge density for the molar ratio $M^{3+}/(M^{2+} + M^{3+})$.

One of the most important properties of the hydrotalcite-like compounds is their high anionic exchange capacity that is related to their lamellar structure. This allows the exchange of their original anions with those present in an aqueous solution [1–4]. LDHs are subject to increasing interest due to their numerous potential applications and they are simple and relatively cheap to prepare [5].

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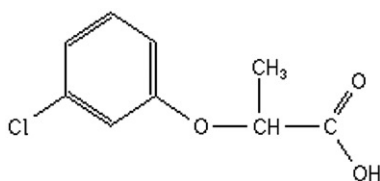


Figure 1. Molecular structure of 3(2-chlorophenoxy)propionic acid (CPPA).

LDHs find widespread applications in many fields including industrial catalytic processes [6], pharmaceuticals [7], polymer reinforcement [8,9], environmental cleanup by ion exchange [10], matrix for control release formulation [11] and electroactive material [12].

Intercalations of various anions into LDHs have been accomplished using various methods: co-precipitation [13,14], ion exchange [15–17], calcination–rehydration [18–20], thermal reaction [21] and hydrothermal reaction [22]. The co-precipitation and anion exchange methods have often been used for the formation of organo-LDH nanohybrids. A set of different methods of preparation have been performed to insert [2-(2,6-dichlorophenylamino)-phenyl]acetic acid (DPAPAc) into a Mg:Al (2:1) LDHs, and it was shown that different methods gave different expansion of the interlayer spacing [23].

In this study, the intercalation of 3(2-chlorophenoxy)propionate (CPPA) into the interlamellae of Zn/Al-LDH synthesised at Zn to Al molar ratio, $R=3$ and pH 7.5 was accomplished by anion exchange method for the formation of organic–inorganic nanohybrid material. The physicochemical properties of the resulting nanohybrid material will be studied and discussed.

2. Results and discussion

2.1. Powder X-ray diffraction

An organic anion, 3(2-chlorophenoxy)propionic acid (CPPA) (Figure 1), a derivative of phenoxyalkane carboxylic acid that acts as a plant growth regulator as well as herbicide, is commonly used for the control of weeds in wheat, rice, maize and aquaculture. The anion, as a guest, will be intercalated into the inorganic host interlamellae Zn/Al-LDH for the formation of host–guest, organic–inorganic nanohybrid material.

Figure 2 shows the powder X-ray diffraction (PXRD) patterns of the Zn/Al-LDH and its nanohybrid compounds, CPPAEX, prepared using various concentrations of CPPA from 0.009 to 0.05 M. As shown in the figure, the basal spacing of Zn/Al-LDH, which contains nitrate as the counter anion in the interlayer, was recorded to be 8.9 Å, which is in good agreement with the sum of the thickness of the anion, NO_3^- (4.1 Å), and that of brucite-like layer (4.8 Å) [24]. The intercalation of CPPA phenoxyherbicides gave materials exhibiting the diffraction pattern characteristic of a well-crystallised LDH structure with a sharp (003) diffraction peak at 19.6–21.0 Å. The expansion of basal spacing from LDH to CPPAEX is due to the inclusion of CPPA into the LDH interlamellae with orientations that warrant the expansion of the LDH lamella.

The interlayer distance of the CPPAEX decreased slightly from 21.0 to 19.6 Å with the increase in the concentration of CPPA used during the sample preparation. This is due to

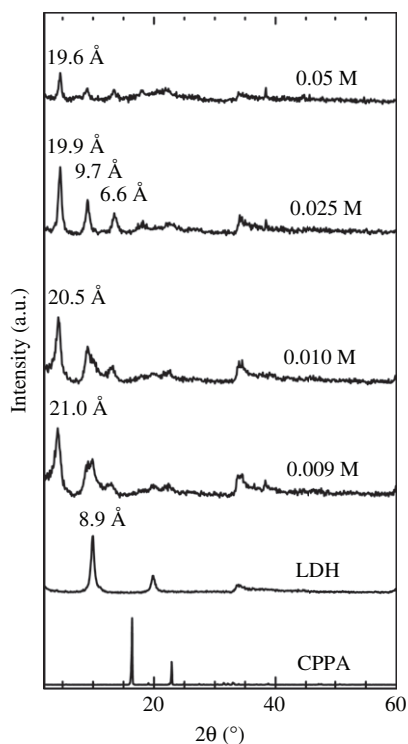


Figure 2. PXRD patterns of Zn/Al-LDH and its nanohybrids prepared at various concentrations of CPPA, 0.009–0.05 M.

the different spatial orientation and the environment of CPPA molecules inside the interlamellae of the nanohybrid. The co-presence of nitrate anion inside the interlamellae cannot be ruled out, as indicated by nonsymmetrical 003 reflections and overlapping of the 006 reflections with 003 reflection of the Zn/Al-LDH for the samples that were synthesised at 0.009 and 0.01 M CPPA. At 0.009 and 0.01 M CPPA, the formation of a transitional phase, i.e. a phase in which both nitrate and CPPA anions are co-intercalated occurs, resulting in the expansion of the inorganic interlamellae. When a higher concentration of CPPA is used, more nitrate anion is exchanged with CPPA and results in the formation of the nanohybrid phase, which becomes dominant and therefore the phase becomes purer. As a result, less co-intercalation of nitrate occurs, and hence the basal spacing decreases due to the spatial re-orientation of CPPA. Subsequently, a pure LDH phase was completely transformed to pure nanohybrid. This process was accomplished at 0.025 M with a further reduction of the basal spacing. This led to the inorganic interlayers re-adjusted and re-oriented themselves to balance the CPPA-charged anions in order to maximise the interaction with their surrounding [25]. As a result of the complete exchange of the nitrate anion, the nanohybrid, CPPAEX, prepared using 0.025 M anion produced sharp, symmetrical and intense peaks, especially for the (003) peak. This particular sample was then chosen as the phase pure well-ordered nanohybrid material and used for further characterisations.

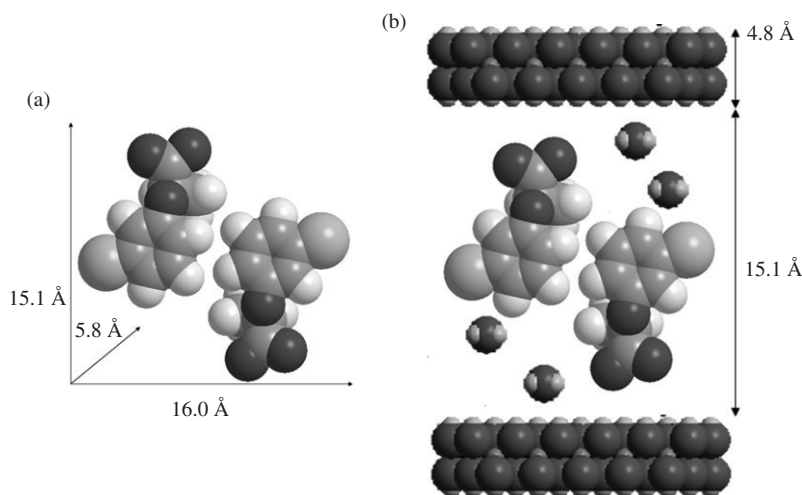


Figure 3. Schematic representation of (a) the CPPA molecules in 3-D space and (b) the proposed spatial arrangement of CPPA molecules intercalated into the Zn/Al-LDH inorganic interlayer.

The results based on the PXRD patterns show that the intercalated CPPA anion bound to the matrix by electrostatic interactions and hydrogen bonding has an interlayer distance of 19.9 Å. The inorganic brucite-like layer thickness and the hydrogen bond distance is known to be 4.8 Å [26] and this gives the interlayer space available for the CPPA anion as 15.1 Å. By using ChemOffice software the calculation of molecular dimensions was made and it provides spatial dimension with a longer axis of 16.0 Å; a shorter axis of 15.1 Å and a thickness of 5.8 Å, as shown in Figure 3(a). Therefore, the spatial orientation for the three-dimensional (3-D) molecule of CPPA phenoxyherbicides intercalated between the layers can be proposed, as shown in Figure 3(b). This shows that two CPPA anions are vertically aligned so that the basal spacing of 19.9 Å is obtained.

2.2. FT-IR spectroscopy

The presence of the intercalated species in the Zn/Al-LDH was also supported by FT-IR results. The FT-IR spectra of Zn/Al-LDH, CPPAEX and CPPA in the region between 400 and 4000 cm^{-1} are illustrated in Figure 4.

The FT-IR spectrum of the Zn/Al-LDHs is shown in Figure 4. Broad absorption peaks in the region of 2800–3800 cm^{-1} centred at 3454 cm^{-1} are assigned to O–H stretching mode due to the LDH brucite-like layer and/or interlayer water molecules. A band observed at 1637 cm^{-1} is assigned to the bending vibration of interlayer water molecules and the presence of NO_3^- is shown by a very strong absorption peak at 1378 cm^{-1} . This disappears after the intercalation process, indicating that NO_3^- was completely replaced by the CPPA. A band at the lower wavenumber region corresponds to the lattice vibration mode such as the translational vibrations of Zn–OH at 611 cm^{-1} and deformation vibration of OH–Zn–Al–OH at 407 cm^{-1} [27,28].

The FT-IR spectrum of the pure CPPA is also illustrated in Figure 4 and shows a broad band at 3459 cm^{-1} , which can be attributed to the O–H stretching vibration.

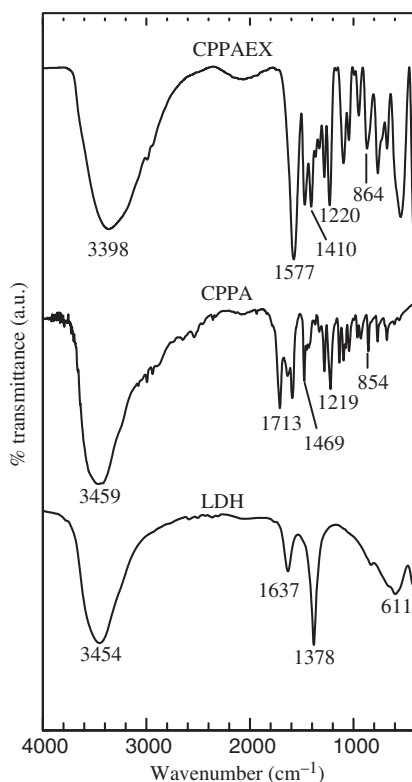


Figure 4. FT-IR spectra of Zn/Al-LDH, CPPA and CPPA-LDH nanohybrid, CPPAEX.

A sharp band observed at 1713 cm^{-1} is due to the C=O stretching. Bands at 1469 and 1400 cm^{-1} are attributed to the stretching vibrations of aromatic ring C=C and strong bands at 1288 and 1219 cm^{-1} are due to the symmetric and asymmetric stretching modes of C–O–C. A sharp band at 854 cm^{-1} is attributed to C–Cl stretching [29].

The FT-IR spectrum of CPPAEX synthesised by using 0.025 M CPPA is shown in Figure 4. As expected, the spectrum resembles a mixture of both the FT-IR spectra of CPPA and Zn/Al-LDH, indicating that both functional groups of CPPA and Zn/Al-LDH are present together, except for the peak at 1378 cm^{-1} corresponding to the nitrate anions. All these confirm that all the interlayer nitrate anions have been fully replaced by CPPA. The most important feature in the FT-IR spectra of the nanohybrid is the disappearance of a band at 1713 cm^{-1} (which is due to the carboxylic group in CPPA) and the presence of new bands at around 1577 cm^{-1} and 1410 cm^{-1} . These new bands are due to the C=O carboxylate anion, which confirm the presence of CPPA in the anionic form in the interlayer of the LDH [29].

2.3. Organic–inorganic composition

Elemental analysis (Table 1) shows that the molar ratio of Zn to Al in both Zn/Al-LDH and CPPAEX is 2.8 compared to 3.0 for the value initially prepared for the mother liquor. This indicates that the Zn to Al molar ratio in the resulting synthesised materials were

Table 1. Basal spacing and chemical composition of Zn/Al-LDH (LDH) and its nanohybrid, CPPAEX.

Sample	d (Å)	Zn/Al molar ratio	Mole fraction (x_{Zn})	N (%)	C (%)	Anion ^a (%w/w)
LDH	8.9	2.8	0.74	3.0	0.0	–
CPPAEX	19.9	2.8	0.74	0.0	24.4	42.3

^aEstimated from CHNS analysis.

adjusted accordingly for the formation of the positively charged inorganic layers to compensate the negatively charged intercalated anion so that the resulting materials Zn/Al-LDH and CPPAEX are charged neutral.

The percentage of nitrogen in Zn/Al-LDH agrees with the information obtained from the FT-IR spectrum (Figure 4) which shows a broad absorption band at 1379 cm^{-1} , which is due to NO_3^- and the presence of 24.4% carbon in the CPPAEX is due to the intercalation of CPPA into the interlayer of Zn/Al-LDH. As shown in Table 1, the estimated percentage of CPPA intercalated into the interlayer is 42.3%.

The theoretical exchange capacity of the fully exchanged LDH was calculated to be 32.4% compared to about 42.3% w/w, estimated by thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) (Table 1). PXRD study shows that no CPPA phase can be found in the nanohybrids (Figure 2) which means there is no adsorption of un-intercalated CPPA species at the outer layers of the nanohybrid. Due to the fact that, in general, PXRD technique will give a phase pure material at around 97%, and the purity of CPPA is not 100% (as assumed in the TGA–DTA technique) and that the water content varies from the LDH to its nanohybrid compound, we believe that the discrepancy is due to these factors.

2.4. Thermal analysis

The TGA/DTA thermogravimetric analyses obtained for the LDH, CPPAEX and CPPA are reported in Figure 5 (a)–(c) and Table 2. For CPPA and LDH, thermal studies show temperature maxima at 204.3°C and 234.8°C , compared to 348.8°C for the CPPAEX nanohybrid. This indicates that CPPA encapsulated into the inorganic interlamellae is thermally more stable than its counterpart in the sodium salt form.

For both LDH and its nanohybrids, three stages of weight loss were observed. The first stage is the weight loss due to the physically adsorbed water, interlayer water can be observed at around $35\text{--}200^\circ\text{C}$. This is followed by weight loss due to the removal of an interlayer anion and dehydroxylation of the hydroxyl layer, which can be observed at $201\text{--}600^\circ\text{C}$. Weight loss due to the decomposition of the nitrate anion for Zn/Al-LDH occurred at 234.8°C , while for the encapsulated organic moiety of the nanohybrid it occurred at 348.8°C . The third stage was characterised by the combustion of the organic species, leaving a relatively less volatile metal oxide.

2.5. Surface morphology and surface properties

Surface morphology study of the LDH and its nanohybrid were carried out using a scanning electron microscope (Figure 6). The morphology of LDH and its nanohybrid

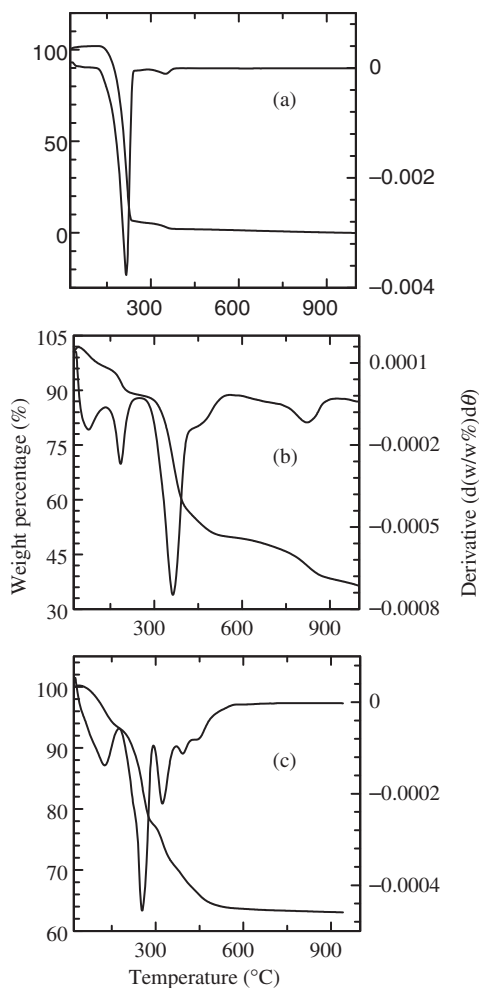


Figure 5. (a) TGA–DTA thermograms of CPPA, (b) its nanohybrid, CPPAEX and (c) Zn/Al-LDH (LDH). The analysis is given in Table 2.

Table 2. TGA–DTA data for Zn/Al-LDH (LDH), CPPA and its nanohybrid, CPPAEX.

	Weight loss			Total weight loss (%)
	(35–200°C)	(201–600°C)	(601–1000°C)	
LDH	6.8 ($T_{\max} = 112.9^{\circ}\text{C}$)	29.0 ($T_{\max} = 234.8^{\circ}\text{C}$)	–	35.8
CPPAEX	12.0 ($T_{\max} = 175.9^{\circ}\text{C}$)	38.4 ($T_{\max} = 348.8^{\circ}\text{C}$)	16.6 ($T_{\max} = 779.1^{\circ}\text{C}$)	67.0
CPPA	–	98.3 ($T_{\max} = 204.3^{\circ}\text{C}$)	–	98.3

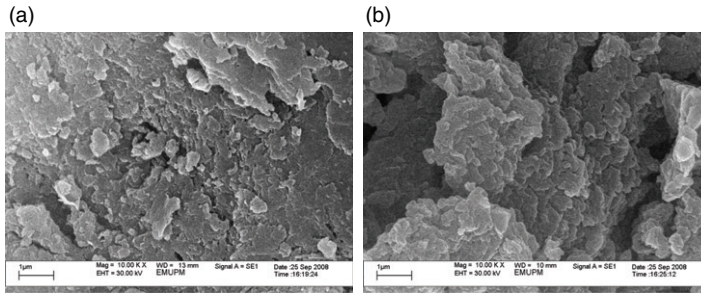


Figure 6. Surface morphology of (a) Zn/Al-LDH (LDH) and (b) its nanohybrid, CPPAEX.

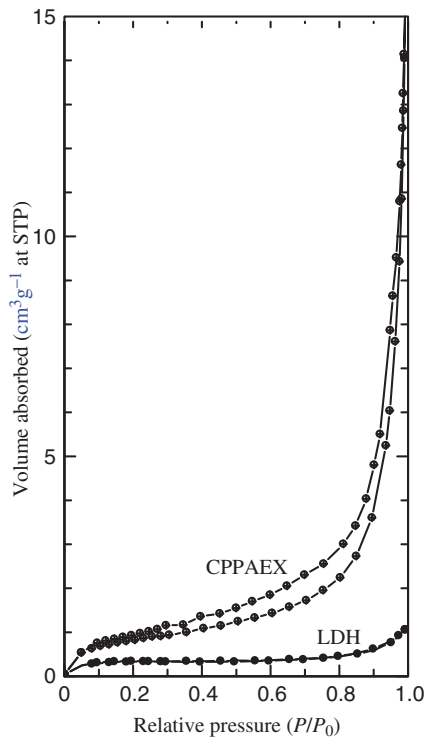


Figure 7. Nitrogen adsorption-desorption isotherms for Zn/Al-LDH (LDH) and its nanohybrid CPPAEX.

shows an agglomerate and nonporous structure in which the presence of the intercalated anion in the interlayer did not greatly influence the morphology of the resulting materials.

The nitrogen adsorption-desorption isotherms (Figure 7) for LDH and CPPAEX show the features which can be ascribed to Type IV in the IUPAC classification, indicating the mesopore-type of material [30]. The adsorption of LDH and the nanohybrid increased slowly at low relative pressure in the range 0.0–0.8 followed by the rapid adsorption

of the adsorbent at 0.8 and higher. The desorption branch of the hysteresis loop for LDH is narrower compared to CPPAEX, indicating different pore texture of the materials.

3. Experimental

3.1. Synthesis

All chemicals used in this synthesis were obtained from various chemical suppliers and used without any further purification. All solutions were prepared using deionised water.

Synthesis of LDH was done by preparing the mother liquor containing Zn^{2+} and Al^{3+} cations with Zn to Al initial molar ratio, $R=3.0$. The resulting solution was adjusted to $\text{pH } 7.50 \pm 0.02$ by the dropwise addition of aqueous NaOH (2.0 M). The reaction was carried out under nitrogen atmosphere. The precipitate was aged at 70°C in an oil bath shaker for 18 h. The synthesised material was then centrifuged, thoroughly washed with deionised water and dried in an oven at 70°C . The resulting LDH was then finely powdered, kept in a sample bottle and stored in a vacuum desiccator.

In the anion exchange method, LDH of Zn/Al with nitrate as the interlayer gallery anion was exchanged with CPPA as a guest anion to form an Zn/Al-CPPA nanohybrid. About 0.500 g Zn/Al-LDH was put in contact with 100 mL aqueous solution of CPPA and kept for 18 h at 70°C , at various concentrations (0.009–0.05 M) of guest anions solution. The solution was kept for another 18 h at 70°C . The slurry was centrifuged, washed with deionised water and then dried in an oven at 70°C , powdered and kept in a sample bottle and stored in a vacuum desiccator for further use and characterisations.

3.2. Characterisation

PXRD patterns were recorded at $2\text{--}60^\circ$ on an ITAL 2000 diffractometer using Cu-K α radiation at 40 kV and 30 mA. FT-IR spectra of the materials were recorded over the range $400\text{--}4000\text{ cm}^{-1}$ on a Perkin-Elmer 1752X spectrophotometer using the KBr disc method. A CHNS analyser, model CHNS-932 of LECO Instruments was used for CHNS analysis. The Zn to Al molar ratio of the resulting Zn/Al-LDH-nanohybrid was determined by an inductively coupled plasma atomic emission spectrometry (ICP-AES) with a Perkin-Elmer spectrophotometer model Optima 2000DV under standard conditions. TGA/DTA were carried out using a Mettler Toledo TGA/SDTA851 thermogravimetric analyser with a heating rate of $10^\circ\text{C min}^{-1}$ between 35°C and 1000°C , under a nitrogen flow rate of about 50 mL min^{-1} . The Brunauer–Emmett–Teller (BET) surface area of the samples was determined by a BEL Japan, Belsorp mini using nitrogen gas adsorption–desorption technique at 77 K together with the BET equation.

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