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Preparation and characterisation of novel paddy cultivation herbicide nanocomposite from zinc/aluminium layered double hydroxide and quinclorac anion*

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ABSTRACT
Zn/Al-layered double hydroxide-quinclorac (Zn/Al-LDH-QC) nanocomposite has been synthesised via co-precipitation method. The versatility of the Zn/Al-LDH enables this host material to be intercalated with quinclorac (QC), a type of auxin agonist herbicide that was widely used in paddy cultivation. The PXRD analysis shows that the basal spacing of the Zn/Al-LDH-QC nanocomposite expanded in the range of 15.8–16.7 Å (from 8.8 Å in Zn/Al-LDH), therefore indicating the successful intercalation of QC into the interlayer gallery of Zn/Al-LDH. The intercalation was also proven from the FTIR and elemental analysis. The thermogravimetric analysis conducted using TGA/DTG shows that the Zn/Al-LDH-QC exhibits better thermal stability compared to the pure QC herbicide. Based on the results collected from the ICP-OES, CHNS analyser, and TGA/DTG, the chemical formula of Zn/Al-LDH-QC was proposed as $[Zn_{0.75}Al_{0.25}(OH)_2][C_9H_4Cl_2NCOO]^-_{0.25}0.90H_2O$. This study shows that the Zn/Al-LDH has potential to be used as a host material for herbicide in paddy cultivation sector.

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Nanocomposite; quinclorac; Zn/Al-layered double hydroxide; intercalation; co-precipitation

Introduction

Layered double hydroxide (LDH), which is also known as anionic clay has attracted considerable interest of worldwide researcher due to their amazing properties, including huge surface area, remarkable anion exchange capability, great biomedical properties, chemical inertness and low toxicity [1]. The structure of LDH comprises positively charged edge sharing octahedra, which forming host layers with a brucite-like structure. The substitution of divalent and trivalent cations in the LDH structure generates excessive positive charges in the interlayer, which need to be counterbalanced by the interlayer anions [2]. Their general formula can be written as $[M^{2+}_{(1-x)}L^{3+}_x(OH)_2]^{x+}A^{m-}{}_{x/m}{\cdot}nH_20$, where $M^{2+}$and L^{3+} represent divalent and trivalent metal cations, respectively, whereas A stands for an anion [3]. The ratio of the divalent and trivalent cations can be varied to control the charge density and the anion exchange capacity of the particular LDH [4].

Due to the remarkable anion exchange capacity possesses by LDH, this layered material has been reported to be intercalated with a wide range of anions, such as (4-chloro-2-methylphenoxy)acetate [5], glyphosate [6], chlorpyrifos [7], linuron, metamitron and 4-(2,4-dichlorophenoxy)butyrate [8]. Other interesting quality own by LDHs is regarding their obtainability, as LDHs are naturally plentiful, readily manufactures at industrial scale, easily prepared and more economical [9,10]. LDHs were reported to be synthesised using various different method, including ion exchange method [11], co-precipitation method [12] and reconstruction method [13]. Amongst these methods, co-precipitation seems to be the most favoured in synthesising LDHs, as the LDHs can be directly intercalated with the desired anion to produce well-crystallized nanocomposite [14–16]. The co-precipitation method also allowed the production of intercalated LDH nanocomposite in huge quantity, by simply scaling up the starting material [10].

Quinclorac (QC), which is also known as 3,7-dichloro-8-quinolinecarboxylic acid is a type of herbicide used for preemergence and post emergence control of weedy rice, common barnyardgrass, heartleaf false pickerelweed and several type of broadleaf weeds found in paddy cultivation area [17]. The chemical structure of QC is shown in Figure 1. With similar behaviour as dicamba and 2,4-dichlorophenoxyacetic acid, this colourless crystal is also categorised as an auxin agonist. The classification is mainly founded on the morphological response observed on the dicots plants once treated with QC and the rise of ethylene detected in the susceptible plants. Nevertheless, the ethylene evolution caused by QC is apparently less than those induced by 2,4-dichlorophenoxyacetic acid [18].

QC acts on the applied grass by constraining the growth of roots and shoots, causing the leakage of electrolyte in young roots and shots tissues, thus resulting the formation of necrotic band in the elongation zone of both parts. QC is not only can

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*This research showed that the quinclorac (QC) can be intercalated into the interlayer gallery of Zn/Al-layered double hydroxide via co-precipitation method. This method is the simplest and economical method which uses $Zn(NO_3)_2$, $Al(NO_3)_3$ and QC as a precursor. The resulting nanocomposite exhibit pure phase and high crystilinity with an improved thermal stability compared to the pure form of QC.

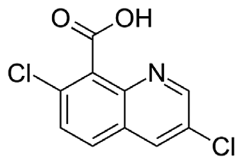

Figure 1. The chemical structure of QC.

be absorbed at the roots and shoots of the treated plants, this pesticides may also transported throughout the phloem and xylem [17]. In this present paper, the intercalation of anion QC into the interlayer gallery of Zn/Al-LDHs were accomplished using co-precipitation method. To the best of our knowledge, the novel nanocomposite synthesised, Zn/Al-LDH-Quinclorac (Zn/Al-LDH-QC) have not yet been published in any publication. Hopefully, the novel Zn/Al-LDH-QC nanocomposite synthesised can be used to benefit the paddy cultivation sector in the future.

Experimental

Materials and methods

All the reagents used to synthesise Zn/Al-LDH-QC in this study were used as received, no further purification was performed. The main reagents, $Zn(NO_3)_2 \bullet 6H_2O$ (purity 98%) and $Al(NO_3)_3 \bullet 9H_2O$ (purity 98%) were purchased from Systerm (Malaysia). The intercalated anion, QC with purity of 95% was obtained from Essense (China). The NaOH and HCl that were used to control the pH of the solution were supplied from HmbG Chemicals (Germany) and Sigma-Aldrich (U.S.A.), respectively. All solutions used in this study were prepared using deionised water.

Synthesis of Zn/Al-LDH-QC nanocomposite

The Zn/Al-LDHs were prepared by conventional co-precipitation method using $Zn(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ as precursors, under nitrogen gas atmosphere [19]. The mixed solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.1 M) and $Al(NO_3)_3 \cdot 9H_2O$ (0.033 M), with molar ratio, $R = 3$ was prepared by dissolving the salts in 250 mL of deionised water. The mixed solution was continuously stirred and purged with nitrogen gas to prevent any contamination from atmospheric CO_2. 50 mL of QC solution (0.05, 0.1 and 0.2) was added into the mixture and continuously stirred 5. 2 M NaOH was titrated into the mixed solution until the desired pH (pH 7.5 ± 0.05) was obtained. The aqueous solution was aged at 70 °C in an oil bath shaker for 24 h. The resulting white precipitate was collected by centrifuge (40 rpm for 5 min). The precipitate obtained was washed with deionised water thoroughly, dried in oven until completely dried (at 60 °C) and ground into fine powder. The Zn/Al-LDH-QC obtained was kept in sample bottle, so that it can be used for the characterisation purpose.

Characterisation of Zn/Al-LDH-QC nanocomposite

The Zn/Al-LDH-QC nanocomposite synthesised were characterised by Powder X-ray Diffraction (PXRD) Bruker AXS, model D8 Advance in the range of 2–60°. The PXRD patterns of the nanocomposite were recorded using Cu K_α irradiation ($\lambda = 0.15406$ nm) at 60 kV, 60 mA and 0.025° s^{-1}. The Fourier transform infrared (FTIR) spectra of the nanocomposites were

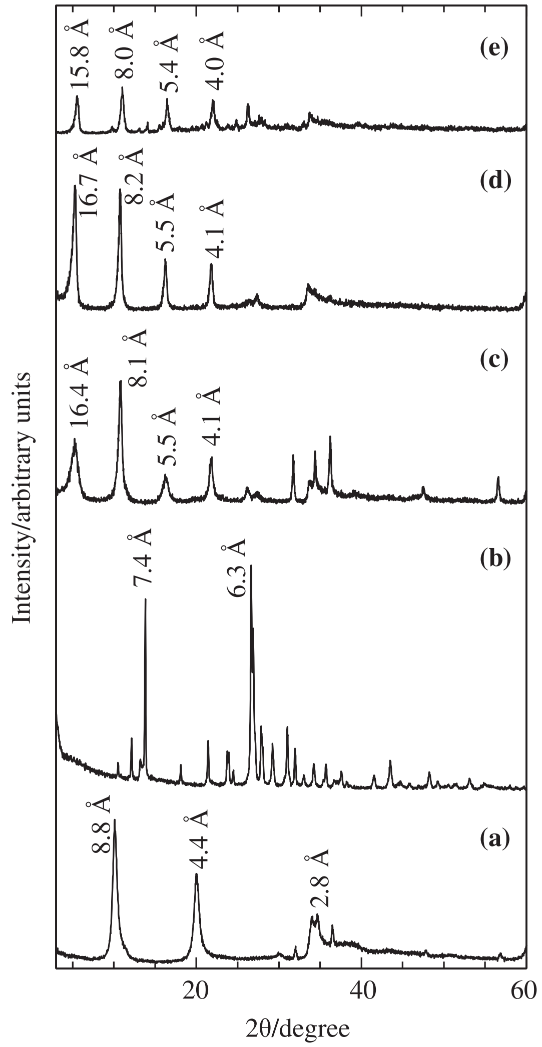

Figure 2. PXRD patterns of (a) Zn/Al-LDH, (b) QC, and the Zn/Al-LDH-QC nanocomposites prepared using (c) 0.05 M QC (d) 0.1 M QC and (e) 0.2 M QC.

obtained using a Nicolet FTIR spectrometers from Thermo Electron Corporation, with the KBr pellet method in the range of 400–4000 cm^{-1}. The percentage of the metal content and the percentage of carbon, hydrogen and nitrogen in the nanocomposite were determined using inductively coupled plasma optical emission spectrometry (ICP-OES), model Perkin-Elmer Plasma 1000 and CHNS elemental analyser, model CHNS-932 LECO, respectively. The thermal stability of the nanocomposite was studied in the range of 35–1000 °C using Perkin-Elmer Pyris 1 TGA Thermo Balance, with heating rate of 10 °C min^{-1} and under a constant flow of nitrogen gas. The surface morphology of the nanocomposite was determined using field emission scanning electron micrographs (FESEM) Hitachi SU 8020 UHR instrument.

Results and discussion

PXRD analysis

Figure 2 shows the PXRD patterns of Zn/Al-LDH (Figure 2(a)), QC (Figure 2(b)), and the Zn/Al-LDH-QC nanocomposites at different concentrations of QC (Figure 2(c), (d) and (e)). The Zn/Al-LDH exhibit well crystalline structure and possess all the characteristic diffraction peak of Zn/Al-LDH (JCPDS card No.51-1528). Three peaks can be observed on the PXRD pattern of Zn/Al-LDH (0 0 3, 0 0 6, and 0 0 9), with basal spacing of 8.8 Å, 4.4 Å and 2.8 Å, respectively. The (0 0 3) Bragg reflection which corresponding to the basal spacing of 8.8 Å, signifies the presence of nitrates as the counterbalance ions [20,21]. The basal spacing of the synthesised nanocomposite, Zn/Al-LDH-QC seems to expand in the range of 15.8–16.7 Å, thus indicate the success intercalation of QC into the interlayer gallery of Zn/Al-LDH. The presence of divalent cation (Zn^{2+}) and trivalent cations (Al^{3+}) lead to the formation of excess positive charge on the LDH layer, therefore, promote the intercalation of QC into the interlayer gallery of Zn/Al-LDH via electrostatic interaction. The Zn/Al-LDH-QC nanocomposite obtained exhibit symmetrical, sharp and intense reflection, thus signifies the formation of well-ordered layered structures. Based on the PXRD patterns, it can be observed that the Zn/Al-LDH-QC nanocomposite synthesised using 0.1 M QC possess higher intensity and better crystallinity, than the other Zn/Al-LDH-QC nanocomposite that were synthesised using 0.05 M and 0.2 M of QC. Therefore, this nanocomposite was selected to be used for further characterisation.

Spatial orientation of QC in the Zn/Al-LDH interlayer

The PXRD patterns show that the basal spacing of the Zn/Al-LDH-QC nanocomposite is 16.7 Å. By referring to the value of basal spacing of the Zn/Al-LDH-QC nanocomposite and the thickness of Zn/Al-LDH (4.8 Å) [22], the gallery height of the Zn/Al-LDH after the intercalation of the QC is calculated as 11.9 Å. Consequently, the spatial orientation of QC in the Zn/Al-LDH interlayer can be predicted using Chem 3D Ultra 8.0 software (Figure 3). The intercalated QC was believed to exhibit a monolayer arrangement in the interlayer gallery of Zn/Al-LDH, and were held by the electrostatic interaction. The x, y and z axes of QC were calculated and determined to be 11.8, 9.2 and 4.1 Å, respectively. The three-dimensional molecular size of the QC was determined using Chem 3D Ultra 8.0 software, and was shown in Figure 4.

FTIR analysis

The FTIR analysis was also performed on the Zn/Al-LDH, QC and Zn/Al-LDH-QC nanocomposite, so as to observe the changes of their functional group after the occurrence of the intercalation. The FTIR analysis was conducted in the region between 400–4000 cm^{-1}, as shown in Figure 5. In the FTIR spectra of Zn/Al-LDH (Figure 5(a)), a broad absorption peak was observed at 3450 cm^{-1}, which represent the O–H group which are found in both interlayer water and hydroxide basal layer [21,23]. A strong and sharp peak was observed at 1385 cm^{-1}, signify the symmetric stretching of the NO_3^-, whereas another two weak peaks were emerging at 604 and 432 cm^{-1}, represent the bending vibration of Al–OH and Zn–Al–OH, respectively [24].

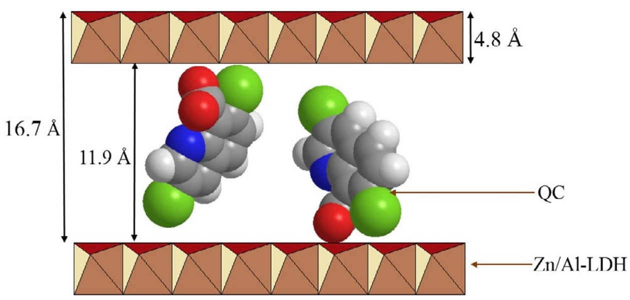

Figure 3. Spatial Orientation of QC in the interlayer gallery of Zn/Al-LDH.

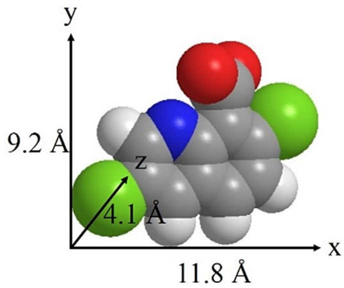

Figure 4. Three-dimensional molecular structure of the QC.

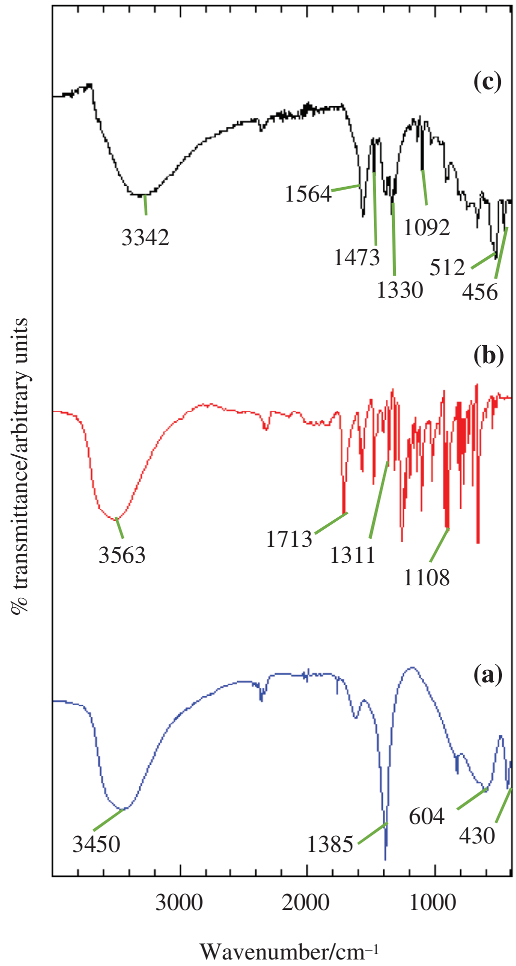

Figure 5. FTIR spectra of (a) Zn/Al-LDH, (b) QC and (c) Zn/Al-LDH-Q nanocomposite.

It can be seen that in the FTIR spectra of QC (Figure 5(c)), there are several peaks that were appearing in both FTIR spectra of Zn/Al-LDH and Zn/Al-LDH-QC nanocomposite, while certain peaks disappeared after the intercalation. The bending vibration of Al–OH and Zn–Al–OH were also present in the FTIR spectra of Zn/Al-LDH-QC nanocomposite at 512 and 456 cm^{-1}, respectively. A weak peak that represents C–N stretching mode in aromatic compound was observed in the FTIR spectra of QC and Zn/Al-LDH-QC nanocomposite at 1311 and 1330 cm^{-1}, respectively. A notable peak that was representing the co-intercalated nitrate in the Zn/Al-LDH at 1385 cm^{-1} was disappeared after the intercalation, hence indicate that the NO_3^- has been replaced with the QC anion. A sharp peak was also present in the FTIR spectra of QC

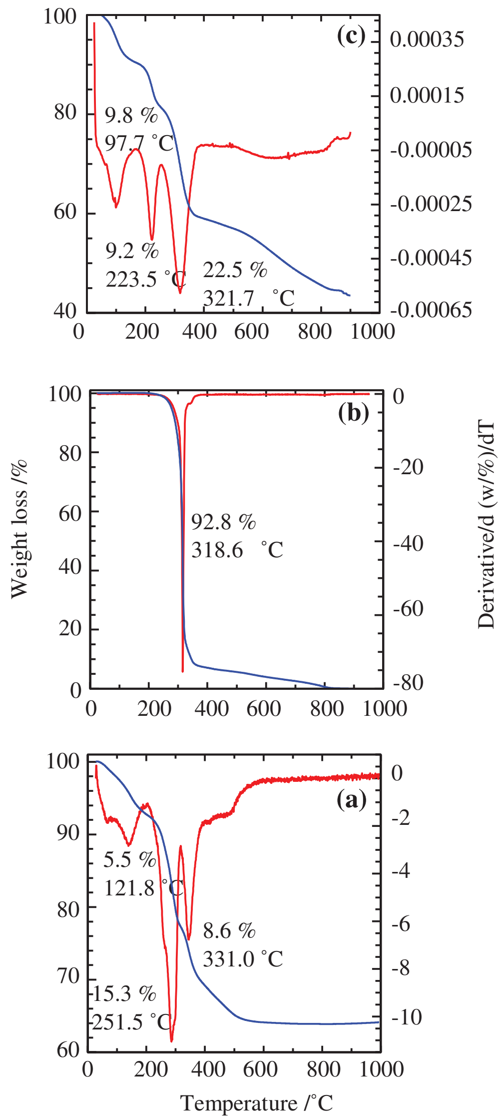

Figure 6. TGA/DTG curves of (a) Zn/Al-LDH, (b) QC and (c) Zn/Al-LDH-Q nanocomposite.

around 1108 cm^{-1} and the FTIR spectra of Zn/Al-LDH-QC nanocomposite around 1092 cm^{-1}, due to stretching of C–O. The asymmetric stretching peak of carboxylic group in QC at 1713 cm^{-1} seems to disappear, and were replaced with peaks at 1564 and 1414 cm^{-1} which represent the stretching mode of the carboxylate anion found in the QC [25]. These peaks, therefore, show that the species that were intercalated into the interlayer gallery of Zn/Al-LDH are in the anionic form of QC.

The result obtained from the FTIR analysis reveals that the characteristic peaks of pristine QC are also found in the FTIR spectra of Zn/Al-LDH-QC nanocomposite, hence confirm the presence of QC in the interlayer gallery of Zn/Al-LDH. The positions of certain peaks were, however, to some extent shifted owing to the interaction between the QC anion and Zn/Al-LDH resulting from the intercalation [26].

Thermal studies

The thermal decomposition behaviour of Zn/Al-LDH, QC and Zn/Al-LDH-QC nanocomposite were performed and the result obtained from the studies was provided in Figure 6. The thermal analysis on Zn/Al-LDH reveals that this host material decompose in three stages (Figure 6(a)). The first decomposition, which occurred at 121.8 °C with 5.5 % of weight loss is referring to the elimination of water that was physisorbed on the outer surface of Zn/Al-LDH. The second decomposition, at 251.5 °C with 15.3% of weight loss was resulting from the removal of interlayer water. Whereas the third stage of the Zn/Al-LDH decomposition, taken place at 331.0 °C with 8.6% of weight loss was due to the dihydroxylation of Zn/Al-LDH [27].

Figure 6(b) show thermal analysis of pure QC, it can be seen that a sharp weight loss of 92.8% with maximum decomposition temperature was occurring at 318.6 °C (Figure 6(b)). The major weight loss indicates that the pure QC was almost completely decomposed during this stage. The Zn/Al-LDH-QC nanocomposite synthesised seems to demonstrate better thermal stabilities compare to the pure QC. Three thermal events of weight loss can be observed from the TGA/DTG curve of Zn/Al-LDH-QC nanocomposite, which happened at 97.7, 223.5 and 321.7 °C with 9.8, 9.2, and 22.5 % of weight loss, respectively. Similar to the Zn/Al-LDH host material, the first two weight loss were occurred due to the removal of water molecule from the external surface of Zn/Al-LDH and their interlayer gallery [28]. Whereas for the third weight loss, the maximum decomposition was correspond to the combustion of the organic moiety in the interlayer gallery of Zn/Al-LDH. The maximum decomposition temperature of Zn/Al-LDH-QC at 321.7 °C is higher than pure QC at 318.6 °C, thus signifies better thermal stability possess by the Zn/Al-LDH-QC nanocomposite.

Elemental analysis

The elemental analysis of Zn/Al-LDH, QC and Zn/Al-LDH-QC nanocomposite obtained from ICP-OES and CHNS analyser were summarised in Table 1. Referring to the table, it was shown that the final molar of Zn/Al in the Zn/Al-LDH is 2.9, even though their initial molar ratio in the mother liquor is 3.0. The reduction of the Zn/Al molar ratio indicates the incomplete precipitation of Al^{3+} during the formation of positively charged layer in the Zn/Al-LDH [29]. Using the carbon percentage of Zn/Al-LDH-QC determined by the CHNS analyser (16.88%), the percentage loading of the QC in the interlayer Zn/Al-LDH is calculated to be 33.87%. Therefore, these results confirm the success intercalation of QC in the interlayer gallery of Zn/Al-LDH host. Based on the elemental analysis and thermogravimetric studies, the chemical formula of Zn/Al-LDH-QC synthesised can be proposed as $[Zn_{0.75}Al_{0.25}(OH)_2]\ [C_9H_4Cl_2NCOO]^-_{0.25}\ 0.90H_2O$.

Surface morphology analysis

The scanning electron micrograph for Zn/Al-LDH and Zn/Al-LDH-QC nanocomposites were illustrated in Figure 7(a) and (b), respectively. The morphology of Zn/Al-LDH shows a typical non-uniform, irregular and non-porous plate-like structures, whereas the morphology of Zn/Al-LDH-QC nanocomposite show a fine plate-like structure, with irregular and smaller particle size. The intercalation of QC into the interlayer gallery of Zn/Al-LDH, is therefore, change the surface morphology of the pristine Zn/Al-LDH.

Table 1. Elemental chemical composition of Zn/Al-LDH, QC and Zn/Al-LDH-Q nanocomposite.

Sample	Zn/Al molar ratio (R_f)	C (%)	H (%)	N (%)	Mole fraction X_{Zn}	Mole fraction X_{Al}	QC(%w/w)[a]	Formula[b]
Zn/Al-LDH	2.9	–	3.80	2.40	0.74	0.26	–	$[Zn_{0.74}Al_{0.26}(OH)_2]\,(NO_3^-)_{0.26}\cdot 0.22H_2O$
QC	–	48.76	1.85	5.17	–	–	–	$C_{10}H_5Cl_2NO_2$
Zn/Al-LDH-QC	3.0	16.88	2.53	2.24	0.75	0.25	33.87	$[Zn_{0.75}Al_{0.25}(OH)_2]\,[C_9H_4Cl_2NCOO]^-_{0.25}$ $0.90H_2O$

Notes: [a]Estimated from CHNS analysis.
[b]Estimated from ICP-OES, CHNS and TGA/DTG analysis.

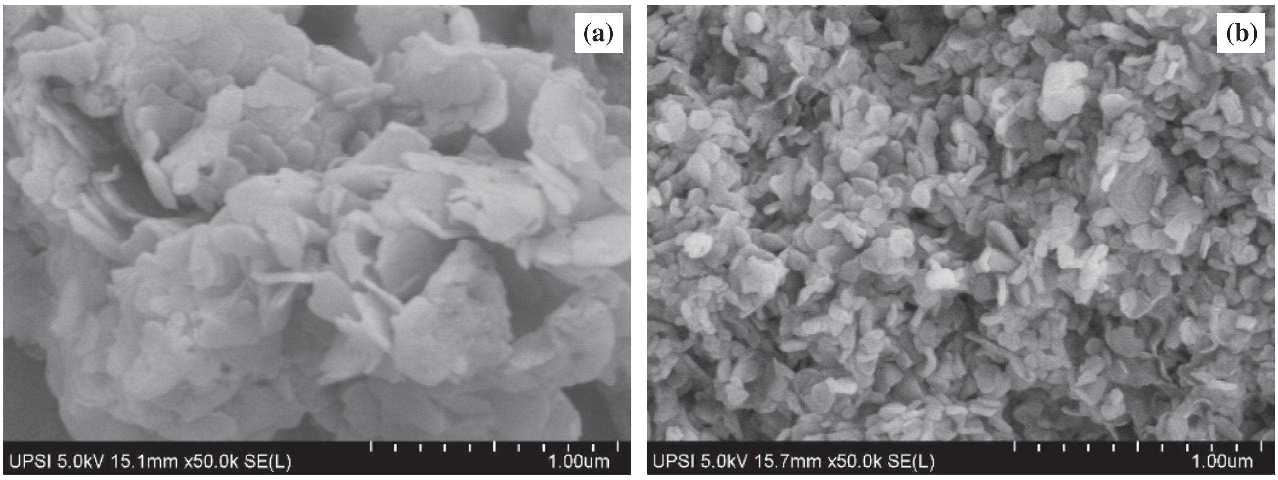

Figure 7. Surface morphology of (a) Zn/Al-LDH, (b) Zn/Al-LDH-QC nanocomposite.

Conclusion

The QC anion has been successfully intercalated into the interlayer gallery of Zn/Al-LDH using co-precipitation method. The basal spacing of Zn/Al-LDH before intercalation is 8.8 Å. The emergence of a new peak at a lower angle of 2θ with the basal spacing of 15.8–16.7 Å can be observed in the PXRD pattern of the Zn/Al-LDH-QC nanocomposite, thus indicate the success intercalation of QC into the interlayer gallery of Zn/Al-LDH. The characterisation studies that were performed on the Zn/Al-LDH-QC nanocomposite confirmed the occurrence of the intercalation, and the chemical formula of the nanocomposite can be proposed as $[Zn_{0.75}Al_{0.25}(OH)_2][C_9H_4Cl_2NCOO]^-_{0.25}$ $0.90H_2O$. Hence, it can be suggested that the Zn/Al-LDH has potential to be used as a host material for quinclorac herbicide in paddy cultivation sector.

Contributors

SNMS conceived and designed the study, collected and analysed the data, wrote the article in whole/part, revised the article. NH conceived and designed the study, obtained funded and ethics approval, wrote the article in whole/part, revised the article. IMI conceived and designed the study, obtained funded and ethics approval, wrote the article in whole/part, revised the article. NMA wrote the article in whole/part, revised the article. SAB wrote the article in whole/part, revised the article. MZH wrote the article in whole/part, revised the article. MM collected and analysed the data, wrote the article in whole/part and revised the article. BNA wrote the article in whole/part, revised the article. MWRW wrote the article in whole/part, revised the article.

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Disclosure statement

No potential conflict of interest was reported by the authors

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