Synthesis and characterization of mesoporous zinc layered hydroxide-isoprocarb nanocomposite

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Intercalation; Characterization; Zinc layered hydroxide; Isoprocarb; Mesoporous

Abstract
The ion exchange method was used to intercalate a poor water-soluble insecticide, isoprocarb into zinc layered hydroxide (ZLH). PXRD analysis indicated the successful intercalation with good crystallinity for the resulting nanocomposite, with a basal spacing of 33.1 Å. FTIR analyses showing the resemblance of an absorption peak of the nanocomposite with the host and the guest anion. The thermal analysis confirmed that the nanocomposite had better thermal stability compared to the pristine isoprocarb. The nanocomposite also characterized by elemental and surface morphology analysis. The surface analyses of the host and nanocomposite showed mesoporous-type material characteristics. On the whole, the intercalation process decreased the pore size of the nanocomposite compared to the pristine host, layered zinc layered hydroxide-sodium dodecyl sulphate (ZLH-SDS). The obtained material is believed has a great potential as an environmentally friendly insecticide.

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1. Introduction

Layered metal hydroxide compounds can be classified into two main types, namely layered double hydroxide and layered hydroxide salt. One example is zinc layered hydroxide (ZLH) [1–3]. ZLH have a structure like brucite, but instead of metal replacement, hydroxide ions are removed from the structure and replaced by water molecules. Oxoanions are then positioned in the second coordination sphere of the metal to stabilize the electrostatic charge, or by the direct substitution of other single charged anions [3,5]. This layered material has potential for ion exchange, where the general formula can be represented by $M^{2+}(OH)_{2-x}(A^{m-})_{x}nH_{2}O$, in which $M^{2+}$ is a metallic cation, such as $Cu^{2+}$, $Co^{3+}$, $Ni^{2+}$, $Mn^{2+}$ or $Zn^{2+}$ and $A$ is the oxoanion with an $m-$ charge [5].

Synthesis of mesoporous materials has attracted huge consideration recently due to its prevalent applications such as optical, electronic, and electrochemical devices [6]. Many framework compositions (e.g., silica, organosilica, metal, and non-siliceous oxides) [7–9] and various morphologies (e.g., nanoparticle, monolith, and film) [6,10] have been synthesized under various synthetic conditions. ZLH is one of mesoporous material that has attracted considerable attention due to their ion exchange properties and mesoporous structures. There have been a number of recent reports of ZLH nanocomposites with mesoporous properties, such as zinc layered hydroxide-salicylate [11], zinc layered hydroxide-protocatechuate [12], undoped and doped zinc layered gallate nanohybrid with $Fe^{3+}$, $Co^{2+}$, and $Ni^{2+}$ [13], zinc hydroxide nitrate-3-(4-methoxyphenyl) propionate [14] and zinc layered hydroxide-para-amino salicylate [15].

Isoprocarb, or 2-isopropylphenyl-N-methylcarbamate, is one of the most important carbamate insecticides, and exists as a poor water-soluble insecticide [16]. It is used against various types of parasites for plants in tropical and subtropical regions, such as fulgorids rice and cotton leafhopper [16]. A poor water-soluble insecticide is usually dependent on an anionic surfactant that forms a hydrophobic region in the interlayer of layered material [17].

The final properties of inorganic-organic functional hybrids are controlled by interactions between a host (inorganic layered matrix) and guest (functional organic molecule), because the strength and directionality of interactions affect the distribution, orientation and electronic properties of guest molecules [18].

Therefore, in this study, we have synthesized zinc layered hydroxide-sodium dodecyl sulphate-isoprocarb nanocomposite (ZLH-SDS-ISO) by intercalating isoprocarb into the interlayer ZLH modified with sodium dodecyl sulphate (SDS) surfactant. The characterization of the nanocomposite has been done using PXRD, FTIR, elemental analysis, thermal study, surface morphology and surface area analysis.

2. Materials and methods

2.1. Materials

Sodium dodecyl sulphate (SDS) and zinc nitrate ($Zn(NO_{3})_{2}$-6$H_{2}O$) were purchased from Systerm Malaysia. Sodium hydroxide, NaOH, was purchased from HmbG Chemicals. Whereas, isoprocarb insecticide, $C_{11}H_{15}NO_{2}$ (ISO), was purchased from Nanjing Essence Fine-Chemical. All solutions were prepared using deionized water. Each chemical utilised in this synthesis was obtained from chemical providers and used without additional purification.

2.2. Synthesis of ZLH-SDS-ISO nanocomposite

Zinc layered hydroxide-sodium dodecyl sulphate (ZLH-SDS) was synthesized by the procedure described elsewhere [17]. Briefly, ZLH-SDS was synthesized using a co-precipitation method by the slow addition of 1.0 M NaOH and 40 mL of 0.5 M of $Zn(NO_{3})_{2}$-6$H_{2}O$ into a solution containing 40 mL 0.25 M SDS under magnetic stirring. The pH value was adjusted to 6.5. The slurry was then centrifuged and dried in an oven at 70 °C.

Preparation of isoprocarb (ISO) intercalated into the interlayer of ZLH-SDS (indicated as ZLH–SDS-ISO) was achieved by an ion exchange method. Various concentrations of isoproc acid solution were prepared at 0.001 M, 0.0025 M and 0.005 M. Then 0.5 g of ZLH-SDS was dissociated in an isoprocarb solution and kept under magnetic stirring for 2 ø h. The slurry was then aged for 24 h in an oil bath shaker at 70 °C. Then the slurry was centrifuged and the final white solid was dried in an oven for 24 h.

2.3. Characterization

There were several instruments involved in the characterization of the ZLH-SDS-ISO nanocomposites. The X-ray diffraction patterns (XRD) were obtained using a Powder X-ray Diffraction (PXRD) Bruker AXS (model D8 Advance, wavelength of 1.5406 Å) with CuKα radiation at 60 kV and a current of 60 mA. The recorded region of 20 was from 2° to 60°, with a scanning rate of 2° min$^{-1}$. The FTIR spectra were collected in a Thermo Nicolet 6700 Fourier Transform Infra-red Spectrometer in the range 400–4000 cm$^{-1}$. The thermal analyses (TGA/DTG) of the sample were obtained with a Perkin Elmer Pyris 1 TGA Thermo Balance with a heating rate of 20 °C min$^{-1}$ (N$_{2}$ flow rate was 50 mL/min, temperatures were 25–900 °C at a rate of 10 K/min). An inductive coupled plasma optical emission spectrometry (ICP-OES), model Agilent, 720 Axial and (CHNO-S), model Thermo Finnigan, Flash EA 1112 was used to study the composition of the samples. The surface morphology of the samples were observed by a field emission scanning electron microscope (FESEM) Hitachi model SU 8020 UHR. Surface characterization of the nanocomposites was carried out by the nitrogen gas adsorption-desorption technique at 77 K using a Quantachrome Autosorb-1 and degassed in an evacuated heated chamber at 120 °C overnight.
3. Results and discussion

3.1. PXRD analysis

The XRD pattern of ZLH-SDS showed a basal spacing of 9.8 Å, corresponding to Zn(OH)$_3$(NO$_3$)$_2$·2H$_2$O, and the peak at 33.0 Å had the same pattern with LDH-SDS that was previously reported by [19]. The resulting ZLH-SDS was well crystallized, without impurities like ZnO, which indicated that a complete reaction occurred during the co-precipitation between zinc nitrate and SDS. Upon dissolving zinc nitrate hexahydrate in water, the zinc species undergoes hydrolysis reactions (Eqs. (1) and (2)) as previously reported by Moezzi et al. [20]

$$Zn(NO_3)_2 \rightarrow Zn^{2+}(aq) + 2(NO_3^{-})(aq)$$  \hspace{1cm} (1)

$$Zn^{2+} + (aq) + H_2O \rightarrow ZnOH^{+} (aq) + H^+(aq)$$ \hspace{1cm} (2)

Zinc hydroxide species can actually further transform into ZnO nanoparticles. However, in the presence of dodecyl sulphate ions, these zinc hydroxide species could cause charge-assemblies to form zinc hydroxide-dodecyl sulphate layered nanosheets. The formulas below represent the main reactions that were previously reported by Liang et al. [21].

$$Zn(OH)_{2-x}\cdot x/4O_2 \rightarrow ZnO + (1-1/2x)H_2O$$ \hspace{1cm} (3)

$$Zn(OH)_{2-x}\cdot xDS^{-} \rightarrow Zn(OH)_2 - xDS_x$$ \hspace{1cm} (4)

The x-ray diffraction pattern of ZLH-SDS-ISO shows a series of basal peaks, indicated by (0 0 3), (0 0 6), (0 0 9) in Fig. 1. A typical of intercalation peak was observed at a lower angle, 2$\theta$, and clearly confirmed the intercalation of isoprocarb anion into the interlayer of ZLH [14]. The intercalation occurred due an ion exchange reaction that took place between the nitrate ion and isoprocarb anion. The intercalation of 0.001 M, 0.0025 M and 0.005 M of isoprocarb insecticide into the nitrate ion and isoprocarb anion. The intercalation of isoprocarb between interlayers of ZLH, with a pure phase of isoprocarb was not present in the ZLH-SDS-ISO nanocomposite. This was due to the successful intercalation peak decreased for 0.005 M isoprocarb due to the presence of the large amount of isoprocarb in the interlayer, as this interfered with the crystal growth during regeneration [25]. For further characterization, a sample of 0.0025 M isoprocarb was chosen as the phase pure well-ordered nanocomposite material.

![X-ray diffraction pattern of ZLH-SDS, isoprocarb and ZLH-SDS-ISO nanocomposite at 0.001 M, 0.0025 M, and 0.005 M concentration of isoprocarb.](image)

3.2. FTIR

As shown in Fig. 2, the FTIR spectra of ZLH-SDS shows a strong and sharp absorption band around 3500–3700 cm$^{-1}$, which corresponds to the stretching vibrations of the OH group of the free water molecule [26]. A strong and broad absorption band centred at 3461 cm$^{-1}$ can be attributed to the OH vibration. This band has a broad base due to the hydrogen bonds associated with the water molecule [5]. Another bending vibration at 1637 cm$^{-1}$ is due to the H–O–H bending of the water molecule in the interlayer of ZLH-SDS. Two main doublet absorption bands appear in the 2850–2950 cm$^{-1}$ region, which are due to the stretching vibration of the aliphatic group. Another band at 1350–1480 cm$^{-1}$ is due to bending vibration of the aliphatic group. The stretching vibration at 1210–1240 cm$^{-1}$ was due to the presence of a sulphate group in SDS [27]. A strong absorption band at 1364 cm$^{-1}$ was due to the presence of nitrate, as the salt used for the source of metal ions was zinc nitrate.

The FTIR spectra of ZLH-SDS-ISO resemble the ZLH-SDS and isoprocarb spectra. A strong and broad band at 3438 cm$^{-1}$ was attributed to the stretching vibration of the hydroxyl group of the water molecule. A peak at 1637 cm$^{-1}$...
revealed that there was a free water molecule in the interlayer of the nanocomposite. Sharp doublet absorption of ZLH-SDS-ISO nanocomposite band resembled the peak in ZLH-SDS layer at 2913 and 2846 cm\(^{-1}\), which was due to the stretching vibration of the C-H group that was present in the nanocomposite. The peak at 1458 cm\(^{-1}\), which also resembles the peak in ZLH-SDS, was due to the bending vibration of the aliphatic group, C\(_A\)H. The bands that appeared at 1189 and 1056 cm\(^{-1}\) were assigned to the asymmetric and symmetric stretching vibration of S\(_A\)O\(_A\) [19]. The stretching vibration of S\(_A\)O for ZLH-SDS-ISO particles was shifted to lower frequencies, indicating the configuration variation of the OSO\(_3\) functional group [19]. Those shifts confirm the loss of S\(_A\)O bond strength, and refer to the existence of a hydrogen bond within the ZLH interlayer and sulphate group (S\(_A\)O\(_A\)H--O--Zn), as well as to the electrostatic attraction [19]. The absence of the N--H absorption peak that should appear at 3314 and 1543 cm\(^{-1}\) in the resulting ZLH-SDS-ISO spectra indicated that the isoprocarb molecule was successfully loaded into the ZLH interlayer in an ionic form. After the intercalation, isoprocarb may undergo an elimination mechanism in the hydrolysis reaction [16]. The N--O peak (1364 in ZLH-SDS spectra) also disappeared in ZLH-SDS-ISO spectra, which confirmed the removal of NO\(_3\) \(^{-}\) ion after the intercalation of isoprocarb into the interlayer of ZLH.

The isoprocarb spectra presented an adsorption peak at 2965 and 2868 cm\(^{-1}\), indicating the C--H stretching vibration, while the C--H bending vibration peak appeared at 1447 cm\(^{-1}\). The peak at 1221 cm\(^{-1}\) corresponded to the C--N stretching vibration. Overall, the main FTIR absorption bands for ZLH-SDS-ISO nanocomposite are listed in Table 1.

### 3.3. Spatial orientation

The proposed orientation of the ZLH-SDS-ISO nanocomposite is shown in Fig. 3. Previous studies classified the arrangement of dodecyl sulphate into two structures: an interdigitated monolayer arrangement with the trans-dodecyl chain sandwich [28] and tail-to-tail bilayer arrangement of the dodecyl chain [29]. SDS was intercalated into ZLH as a dodecyl sulphate anion [30]. Dodecyl sulphate and isoprocarb are aligned perpendicular and electrostatically attracted to host layer surface. Hence, the dodecyl sulphate ion is shown...
to be tilted and in a monolayer arrangement, while the isoprocarb anion is in bilayer arrangement. Regarding the size of the isoprocarb molecule and interlayer space height (33.1 Å) of ZLH-SDS-ISO nanocomposite, it is reasonable to conclude that the isoprocarb molecules are intercalated into the hydrophobic region formed by dodecyl sulphate molecules in the interlayer space of ZLH, due to the increase of the ZLH-SDS-ISO nanocomposite basal spacing, as reported elsewhere [19]. The interlayer height of ZLH-SDS-ISO nanocomposite was estimated by the basal spacing obtained from PXRD analysis, which was 33.1 Å. Since the layer thickness was 4.8 Å and the Zn$^{2+}$ moiety of the lattice from the basal spacing was 2.6 Å, the interlayer height of the nanocomposite is estimated to be 25.1 Å.

3.4. Elemental analysis

The composition analysis results for the ZLH-SDS and the ZLH-SDS-ISO nanocomposite are listed in Table 2. CHNS analysis of the ZLH-SDS indicated 2.46% of N, 24.8% of C, 5.48% of H and 3.38% of S. ICP-OES analysis showed a high percentage of Zn (38.87%) for pristine ZLH-SDS used in this work. After the intercalation process, about 61.10% of carbon was detected. The intercalation of isoprocarb anion in the interlayer of ZLH caused the increase in percentage of the carbon. The percentage of S and N in the resulting nanocomposite was 0.77% and the 6.17%, respectively. The S element represents the dodecyl sulphate ion in the interlayer of ZLH. Previously, PXRD analysis confirmed that there was no nitrate ion after intercalation process. Therefore, the N element detected in the resulting nanocomposite came from the amine group in the isoprocarb anion, which confirmed the successful intercalation of isoprocarb in the interlayer of ZLH. The percentage isoprocarb anion intercalated between the interlayer of ZLH region was 83.35%, which was calculated from the percentage of N element in the nanocomposite. ICP-OES detected 38.87% of Zn in the resulting nanocomposite.

3.5. Thermal study

The thermogravimetric analysis, TGA-DTG, obtained for isoprocarb, ZLH-SDS-ISO nanocomposite and ZLH-SDS are reported in Fig. 4. In Fig. 4(a), the thermal study shows that the maximum temperature of pure isoprocarb was observed at 184 °C, with 99.8% of weight loss.

For ZLH-SDS-ISO, three stages of decomposition were observed in Fig. 4(b). The first stage was due to the removal of surface-physisorbed water molecules, and dehydroxylation of the hydroxyl layer which occur at 130 °C with 9.6% of weight loss [31]. The second stage was due to decomposition of isoprocarb, which can be observed at 189 °C with 74.2% weight loss. The final stage was due to decomposition of SDS at 239 °C with weight loss of 13.7%.

Fig. 4 Thermogravimetric curve for (a) isoprocarb anion, (b) ZLH-SDS-ISO nanocomposite and (c) ZLH-SDS.

The ZLH–SDS displayed two stages of weight loss (Fig. 4 (c)). The first stage corresponded to the removal of intercalated water at 107 °C with 3.2% of weight loss [32]. Whereas, the decomposition of SDS took place at 198 °C with 37.0% of weight loss. From Fig. 4(a) and (b), the maximum temperature of the decomposition of isoprocarb in the resulting nanocomposite increased from 184 °C to 189 °C. Therefore, the isoprocarb that intercalated in the ZLH-SDS interlayer was proved to be thermally more stable compared to its prior form. This is due to the electrostatic interaction between anions and ZLH layer [14].

Table 2 The composition analysis of the ZLH-SDS and ZLH-SDS-ISO nanocomposite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N (%)</th>
<th>C (%)</th>
<th>H (%)</th>
<th>S (%)</th>
<th>Anion (% w/w)</th>
<th>% Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZLH-SDS</td>
<td>2.46</td>
<td>24.80</td>
<td>5.48</td>
<td>3.38</td>
<td>–</td>
<td>24.14</td>
</tr>
<tr>
<td>ZLH-SDS-ISO</td>
<td>6.17</td>
<td>61.10</td>
<td>7.14</td>
<td>0.77</td>
<td>83.35</td>
<td>38.87</td>
</tr>
</tbody>
</table>
3.6. Surface morphology

Fig. 5(a) and (b) illustrate the morphology of ZLH-SDS and ZLH-SDS-ISO at 10 k magnification. The FESEM image of ZLH-SDS resembles thin flake-like nanosheets that are expected to be layered materials [1]. The edge of ZLH-SDS sheets was quite fractured, with a cracked surface (Fig. 5(a)). After the intercalation, the crystal size decreased, with irregular thin flakes and in the micrometre range dimension (Fig. 5(b)). The sheets were in stacked plate, sharp edges and smooth surface. The effect of the hydrophobic interaction between the hydrocarbon tails was to facilitate the aggregation of the particle, as previously reported elsewhere [19,27].

3.7. Surface area analysis

The comparison of the surface area and porosity of ZLH-SDS and ZLH-SDS-ISO nanocomposite are given in Table 3. The intercalation of the isopropyl carbion decreased the BET surface area from 7.027 m² g⁻¹ for ZLH-SDS to 1.196 m² g⁻¹ for the ZLH-SDS-ISO nanocomposite. As the surface area is inversely related to particle size, this case is attributed to the increase in the particle size and decrease of the pore volume [33]. Particularly, specific surface area decrease with the increase of particle size as well as pores presence, which lead to the decrease in the specific surface area [34]. This also might be due to a shift in the particle size distribution to a larger mean size [35]. The decrease of surface area may take place due to the collapse of pore structure. The collapse of the interconnected mesoporous enlarged and changed the smaller mesoporous into irregularly shaped larger mesoporous and decreased the surface area value [36].

As shown in Fig. 6, both the host and resulting nanocomposites possessed a relatively narrow distribution of pores, with an average diameter of 27.83 to 25.04 nm, respectively, confirming the formation of regular mesoporous materials. This was due to the closing of the pores from insertion of

<table>
<thead>
<tr>
<th>Samples</th>
<th>Specific BET surface area (m²/g)</th>
<th>Average pore diameter (nm)</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZLH-SDS</td>
<td>7.027</td>
<td>27.83</td>
<td>Mesoporous</td>
</tr>
<tr>
<td>ZLH-SDS-ISO</td>
<td>1.196</td>
<td>25.04</td>
<td>Mesoporous</td>
</tr>
</tbody>
</table>

Fig. 5 FESEM images of (a) ZLH-SDS, and (b) ZLH-SDS-ISO nanocomposite at 10 k magnification.

Fig. 6 Adsorption-desorption isotherms of nitrogen gas for (a) ZLH-SDS and (b) ZLH-SDS-ISO.
the isoprocarb anion into the pores of the ZLH-SDS layer [37,38]. The presence of dodecyl sulphate and isoprocarb anion in the interlayer created a stronger bonding between the ZLH layers and the anion, thus lowering the surface area of the nanocomposite material [22]. A nitrogen-adsorption isotherm for ZLH-SDS and the ZLH-SDS-ISO nanocomposites are a type IV isotherm, with H3 hysteresis loops based on the International Union of Pure and Applied Chemistry (IUPAC) classification [39] indicating mesoporous-type materials. The adsorption slowly increased in low relative pressure in the range of 0.0–0.6 (for ZLH-SDS) and 0.0–0.5 (for ZLH-SDS-ISO), which indicates a surface monolayer adsorption process. Further increases in the relative pressure resulted in a rapid adsorption of the adsorbent, due to the first multilayer adsorption [14]. The optimum uptake for resulting was 5 cm^3/g, which indicates a low capacity for uptake of nitrogen gas compared to the host, which was 32 cm^3/g. This is due to the high capacity of the isoprocarb anion intercalate in the interlayer of ZLH. A similar result was also reported elsewhere [3]. The presence of H3 hysteresis loop in layered ZLH-SDS and the ZLH-SDS-ISO nanocomposite revealed that the pores exhibit slit-shaped pores with non-uniform shape and sizes.

The Barret-Joyner-Halenda (BJH) pore size distribution for ZLH-SDS and the ZLH-SDS-ISO nanocomposite are shown in Fig. 7. The pore size distribution of ZLH-SDS and ZLH-SDS-ISO is almost the same, with features centred at around 14 and 21 nm. In particular, the pore size distributions show the formation of regular mesoporous in the layered ZLH nanocomposites.

4. Conclusion

In conclusion, this study showed the successful intercalation of isoprocarb into the ZLH interlayer by an ion exchange method. The SDS surfactant provided a great impact in order to intercalate the poor water-soluble insecticide, like isoprocarb, into the interlayer of ZLH. The crystallinity of the resulting nanocomposite is increase by increasing the amount of isoprocarb anion. A well-crystallized nanocomposite was obtained with basal spacing 33.1 Å. The FTIR spectra of ZLH-SDS-ISO showed a resemblance with ZLH-SDS spectra and isoprocarb spectra. The thermal stability of isoprocarb increased after the intercalation, compared to its pure form. The resulting nanocomposite showed a mesoporous-like characteristic. This study also showed that ZLH can be an excellent host for isoprocarb. Further work in controlled release formulation of this nanocomposite is needed for environmental purposes.

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