Nano Hybrids *Online: 2014-08-18*
ISSN: 2234-9871, Vol. 7, pp 53-67
doi:10.4028/www.scientific.net/NH.7.53

Synthesis and Characterization of Layered-Double Hydroxide 3-(4-Hydroxyphenyl) Propionate Nanocomposite

Siti Nurasikin Ahmad[1,a], Norhayati Hashim[1,2,b*], Nur Hidayah Yusri[3,c], Illyas Md Isa[1,2,d], Azlan Kamari[1,2,e], Azmi Mohamed[1,2,f] and Muhammad Ibrahim Mohd Damanhuri[1,g]

[1]Department of Chemistry, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjong Malim, Malaysia.

[2]Nanothecnology Research Center, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjong Malim, Malaysia.

[3]Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Skudai, Johor Malaysia.

Email: [a]inickin@gmail.com, [b]hyatie@gmail.com (*corresponding author), [c]hidayah1606@gmail.com, [d]ilyas@fsmt.upsi.edu.my, [e]azlan.kamari@fsmt.upsi.edu.my, [f]azmi.mohamed@fsmt.upsi.edu.my, [g]muhdibrahim@fsmt.upsi.edu.my

Keywords: Nanocomposite; Layered Double Hydroxide; 3-(4-hydroxyphenyl)propionic acid; Intercalation

Abstract. A new layered-double hydroxide-3-(4-hydroxyphenyl)propionate (LDH-HPP) has been synthesized by intercalation of 3-(4-hydroxyphenyl)propionic acid (HPP) into Zn-Al-layered double hydroxide (LDH) by ion-exchange method. PXRD, FTIR, TGA/DTG, compositional studies and FESEM were used to characterize the synthesized nanocomposite. The intercalation of HPP into the interlayer gallery space of LDH was characterized by x-ray diffractogram showed expanded basal

spacing of the value of 17.1 Å. The FTIR spectra of LDH-HPP nanocomposite synthesis by 0.025M HPP resembled a mixture of both FTIR spectra of HPP and LDH. Thermal analysis of LDH-HPP nanocomposite shows a better thermal stability as compared to the pure HPP, which proved that the intercalation of HPP into LDH interlayer enhanced the thermal stability of the HPP.

Introduction

Layered nanomaterials are getting lots of attention due to their unique structural felexibility, which is useful for the development of new hybrid materials with controlled functionality [1]. The layered double hydroxide (LDH) is also known as hydrotalcite-like material or anionic clay, are the large group of natural or synthetic materials that are layered, containing the hydroxide of two or more different kinds of metal cations and possessing an overall positive charge, which neutralized by the incorporation of exchangeable anion [2]. The structure of LDH closely related to brucite-like layer, $Mg(OH)_2$, where Mg^{2+} is octahedrally surrounded by six OH^- and share edges to form infinite sheet [3]. Some of the divalent ions are replaced by trivalent ions, resulting in positively charge sheet and compensated by anions in the interlayer galleries along with the water molecules [4-6].

The general formula that represents this class of materials is $[M_{1-x}^{2+} M_x^{3+}(OH)_2]^{x+} (A^{m-})_{x/m}\, nH_2O$, where M^{2+} is divalent cation (Ca^{2+}, Mg^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}), M^{3+} (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 other inorganic anions) [1,7-8]. The *x* value is the charge density for the molar ratio $M^{3+}/(M^{2+}+M^{3+})$ [9]. The monovalent anions such as NO_3^- and Cl^- within the interlayer gallery space can be easily replaced by desired anions [10]. The structure of LDH forms two-dimensional crystals consisting of thin crystalline layered that stacked by van der Waals and/or weak electrostatic interaction; thus various guest anions can be inserted into the LDH interlayer galleries [7]. This material is two dimensional type layered structure consisting of thin crystalline layers with a thickness of a few nanometers [11].

LDHs have anionic exchange capacity and the ability to capture organic and inorganic anions make them almost unique as inorganic materials [12]. LDH has been used in diverse applications such as adsorbents [13], drug delivery [14], controlled release formulation [5], and sensors [15]. There are varied ways to intercalate anions into LDH interlayer gallery, such as co-precipitation method [16], hydrothermal method [14] and ion-exchange method [5].

3-(4-hydroxyphenyl)propionic acid (HPP) is an auxinic growth regulator, it can interfere with RNA production and change the properties and development in the plasma membrane. However, these herbicides can easily wash into the stream or infiltrate the soil eventually contaminating ground water reserves. In this study, 3-(4-hyroxyphenyl)propionic acid (HPP) has been intercalated between the interlayer of LDH by the ion - exchange method. The LDH-HPP nanocomposite was characterized by PXRD, FTIR, TGA/DTG, compositional studies and FESEM to confirm the intercalation. Encapsulation HPP into LDH interlayer would be enhanced thermal stability, release the anion at controlled manner, safer and environmental-friendly agrochemical.

Experimental

Synthesis of LDH-HPP Nanocomposite. The preparation of LDH-HPP was carried out using the ion-exchange method with various concentrations of anions. The solutions containing anions were added to an aqueous solution containing Zn/Al-LDH precursor [5; 17] and the mixture was stirred about two and half hour at room temperature. Then it was aged for 48h at 70 °C in an oil bath shaker. The centrifuged product LDH-HPP was washed with deionised water. Powder nanocomposite was dried in an oven at 60 °C overnight. The sample was kept in the bottle and stored in a vacuum desiccator for further use and characterization.

Characterisation. The powder X-ray Diffraction (PXRD) patterns were recorded by a Shimadzu XRD-6000 x-ray diffractometer using CuK_a at wavelength, $\lambda = 0.1540562$ nm with a scanning rate of 2 degrees min^{-1}. FTIR spectra analysed by using NICOLET model 6700 in the range of 400-4000

cm^{-1} using the KBr disc method. The percentage content of carbon, hydrogen, nitrogen and sulphur in the sample were analysed by CHNS model Thermofinnigan, Flash EA 1112 series and the chemical composition was analyzed by using inductively coupled plasma-optical emission (ICP-OES) model Agilent, 720 Axial. Thermal analyses were carried out by using a Perkin – Elmer TGA 700 thermal analyzer with heating rate of 10 °C min^{-1} between 25 °C to 1000°C under nitrogen flow rate of 50 mL min^{-1}. Surface morphology of the sample was studied by using field emission scanning electron microscope (FESEM) model HITACHI SU 8020 UHR.

Result and Discussion

Powder X-Ray Diffraction. Fig. 1. shows the PXRD pattern of LDH-HPP nanocomposite with various concentration of HPP anions. The main diffraction peak of LDH at 2θ value of 10º with basal spacing 8.9 Å indicates the basal spacing of LDH with NO_3^- anions in the interlayer [18]. The intercalation of HPP anions into LDH interlayer resulted in the diffraction pattern characteristic with a sharp diffraction peak at the low angle of 2θ and the basal interlayer distance increase by replacing the NO_3^- anions with HPP anions [3]. The diffraction peak of LDH-HPP nanocomposite obtained at the lower angle of 2θ with basal spacing of 17.7 Å confirmed the successful intercalation of HPP anions into the LDH interlayer. The LDH-HPP prepared by 0.025 M was chosen for further use and characterisation due to the sharp, symmetrical and intense peak.

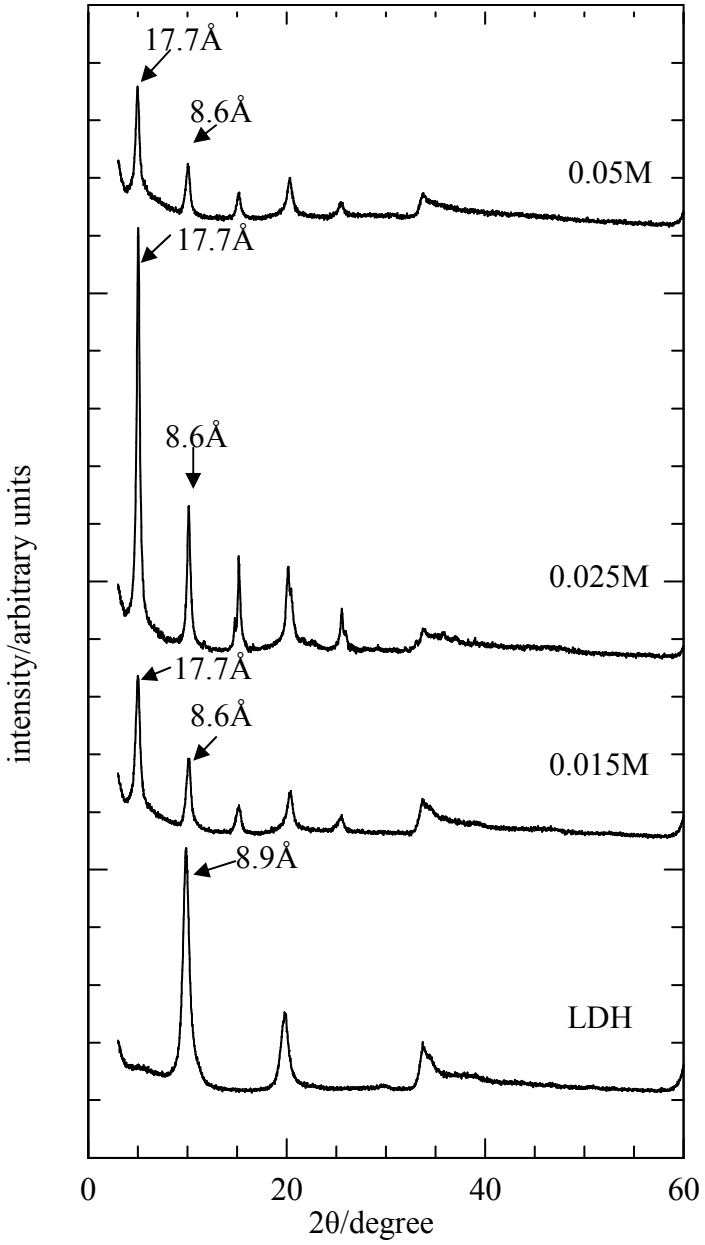

Fig. 1. PXRD patterns of LDH and LDH-HPP nanocomposite at various concentrations of HPP anion.

FT-IR Spectroscopy. FTIR spectra of LDH, HPP anion and LDH-HPP nanocomposite in the region between 400 and 4000 cm^{-1} are shown in the Fig. 2. The FTIR spectra of LDH showed a broad absorption peak centered at 3434 cm^{-1}, which is attributed to OH vibration in the LDH and water molecule while at 1639 cm^{-1} attributed to bending vibration of the interlayer water molecules [19]. The strong absorption peak observed at 1348 cm^{-1} assigned to the presence of NO_3^-. FTIR spectra of pure HPP showed a broad absorption peak at 3406 cm^{-1}, which is assigned to the O-H

stretching vibration of COOH. A sharp band at 1719 cm^{-1} due to the C=O stretching and the stretching vibration for aromatic ring C=C appeared at 1514 cm^{-1}. The band observed at 1302 cm^{-1} is attributed to the C=O stretching of phenol group. The LDH-HPP nanocomposite shows all the characteristic peaks of HPP anion and LDH. The broad band centred at 3406 cm^{-1} attributed to OH stretching, and the absorption peak at 1461 is due to the stretching vibration of the aromatic ring, C=C. The disappearance of the strong peak at 1348 cm^{-1} indicated that NO_3^- have been displaced and presence of the new band around 1583 cm^{-1} is due to the C=O carboxylate ion confirmed the presence of HPP in the interlayer of LDH [20].

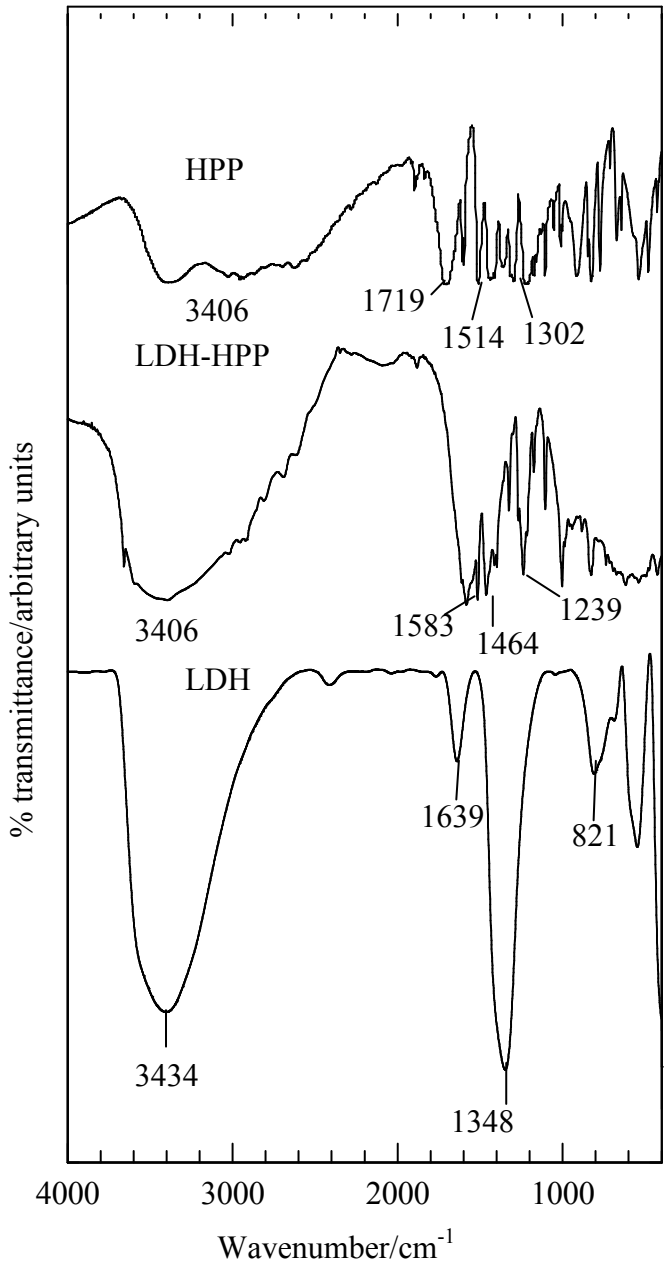

Fig. 2. FTIR spectra of LDH, LDH-HPP nanocomposite and HPP anions.

Spatial Orientation of HPP Anions in the LDH Interlayer. Fig. 3, shows proposed orientation of HPP in the LDH interlayer galleries space by using Chem3D Ultra 8.0. PXRD data show the basal spacing of the LDH-HPP nanocomposite is 17.7 Å. Subtracting 4.8Å of the thickness of LDH composed of the inorganic layer, the interlayer galleries space occupied by HPP anions in the LDH interlayer is 12.9 Å. The molecular size of HPP anions calculated is 11.7Å. Therefore, two HPP anions are needed and arranged in the vertically aligned in order to achieve 12.9 Å basal spacing.

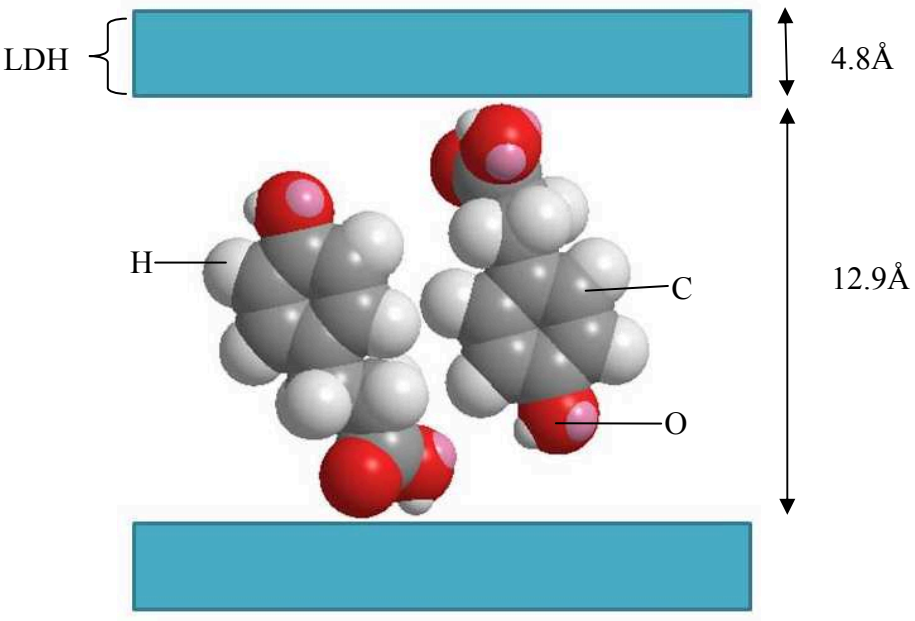

Fig. 3. Proposed spatial orientation of HPP in the LDH inorganic interlayers.

Elemental Analysis. The elemental analysis of LDH and ZLH-HPP nonocomposite are shown in Table 1. Elemental analysis shows the molar ratio of Zn to Al in LDH is 2.9 compared to 0.75 in the LDH-HPP nanocomposite. This indicated that the Zn to Al molar ratio in the resulting nanocomposite was adjusted according to the intercalation of HPP anion into the LDH interlayer. Based on the elemental data, the chemical formula for the LDH-HPP nanocomposite can be express by $[Zn_{0.43}Al_{0.57}(OH)_2](HOC_6H_4C_2H_4COO^-)_{0.57}.0.55H_2O$. The result of CHNS shows that zero percent of N in the LDH-HPP support the disappearance of the strong peak at 1348 cm^{-1} of LDH-HPP FTIR spectra due to the absence of NO_3^- in the nanocomposite. The high percentage of C in the LDH-HPP nanocomposite indicated that the HPP was successfully intercalated into the LDH interlayer. The estimated percentage of HPP prepared by 0.025 M HPP intercalated into the interlayer ZLH estimating from C percentage is 19.6%.

Table 1. Chemical compositions of LDH and its LDH-HPP nanocomposire, Estimate from CHNS and ICP/OES analysis.

Sampel	%N	%C	%H	Mole fraction		[a]Anion [% w/w]	Zn/Al molar ratio	Formula
				(X_{Zn})	(X_{Al})			
LDH	3.8	0	2.4	0.74	0.26	-	2.9	$[Zn_{0.74}Al_{0.26}(OH)_2](NO_3^-)_{0.26}.\ 0.41H_2O$
LDH-HPP	0	12.8	0	0.43	0.57	19.6	0.75	$[Zn_{0.43}Al_{0.57}(OH)_2](HOC_6H_4C_2H_4COO^-)_{0.57}.\ 0.55H_2O$

Thermal analysis. The TGA/DTG thermograms of LDH, HPP and LDH-HPP nanocomposite was shown in Fig. 4. The TGA/DTG curve of pure HPP anions shows that the HPP anions decompose in one stage at 263 ºC, while for the LDH show two stages of decomposition at 95 ºC and 264 ºC with weight loses 5.1 % and 21.5%. Significant changes of thermal behaviour have been observed of the HPP anions when intercalated into LDH interlayer. The thermal analysis of LDH-HPP nanocomposite show that the decomposition occurs in three stages at 73 ºC, 198 ºC and 452 ºC with 8.1%, 11.5% and 37.9% of weight loss. The first stage is due to the loss of water at the external surface. The second weight losses at 198 ºC correspond to the dehydroxylation of LDH sheet, and the last stage is decomposition of intercalated anions and NO_3^-. The thermal behaviour of HPP shows an improvement in LDH-HPP nanocomposite, indicate that the LDH-HPP nanocomposite has better thermal stability than in the pure phase.

Table 2. TGA-DTA data of LDH-HPP nanocomposite and HPP anion.

	Weight loss [%]			Total weight loss [%]
	(35-170°C)	(171-300 °C)	(301-700 °C)	
LDH-HPP	8.1 (T_{max}=73 °C)	11.5 (T_{max}=198 °C)	37.9 (T_{max}=452 °C)	57.5
HPP	-	98.1 (T_{max}=263 °C)	-	98.1
LDH	5.1(T_{max}=95 ºC)	21.5(T_{max}=264 ºC)	-	26.6

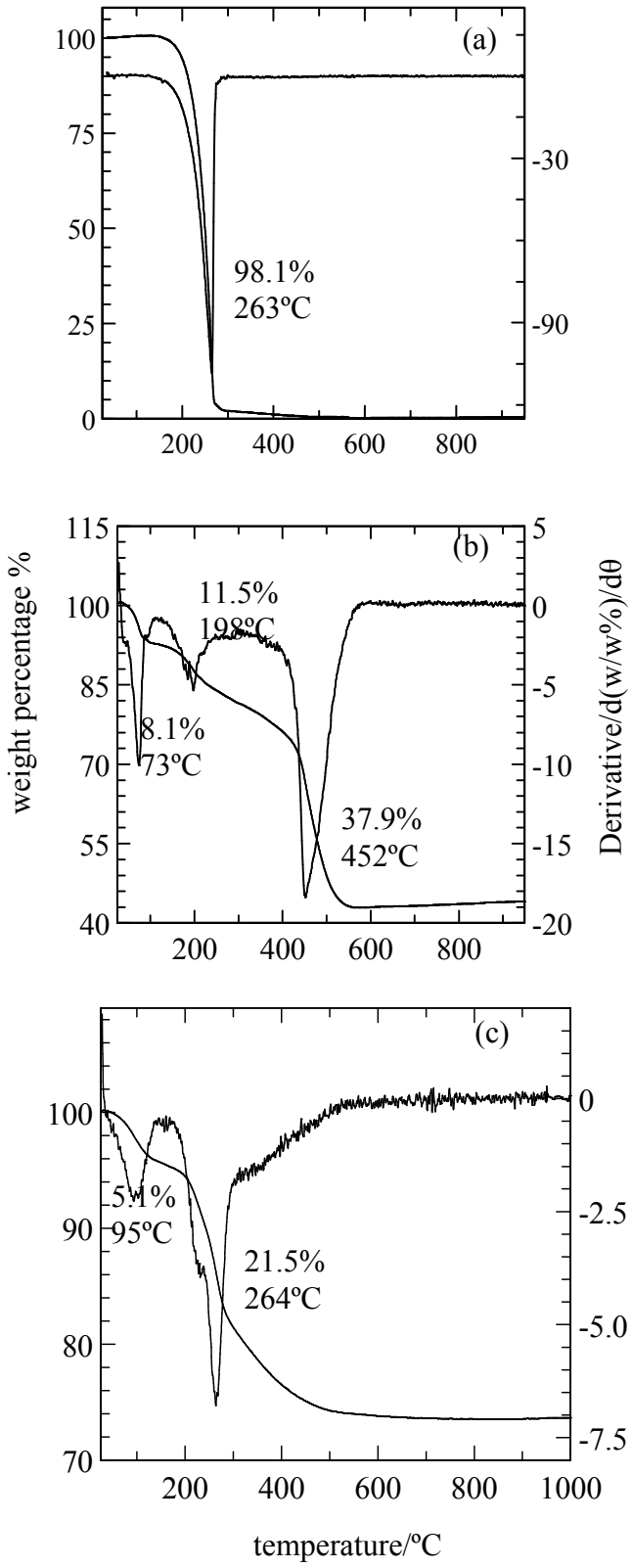

Fig. 4. TGA/DTG spectra of (a) HPP and (b) LDH-HPP nanocomposite (c) LDH.

Surface Morphology. The Fig. 5. shows the FESEM micrograph illustrate the morphologies of LDH-HPP nanocomposite and LDH. Both LDH-HPP nanocomposite and LDH show typical

agglomerated flake-like morphology that has a similar morphology such as in the previous research [21-22,6]. This shows that HPP anion was successfully intercalated into the LDH interlayer.

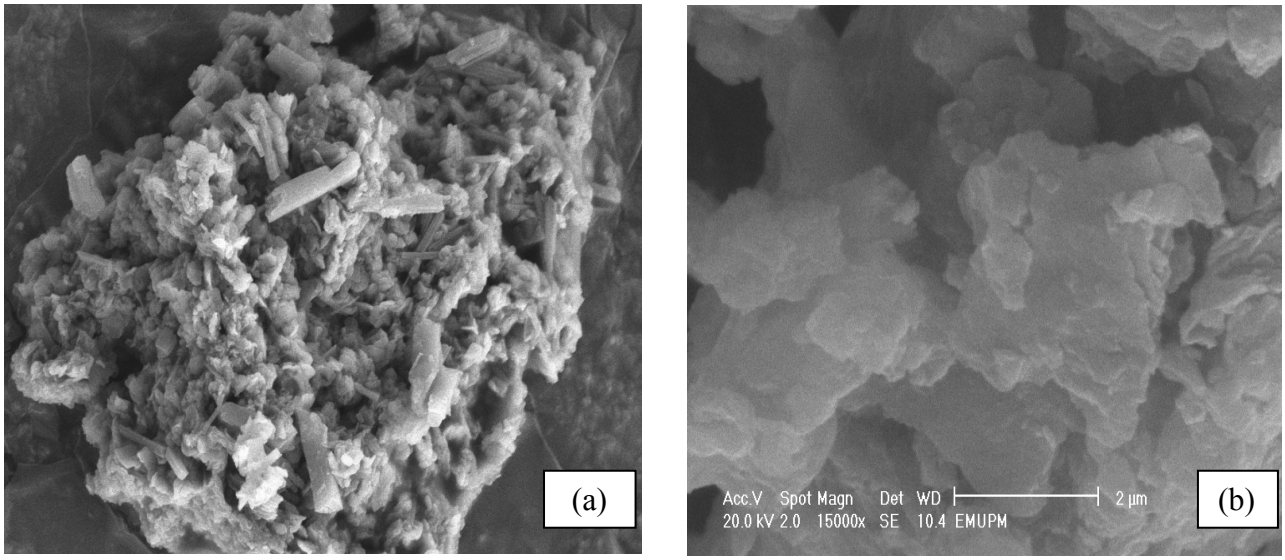

Fig. 5. Field emission scanning electron microscopy image of (a) LDH-HPP nanocomposite and (b) LDH under magnification 10.0k.

Conclusion

A new nanocomposite compound in which is HPP was successfully intercalated into LDH interlayer by ion-exchange method. The intercalation was confirmed by PXRD, FTIR, TGA/DTG, compositional studies and FESEM. Intercalation of HPP into the LDH interlayer shifted the diffraction peak in the lower 2θ with the expansion of basal spacing of 17.7Å. The FTIR spectra of the nanocomposite showed the resemblance of HPP and LDH absorption characteristic with the disappearance of the strong peak at 1348 cm^{-1} indicated that NO_3^- have been displaced and presence of the new band around 1583 cm^{-1} and is due to the C=O carboxylate ion and again indicates the successful intercalation. The estimated percentage of HPP prepared by 0.025 M HPP intercalated into the interlayer LDH estimating from C percentage is 19.6%. Thermal analysis showed that the thermal stability of HPP was enhanced when intercalated into the LDH interlayer with maximum

temperature 452 ºC instead of 263 ºC in pure phase. LDH was found to have plenty of benefits could be proposed for controlled release formulation of herbicides in agriculture due to their unique properties in ion-exchange, easy preparation and low toxicity.

Acknowledgement

The support of the research by KPM under RACE Grant no. 2012-0151-101-62. SA thanks UPSI for all affords and support in this research.

References

[1] J. M. Oh, T. T. Biswick, J. H. Choy, Layered material for green materials, J. Mater. Chem. 19 (2009) 2553-2563.

[2] P.S. Braterman, Z.P. Xu, F. Yarberry, Layered Double Hydroxide, in: S. M.Aubach, K. A. Carrado, and P.K Dutta (Eds.), Handbook of layered materials, Marcel Dakker., New York, 2004, pp. 373-450.

[3] F. Cavani, F. Trifiro, A. Vaccari, Hydrotalcite-type anionic clays: preparation, properties and applications, Catal. Today 11 (1991) 173-301.

[4] J. Tronto, K.C. Sanchez, E.L. Crepaldi, Z. Naal, I.K. Stanlei, J.B. Valim, Synthesis, characterization and electrochemical stidy of layered double hydroxide intercalated with 2-thiophenecarboxylate anions, J. Phys. Chem. Solid 65 (2004) 493-498.

[5] M. Silion, D. Hritcu, G. Lisa, M. I. Popa, New hybrid materials based in layered double hydroxides and antioxidant compounds. Preparation, characterization and release kinetic studies, J. Porous Mater.19 (2012) 267-276.

[6] S.H. Sarijo, S.A.I.S.M. Ghazali, M.Z. Hussien, N.J. Sidek, Synthesis of nanocomposite 2-methyl-4-chlorophenoxyacetic acid with layered double hydroxide: physiochemical characterization and controlled release properties, J. Nanopart. Res. 15 (2013) 1356-1365.

[7] S.H. Hwang, Y.S. Han, J.H. Choy, Intercalation of functional organic molecule with pharmaceutical, cosmeceutical and nutraceutical functions into layered double hydroxide and zinc basic salts, Bull. Korean Chem. Soc. 22 (2001) 1019-1022.

[8] J.W. Lee, W.C. Choi, J.D. Kim, Size-controlled layered hydroxide intercalated with dodecyl sulphate: effect of alcohol type on dedocyl sulphate template, CrystEngComm. 12 (2010) 3249-3254.

[9] M.Z. Hussien, A.M. Jaafar, A. Yahaya, Z. Zainal, The effect of single, binary and ternary anion chloride, carbonate and phosphate on the release of 2,4-dichlorophenoxyacetate intercalated into the Zn-Al layered double hydroxide nanohybrid, Nanoscale Res. Lett. 4 (2009) 1351-1357.

[10] W.G. Hou, Z.L. Jin, Synthesis and characterization of Naproxen intercalated Zn-Al layered double hydroxides, Colloid. Polym. Sci. 285 (2007) 1449-1454.

[11] S. Sasaki, S. Aisawa, H. Hirahara, A. Sasaki, H. Nakayama, E. Narita, Synthesis of p-sulfonated calyx[4]arene-intercalated layered double hydroxide and their adsorption properties for organic molecules, J. Eur. Ceram. Soc. 26 (2006) 655-659.

[12] F. Li, X. Duan, Applications of layered double hydroxide, Struct. Bond. 119 (2006) 193-223.

[13] F. Bruna, R. Celis, I. Pavlovic, C. Barriga, C. Cornejo, M.A. Ulibarri, Layered double hydroxide as adsorbent and carries of the herbicides (4-chloro-2-methylphenoxy)acetic acid (MCPA) system Mg-Al, Mg-Fe and Mg-Al-Fe, J. Hazard. Mater. 168 (2009) 1476-1481.

[14] X. Kong, S. Shi, J. Han, F. Zhu, M. Wei, X. Duan, Preparation of Glycy-L- Tyrosine intercalated layered double hydroxide film and its in vitro release behaviour, Chem. Eng. J. 157 (2010) 598-604.

[15] I.M. Isa, N. M. Sohaimi, Hashim, N.A. Kamari, A. Mohamed, M. Ahmad, S.A. Ghani, Suyanta, Determination of salicylate ion by potentiometric membrane electrode base on zinc aluminium layered hydroxide-4(2,4-dichlorophenoxy)butrate nanocomposite, Int. J. Electrochem. Sci. 8 (2013) 2112-2121.

[16] M. Yadollahi, H. Namazi, Synthesis and characterization of carboxymethyl cellulose/ layered double hydroxide nanocomposite, J. Nanopart. Res. 15 (2013) 1563-1572.

[17] M.Z. Hussein, N. Hashim, A.H. Yahaya, Z. Zainal, Synthesis of an herbicides-inorganic nanohybrid compound by ion exchange-intercalation of 3(2-chlorophenoxy)propionate into layered double hydroxide, J. Exp. Nanosci. 5 (2010) 548-558.

[18] N. Hashim, M.Z. Hussein, I.M. Isa, A. Kamari, A. Mohamed, M. S. Rosmi, A. M. Jaafar, Layered double hydroxide as a potential matrix for controlled release formulation of phenoxyherbicides, Jurnal Sains dan Matermatik 4 (2012) 22-36.

[19] M.Z. Hussein, N. Hashim, A. Yahaya, Z. Zainal, Synthesis of Dichloroprop-Zn/Al-hydritalcite nanohybrid and its controlled release property, Sains Malaysiana, 40 (2011) 887-896.

[20] M.Z. Hussein, N.S.A. Rahman, S.H. Sarijo, Z. Zainal, Synthesis of a monophasic nanohybrid for a controlled release formulation of two active agents simultaneously, Appl. Clay Sci. 58 (2012) 60-66.

[21] M.Z. Hussein, C.W. Long, Synthesis of organo-mineral nanohybrid material: indole-2-carboxylate in the lamella of Zn-Al- layered double hydroxide, Mater. Chem. Phys. 85 (2004) 427-431.

[22] M.Z. Hussein, A.H. Yahaya, Z. Zainal, L.H. Kian, Nanocomposite-based controlled release formulation of an herbicide, 2,4-dichlorophenoxyacetate incapsulated in zinc-aluminium-layered double hydroxide, Sci. Technol. Adv. Mat. 6 (2005) 956-962.