



UNIVERSITI PUTRA MALAYSIA

**SYNTHESIS OF ZINC-ALUMINIUM-HIPPURATE
NANOCOMPOSITE BY VARIOUS METHODS.**

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**SYNTHESIS OF ZINC-ALUMINIUM-HIPPURATE NANOCOMPOSITE BY
VARIOUS METHODS.**

By

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SYNTHESIS OF ZINC-ALUMINIUM-HIPPURATE NANOCOMPOSITE BY VARIOUS METHODS.

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Faculty : Institute of Advanced Technology

Zinc-aluminium-layered double hydroxide (ZAL) with nitrate as counter anion was prepared by direct co-precipitation method at constant pH, 7.5 under N₂ (g) atmosphere. The anion of hippuric acid (HA), as an organic guest was chosen to be intercalated into the interlayers of Zn-Al-layered double hydroxide (ZAL) inorganic host by direct co-precipitation method for the formation of Zn-Al-hippurate nanocomposite (ZAH), a host-guest type of material.

Various parameters, such as Zn to Al initial molar ratios, R_i which are 2, 3, 4, 5 and concentrations of hippurate anion in a range of 0.06 to 0.15 M, have been studied for



the formation of Zn-Al-hippurate nanocomposite synthesised by direct co-precipitation method (ZAHDM). X-ray diffraction pattern shows expansion of the precursor basal spacing compared to ZAL in order to accommodate the hippurate anion, which is larger in size than the nitrate. ZAHDMs synthesised at 0.15 M HA for all the ratios were chosen for further characterizations because sharper, symmetrical and more intense peaks were observed for these samples compared with samples prepared with other concentrations. In this study, ZAHs was also prepared by indirect anion exchange method (ZAHXMs) and reconstruction method (ZAHHRMs).

The nanocomposites prepared by these different methods show that the highest basal spacing values were observed for the nanocomposite synthesis by direct co-precipitation method (ZAHDMs) and the lowest were obtained by using anion exchange method (ZAHXMs). This shows that different crystalline structure was observed for the different method of synthesis of the nanocomposites. The final ratio, R_f value for ZAHDM and ZAHHRM nanocomposites were near to its initial molar ratio, R_i but for ZAHXMs (synthesis by anion exchange method), the R_f obtained are only in the range of 0.90 – 1.72 compared to their R_i of 2 – 5. The BET specific surface area values obtained for ZAHXM also show the lowest value compared to ZAHDM and ZAHHRM nanocomposites. These show that the method of synthesis also plays the role in determining the resulting properties of the nanocomposites.

For ZAHDMs and ZAHXMs nanocomposites, the accumulated release profile of HA from the interlayer of the nanocomposite in a sodium aqueous solution were studied and values of the percentage release were obtained by separately put each of the



nanocomposite into the sodium carbonate aqueous solutions at various concentrations of 0.0025, 0.005 and 0.01 M. The release rate of HA was found to be faster for nanocomposite prepared by indirect anion exchange method, compared to the one synthesised by direct co-precipitation method. The data of the HA released from the nanocomposites into various aqueous carbonate solutions were then fitted into various models of release kinetics. In which, the release of the intercalated guest for both ZAHDM and ZAHXM were found to be governed by pseudo-second order kinetic.



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**SINTESIS ZINK-ALUMINIUM HIPPURAT NANOKOMPOSIT DENGAN
PELBAGAI KAEDAH.**

BY

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Hidroksida berlapis ganda Zink-Aluminium (ZAL) dengan nitrat sebagai anion lawan di dalam ruang hidroksida berlapis ganda disintesis melalui kaedah pemendakan bersama serentak pada pH 7.5 di dalam keadaan dialirkan gas nitrogen. Asid hippurik, iaitu satu bahan organik telah dipilih untuk disisipkan ke dalam ruang antara lapisan hidroksida berlapis ganda Zink-Aluminium (ZAL) melalui kaedah pemendakan serentak untuk membentuk nanokomposit Zn-Al-hippurat (ZAH).

Pelbagai parameter, seperti nisbah kandungan logam Zn/Al dalam bahan pemula iaitu 2, 3, 4 dan 5 dan kepekatan anion hippurat dari 0.06 – 0.15 M telah diuji dalam pembentukan nanokomposit Zn-Al-hippurat yang disintesis melalui kaedah



pemendakkan bersama serentak (ZAHDM). Corak pembelauan sinar-x menunjukkan berlakunya pengembangan jarak antara ruang bagi perumah bagi menempatkan anion hippurat, yang saiznya lebih besar berbanding anion nitrat. ZAHDM yang disintesis pada kepekatan HA 0.15 M bagi setiap nisbah yang telah dipilih bagi pencirian selanjutnya kerana ia menunjukkan puncak yang simetri dan tajam jika dibandingkan dengan sampel lain yang disintesis pada kepekatan berbeza. Di sini, nanokomposit juga disintesis melalui kaedah penukaran anion secara tak langsung dan kaedah pembinaan semula.

Nanokomposit yang disintesis melalui tiga kaedah yang berbeza menunjukkan jarak antara ruang bagi nanokomposit yang disintesis melalui kaedah pemendakan bersama serentak (ZAHDM) adalah yang tertinggi dan jarak antara ruang yang terendah diperolehi melalui kaedah penukaran anion secara tak langsung (ZAHXM). Ini menunjukkan perbezaan struktur hablur dapat diperhatikan pada semua kaedah yang berbeza dalam penyediaan nanokomposit. Nilai nisbah akhir, R_f bagi ZAHDM dan ZAHXM nanokomposit menghampiri nilai nisbah awal, R_i tetapi bagi ZAHXM yang disediakan melalui kaedah penukaran anion secara tak langsung, nilai R_f yang diperolehi cuma pada julat 0.90 – 1.72 berbanding nilai R_i iaitu 2 hingga 5. Nilai luas permukaan spesifik yang diperolehi oleh ZAHXM juga menunjukkan nilai terendah jika dibandingkan dengan ZAHDM dan ZAHXM nanokomposit. Ini menunjukkan bahawa kaedah yang berbeza juga memainkan peranan dalam penentuan ciri-ciri nanokomposit.

Bagi nanokomposit ZAHDM dan ZAHXM, profil pelepasan terkumpul HA^- dari ruang lapisan nanokomposit di dalam larutan akues natrium diselidiki dan nilai peratusan pelepasan HA^- diperolehi dengan memasukkan setiap nanokomposit secara berasingan ke dalam larutan akues natrium karbonat pada pelbagai kepekatan iaitu 0.0025, 0.005 dan 0.01 M. Kadar pelepasan HA^- didapati lebih cepat bagi nanokomposit yang disediakan melalui kaedah pertukaran anion secara tak langsung berbanding dengan kaedah pemendakkan serentak. Data dari profil pelepasan telah dipadankan kepada beberapa model pelepasan kinetik. Didapati bahawa, pelepasan anion HA yang tersisip pada ZAHDM and ZAHXM didapati mengikuti kinetik tertib kedua.



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I certify that an Examination Committee has met on 17 December 2009 to conduct the final examination of Faiza binti Abdul Bahar on her Master of Science thesis entitled “Layered Double Hydroxide as a Host for the Formation of a New Nanocomposite Material Prepared by Various Methods” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the student be awarded the relevant degree.

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

Faiza binti Abdul Bahar
Date: 17 December 2010



TABLE OF CONTENTS

	Page
ABSTRACT	i
ABSTRAK	iv
ACKNOWLEDGEMENTS	vii
APPROVAL	viii
DECLARATION	x
LIST OF TABLES	xiv
LIST OF FIGURES	xvii
LIST OF ABBREVIATIONS	xxiii
CHAPTER	
1 INTRODUCTION	1
2 LITERATURE REVIEW	6
2.1 Layered Double Hydroxide (LDH)	6
2.1.1 Historical background	7
2.1.2 Structural properties of layered double hydroxide	8
2.1.3 Syntheses of layered double hydroxide	10
2.1.4 Application of layered double hydroxide	10
2.2 Anion in the interstitial region	11
2.3 Guest anion : Hippuric acid (HA)	12
2.4 Nanocomposite	14
2.4.1 Syntheses of nanocomposite materials	15
2.4.2 Previous studies in nanocomposite	17
3 MATERIALS AND METHODS	21
3.1 Materials	21
3.2 Apparatus and instrumentation	22
3.3 Syntheses of layered double hydroxide	22
3.3.1 Preparation of Zn-Al-NO ₃ ⁻ - layered double hydroxid (ZAL)	23
3.4 Syntheses of Zn-Al-hippurate nanocomposite	23
3.4.1 Direct co-precipitation method	24
3.4.2 Anion exchange method	25
3.4.3 Reconstruction method	26
3.5 Controlled release study of the guest anion, HA into aqueous solution	26
3.6 Physico-chemical analyses and characterization	27
3.6.1 Powder X-ray diffraction (PXRD)	27
3.6.2 Fourier transform infrared spectroscopy (FTIR)	28
3.6.3 Elemental analysis	28
3.6.4 Carbon-Hydrogen-Nitrogen Analysis (CHN)	29



3.6.5	Thermogravimetric and differential thermal gravimetric analyses (TGA/DTG)	29
3.6.6	Surface area and porosimetry analyses (ASAP)	30
3.6.7	Scanning electron microscopy (SEM)	30
3.6.8	Ultra-violet / visible spectrosscopy (UV/VIS)	31
4	RESULTS AND DISCUSSION	32
4.1	Physico-chemical properties of Zn-Al- NO ₃ ⁻ - layered double hydroxide (ZAL)	32
4.1.1	Powder X-ray diffraction	32
4.1.2	Fourier transform infrared spectroscopy	33
4.1.3	Elemental analysis	35
4.1.4	Thermal analysis	39
4.1.5	Surface properties	45
4.1.6	Surface morphology	47
4.2	Physico-chemical properties of Zn-Al-hippurate nanocomposite by direct co-precipitation method (ZAHDM)	50
4.2.1	Powder X-ray diffraction	50
4.2.2	Fourier transform infrared spectroscopy	52
4.2.3	Elemental analysis	56
4.2.4	Thermal analysis	59
4.2.5	Surface properties	61
4.2.6	Surface morphology	72
4.3	Controlled release study of hipurate anion, (HA) from the interlayer of ZAHDM	73
4.3.1	Release kinetics of HA	76 79
4.4	Physico-chemical properties of Zn-Al-hippurate nanocomposite by anion exchange method (ZAHXM)	79
4.4.1	Powder X-ray diffraction	79
4.4.2	Fourier transform infrared spectroscopy	84
4.4.3	Elemental analysis	87
4.4.4	Thermal analysis	90
4.4.5	Surface properties	92
4.4.6	Surface morphology	102
4.5	Controlled release study of hipurate anion, (HA) from the interlayer of ZAHXM	102
4.5.1	Release kinetics of HA	106
4.6	Physico-chemical properties of Zn-Al-hippurate nanocomposite by reconstruction method (ZAHRM)	111



4.6.1	Calcination of the LDH	111
4.6.2	Formation of Zn-Al hippurate nanocomposite by reconstruction method (ZAHRM)	120
4.7	Comparison of chemical properties between nanocomposite synthesised through three different methods.	145
4.7.1	Comparison of nanocomposites prepared by direct co-precipitation and indirect anion exchange method	145
4.7.2	Comparison of ZAHDm4, ZAHXM4 and ZAHRM300 nanocomposites	152
		155
5	CONCLUSION	
	REFERENCES	158
	APPENDICES A	163
	APPENDICES B	165
	APPENDICES C	167
	APPENDICES D	168
	BIODATA OF STUDENT	171
	LIST OF PUBLICATION	172



LIST OF TABLES

Table		Page
1	Elemental composition of ZAL synthesised at various R and at pH 7.5.	38
2	Weight percentage of H and N in ZAL synthesised at various R and at pH 7.5.	38
3	Thermal properties of ZAL synthesised at various R and at pH 7.5	40
4	Surface properties of ZAL synthesised at $R_i = 2, 3, 4$ and 5	47
5	Elemental composition of ZAHDM synthesised at $R_i = 2, 3, 4, 5$ using 0.15 M hippuric acid at pH 7.5	57
6	Weight percentage of C, H, and N in ZAHDM synthesised at various R using 0.15 M hippuric acid at pH 7.5	59
7	Thermal properties of HA and ZAHDM nanocomposite synthesised by direct method at various R using 0.15 M hippuric acid at pH 7.5	61
8	Surface properties of ZAHDM synthesised at $R_i = 2, 3, 4$ and 5 with ZAL4 as comparison	70
9	Percentage release of HA^- from ZAHDM synthesised at various R into 0.0025, 0.005 and 0.01 M Na_2CO_3 aqueous solutions	75
10	Correlation coefficient (r^2), rate constant (k) and half life ($t_{1/2}$) obtained from the zeroth order by fitting the release data of HA^- from ZAHDMs synthesised at various R into 0.0025, 0.005 and 0.01 M Na_2CO_3 aqueous solutions	80
11	Correlation coefficient (r^2), rate constant (k) and half life ($t_{1/2}$) obtained from the first order by fitting the release data of HA^- from ZAHDM synthesised at various R into 0.0025, 0.005 and 0.01 M Na_2CO_3 aqueous solutions	81
12	Correlation coefficient (r^2), rate constant (k) and half life ($t_{1/2}$) obtained from the pseudo-second order by fitting the release data of HA^- from ZAHDM synthesised at various R into 0.0025, 0.005 and 0.01 M Na_2CO_3 aqueous solutions	82
13	Correlation coefficient (r^2), rate constant (k) and half life ($t_{1/2}$) obtained from the parabolic diffusion equation by fitting the release data of HA^- from ZAHDM synthesised at various R into 0.0025, 0.005 and 0.01 M Na_2CO_3 aqueous solutions	83



14	Elemental composition of ZAHXMs synthesised at at various R using 0.15 M hippuric acid at pH 7.5	89
15	Weight percentage of C, H and N in ZAHXMs synthesised at $R_i = 2, 3, 4, 5$ using 0.15 M hippuric acid at pH 7.5	90
16	Thermal properties of ZAHXM nanocomposites synthesised at various R using 0.15 M hippuric acid at pH 7.5	97
17	Surface properties of ZAHXM synthesised at various R with ZAL4 as comparison	100
18	Percentage release of HA^- ZAHXM synthesised at various R into 0.0025, 0.005 and 0.01 M Na_2CO_3 aqueous solutions	104
19	Correlation coefficient (r^2), rate constant (k) and half life ($t_{1/2}$) obtained from the zeroth order fitting of the release data of HA from ZAHXMs synthesised at various R into 0.0025, 0.005 and 0.01 M Na_2CO_3 aqueous solutions	107
20	Correlation coefficient (r^2), rate constant (k) and half life ($t_{1/2}$) obtained from the first order fitting of the release data of HA^- from ZAHXMs synthesised at various R into 0.0025, 0.005 and 0.01 M Na_2CO_3 aqueous solutions	108
21	Correlation coefficient (r^2), rate constant (k) and half life ($t_{1/2}$) obtained from the pseudo-second order fitting of the release data of HA^- from ZAHXMs synthesised at various R into 0.0025, 0.005 and 0.01 M Na_2CO_3 aqueous solutions	109
22	Correlation coefficient (r^2), rate constant (k) and half life ($t_{1/2}$) obtained from the parabolic diffusion equation fitting of the release data of HA^- from ZAHXMs synthesised at various R into 0.0025, 0.005 and 0.01 M Na_2CO_3 aqueous solutions	110
23	Surface properties of ZAL4 and its calcined products obtained by heating ZAL4 at different temperatures: 100, 200, 300, 400, 500, 600, 700 and 800 °C	120
24	Elemental composition of ZAHRM100 – ZAHRM 800 synthesised by reconstruction method at Zn to Al molar ratio 4 at pH 7.5	128
25	Weight percentage of C, H and N in ZAHRM100 – ZAHRM800 synthesised by reconstruction method at Zn to Al molar ratios 4 and at pH 7.5	128
26	Thermal properties of ZAHRM100- ZAHRM800 synthesised by reconstruction method using calcined oxides obtained at different temperature: 100, 200, 300, 400, 500, 600, 700 and 800 °C	130



27	Surface properties of ZAHRM100- ZAHRM800 synthesised by reconstruction method using calcined products obtained by calcination at different temperatures, 100, 200, 300, 400, 500, 600, 700 and 800 °C	141
28	Comparison of nanocomposites properties synthesised by direct co-precipitation, indirect anion exchange and reconstruction methods.	154



LIST OF FIGURES

Figure		Page
1	Schematic representation of LDH structure	8
2	The molecular structure of hippuric acid	12
3	PXRD patterns of ZAL synthesised at various $R_i = 2, 3, 4, 5$ at pH 7.5	34
4	FTIR spectrum of ZAL synthesised at various $R_i = 2, 3, 4, 5$ at pH 7.5	36
5	Plot of Al (x_{Al}) of ZAL against initial molar ratio, Zn/Al	37
6	TGA-DTG thermograms for ZAL2	41
7	TGA-DTG thermograms for ZAL3	42
8	TGA-DTG thermograms for ZAL4	43
9	TGA-DTG thermograms for ZAL5	44
10	Adsorption-desorption isotherms for ZAL synthesised at $R_i = 2, 3, 4$ and 5	46
11	Plot of BET surface area against initial molar ratio, Zn/Al of ZAL	47
12	BJH pore size distribution for ZAL synthesised at $R_i = 2, 3, 4$ and 5	48
13	Scanning electron micrographs for ZAL4 at magnifications of a) 1000 X, b) 5 000 X and c) 10000 X.	49
14	PXRD patterns of ZAHDM nanocomposites synthesised at various R and at 0.06 - 0.15 M HA.	51
15	PXRD patterns of ZAL and ZAHDM synthesised at various R using 0.15 M hippuric acid at pH 7.5	53
16	FTIR spectra of HA, ZAL4 and ZAHDM synthesised at various R using 0.15 M hippuric acid at pH 7.5 with ZAL4 for comparison	55



17	Plot of Al (x_{Al}) and percent loading (%) of ZAHDM nanocomposites against molar ratio, Zn/Al	58
18	TGA-DTG thermograms for pure HA	62
19	TGA-DTG thermograms for ZAHDM2	63
20	TGA-DTG thermograms for ZAHDM3	64
21	TGA-DTG thermograms for ZAHDM4	65
22	TGA-DTG thermograms for ZAHDM5	66
23	Plot of total weight loss (%) of ZAHDM nanocomposites against initial molar ratio, Zn/Al	67
24	Adsorption-desorption isotherms for ZAL4 and ZAHDMs synthesised at various R using 0.15 M hippuric acid at pH 7.5.	68
25	Plot of BET surface area against initial molar ratio, Zn/Al of ZAHDM nanocomposites	71
26	BJH pore size distribution for ZAL4 and ZAHDMs synthesised at various R using 0.15 M hippuric acid at pH 7.5.	73
27	Figure 27: Scanning electron micrographs for a) ZAHDM2, b) ZAHDM3, c) ZAHDM4 and d) ZAHDM5 at magnifications of 5 000 X	74
28	Release profiles of HA ⁻ into 0.0025, 0.005 and 0.01 M Na ₂ CO ₃ aqueous solutions from ZAHDM synthesised at various R using 0.015 M hippuric acid at pH 7.5.	77
29	PXRD patterns for the samples recovered from the aqueous solutions after the release of HA ⁻ from the interlayer of ZAHDM5 at various release times from 0 to 16 hours	80
30	Fitting of HA ⁻ release data to zeroth order kinetics for a) ZAHDM2, b) ZAHDM3, c) ZAHDM4 and d) ZAHDM5.	81
31	Fitting of HA ⁻ release data to first order kinetics for a) ZAHDM2, b) ZAHDM3, c) ZAHDM4 and d) ZAHDM5.	82
32	Fitting of HA ⁻ release data to pseudo-second order kinetics for a) ZAHDM2, b) ZAHDM3, c) ZAHDM4 and d) ZAHDM5	83
33	Fitting of HA ⁻ release data using parabolic diffusion equations for a)	85



	ZAHDM2, b) ZAHDM3, c) ZAHDM4 and d) ZAHDM5 using 0.15 M 7.5	
34	PXRD patterns of ZAL and ZAHXMs synthesised at various R using 0.15 M hippuric acid at pH 7.5	87
35	FTIR spectra of hippuric acid, ZAL and ZAHXMs synthesised at various R using 0.15 M hippuric acid at pH 7.5	90
36	Plot of Al (x_{Al}) and percent loading (%) of ZAHXM nanocomposites against initial molar ratio, Zn/Al	92
37	TGA-DTG thermograms for ZAHXM2	93
38	TGA-DTG thermograms for ZAHXM3	94
39	TGA-DTG thermograms for ZAHXM4	95
40	TGA-DTG thermograms for ZAHXM5	96
41	Plot of total weight loss (%) of ZAHXM nanocomposites against initial molar ratio, Zn/Al	97
42	Adsorption-desorption isotherms for ZAL4 and ZAHXMs synthesised at various R using 0.15 M hippuric acid at pH 7.5	99
43	Plot of BET surface area against molar ratio, Zn/Al of ZAHXM nanocomposites	100
44	BJH pore size distribution for ZAHXMs synthesised at various R using 0.15 M hippuric acid at pH 7.5 with ZAL4 for comparison	101
45	Scanning electron micrographs for a) ZAHXM2, b) ZAHXM3, c) ZAHXM4 and d) ZAHXM5 at magnifications of 5 000 X	102
46	Release profile of HA ⁻ into 0.0025, 0.005 and 0.01 M of Na ₂ CO ₃ aqueous solutions from ZAHXM synthesised at various R using 0.015 M hippuric acid at pH 7.5.	103
47	PXRD patterns for the samples recovered from the aqueous solutions after the release of HA ⁻ from the interlayer of ZAHXM5 at various release times, from 0 to 8 hours	105
48	Fitting of HA ⁻ release data to zeroth order kinetics for a) ZAHXM2, b) ZAHXM3, c) ZAHXM4 and d) ZAHXM5.	107
49	Fitting of HA ⁻ release data to first order kinetics for a) ZAHXM2, b)	108



	ZAHXM3, c) ZAHXM4 and d) ZAHXM5.	
50	Fitting of HA ⁻ release data to pseudo-second order kinetics for a) ZAHXM2, b) ZAHXM3, c) ZAHXM4 and d) ZAHXM5.	109
51	Fitting of HA ⁻ release data to parabolic diffusion equations for a) ZAHXM2, b) ZAHXM3, c) ZAHXM4 and d) ZAHXM5.	110
52	PXRD patterns of ZAL4 and its calcined products obtained by heating ZAL4 at different temperatures: 100, 200, 300, 400, 500, 600, 700 and 800 °C	113
53	FTIR spectra of ZAL4 and its calcined products obtained at different temperatures: 100, 200, 300, 400, 500, 600, 700 and 800 °C	115
54	Adsorption-desorption isotherms of ZAL4 and its calcined products obtained at different temperatures: 100, 200, 300, 400, 500, 600, 700 and 800 °C. (Inset: isotherm at 100, 200 and 300 °C)	117
55	BET surface area value versus the calcinations temperature at 100, 200, 300, 400, 500, 600, 700 and 800 °C.	118
56	BJH pore size distribution of ZAL4 and its calcined products obtained at different temperatures: 100, 200, 300, 400, 500, 600, 700 and 800 °C. (Inset: Pore size distribution of 100 - 300 °C)	119
57	PXRD patterns of ZAL4 and the reconstructed samples, ZAHRM prepared with calcined products obtained at different temperatures, 100, 200, 300, 400, 500, 600, 700 and 800 °C	123
58	PXRD intensity of reconstruct nanocomposite (ZAHRM 100 – ZAHRM 800) versus calcinations temperature at 100, 200, 300, 400, 500, 600, 700 and 800 °C	124
59	FTIR spectra of ZALR4 and the reconstructed samples, ZAHRM prepared with calcined products obtained at different temperatures, 100, 200, 300, 400, 500, 600, 700 and 800 °C	125
60	TGA-DTG thermograms of the reconstructed samples ZAHRM100 prepared from calcined product obtained at 100 °C	131
61	TGA-DTG thermograms of the reconstructed samples ZAHRM200 prepared from calcined product obtained at 200 °C	132
62	TGA-DTG thermograms of the reconstructed samples ZAHRM300 prepared from calcined product obtained at 300 °C	133



63	TGA-DTG thermograms of the reconstructed samples ZAHRM400 prepared from calcined product obtained at 400 °C	134
64	TGA-DTG thermograms of the reconstructed samples ZAHRM500 prepared from calcined product obtained at 500 °C	135
65	TGA-DTG thermograms of the reconstructed samples ZAHRM600 prepared from calcined product obtained at 600 °C	136
66	TGA-DTG thermograms of the reconstructed samples ZAHRM700 prepared from calcined product obtained at 700 °C	137
67	TGA-DTG thermograms of the reconstructed samples ZAHRM800 prepared from calcined product obtained at 800 °C	138
68	Adsorption-desorption isotherms of ZAL4 and ZAHRM100- ZAHRM800 synthesised by reconstruction method using calcined products obtained at different calcination temperatures, 100, 200, 300, 400, 500, 600, 700 and 800 °C (Inset: Isotherms of ZAL4 and ZAHRM100)	140
69	BET surface area value versus the calcinations temperature at 100, 200, 300, 400, 500, 600, 700 and 800 °C for the formation of reconstructed nanocomposites.	142
70	BJH pore size distribution of ZAL4 and ZAHRM100- ZAHRM800 synthesised by reconstruction method using calcined products obtained at different calcination temperatures, 100, 200, 300, 400, 500, 600, 700 and 800 °C (Inset: Pore size distribution of ZAL4, ZAHRM100, ZAHRM200 and ZAHRM600)	143
71	Scanning electron micrographs of: a) ZAHRM4 (synthesised by direct method), b) ZAHRM300, c) ZAHRM400, d) ZAHRM700 and e) ZAHRM800 at magnifications of 5000 X.	144
72	Basal spacing (003) against Zn/Al initial molar ratio of ZAHRM and ZAHRM nanocomposites synthesised at Zn to Al molar ratios 2 -5.	146
73	Final molar ratio (R_f) against Zn/Al initial molar ratio of ZAHRM and ZAHRM nanocomposites synthesised at Zn to Al molar ratios 2 -5.	147
74	Percent loading against Zn/Al initial molar ratio of ZAHRM and ZAHRM nanocomposites synthesised at Zn to Al molar ratios 2 -5	148
75	Total weight loss against Zn/Al initial molar ratio of ZAHRM and ZAHRM nanocomposites synthesised at Zn to Al molar ratios 2 -5	149

76	Plot of BET surface area against Zn/Al initial molar ratio of ZAHDM and ZAHXM nanocomposites synthesised at Zn to Al molar ratios 2 -5	150
77	Saturated percentage release at 0.0025 M of Na ₂ CO ₃ aqueous solution against Zn/Al initial molar ratio of ZAHDM and ZAHXM nanocomposites synthesised at Zn to Al molar ratios 2 -5	151
78	Saturated percentage release at 0.005 M of Na ₂ CO ₃ aqueous solution against Zn/Al initial molar ratio of ZAHDM and ZAHXM nanocomposites synthesised at Zn to Al molar ratios 2 -5.	152
79	Saturated percentage release at 0.01 M of Na ₂ CO ₃ aqueous solution against Zn/Al initial molar ratio of ZAHDM and ZAHXM nanocomposites synthesised at Zn to Al molar ratios 2 -5	153



LIST OF ABBREVIATIONS

ASAP	Analysis of surface area and porosity
BET	Brunauer, Emmett and Teller
BJH	Barett, Joyner and Halenda
C	constant
CHN	carbon-hydrogen-nitrogen
FTIR	Fourier transform infrared
HA	hippuric acid
HA ⁻	hippurate
k	rate constant
LDH	Layered double hydroxide
M ²⁺	Divalent metal cation
M ³⁺	Trivalent metal cation
M _f	final concentration of HA ⁻
M _i	initial concentration of HA ⁻
PXRD	Powder x-ray diffraction
R	Ratio
R _f	Final ratio
R _i	Initial ratio
SEM	Scanning electron microscopy
t _{1/2}	time taken for the HA concentration to increase to half of its initial values

