



**UNIVERSITI PUTRA MALAYSIA**

**SYNTHESIS OF LAYERED DOUBLE HYDROXIDE-  
NANOCOMPOSITES USING N-(2-HYDROXYETHYL)-  
ETHYLENEDIAMINE TRIACETATIC ACID AND ANTHRAQUINONE-2-  
SULPHONIC ACID AS GUEST ANIONS**

**MAZLINA BINTI MUSA.**

**ITMA 2005 1**



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**By**

**MAZLINA BINTI MUSA**

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in  
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**December 2005**



Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

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USING *N*-(2-HYDROXYETHYL)-ETHYLENEDIAMINE TRIACETATIC ACID  
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**December 2005**

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The synthesis of a new nanocomposite material consisting of inorganic layers, Mg/Al-NO<sub>3</sub><sup>-</sup> (MAL) and Co/Al-NO<sub>3</sub><sup>-</sup> (COAL) as hosts and *N*-(2-hydroxyethyl)-ethylenediamine triacetate (HEDTA), an guest anion was successfully done by using conventional method. The PXRD results showed that the intercalation of HEDTA anion into the Mg/Al-NO<sub>3</sub><sup>-</sup> and Co/Al-NO<sub>3</sub><sup>-</sup> with Mg/Al and Co/Al ratio of 5 were readily accomplished, resulting in the formation of nanocomposite materials, Mg/Al-HEDTA (MATA5) and Co/Al-HEDTA (COATA5), with the expansion of the interlayer spacing from 8.0 Å to 14.8 Å and 8.9 Å to 15.3 Å, respectively. This expansion is to accommodate the HEDTA anion of a larger size than nitrate. FTIR spectra of MATA5 and COATA5 showed a combination pattern of HEDTA with MAL5 and COAL5, respectively. The elemental analysis showed the presence of Mg, Al, C and Co in the surface of the synthesized materials. Thermal analysis showed that the MAL5 and COAL5 gradually collapsed



starting at around 600 °C. Scanning electron microscopy (SEM) study showed no significant difference between the surface morphology of MAL5, COAL5, MATA5 and COATA5.

Anion exchange of anthraquinone-2-sulphonate (AQ2) with nitrate from the Zn-Al layered double hydroxide (ZAL) was accomplished in aqueous environment at various concentrations, temperatures and contact times. The anion exchange procedure produced nanocomposite materials, of which basal spacing was expanded from 9.2 to around 20 Å. This is due to the size and spatial orientation of the anions, which is accommodated in the ZAL inorganic layered structure. Relatively pure phase products were obtained as a result of complete anion exchange process when the concentration of aqueous solutions of AQ2 of 0.01-0.025 M, contact time of 18 h and temperature of 70 °C (ZALAQ2S) were used. However, a relatively impure phase was obtained at lower temperatures, 25-50 °C when 0.025 M AQ2 was used in the anion exchange process for 18 h of contact time. At 0.025 M AQ2, anion exchange process could be observed at room temperature even only after 10 min contact time, but the resulting materials did not afford pure phase even after 48 h. The anion-exchange rate for AQ2 with nitrate was found to be very fast for the first 200 min, followed by a slow process thereafter and finally becomes almost leveled off after 1000 min. FTIR spectrum of ZALAQ2S showed a combined pattern of both the FTIR spectra of ZAL and AQ2. The elemental analyses showed that the presence of Zn, Al and C in the surface of the as-synthesized ZALAQ2S and ZAL. SEM analysis shows that the surface morphology of ZAL at 5000 x magnifications is more compact than ZALAQ2S.



Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**SINTESIS NANOKOMPOSIT HIDROKSIDA BERLAPIS GANDA  
MENGUNAKAN ASID *N*-(2-HYDROXYETHYL)-ETHYLENEDIAMIN  
TRIASETIK DAN ANTHRAQUINON-2-SULFONIK SEBAGAI ANION  
TETAMU**

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Sintesis nanokomposit baru mengandungi lapisan tak organik, Mg/Al-NO<sub>3</sub><sup>-</sup>(MAL) dan Co/Al-NO<sub>3</sub><sup>-</sup>(COAL) sebagai perumah dan HEDTA sebagai anion tetamu telah berjaya disediakan melalui kaedah konvensional. Keputusan daripada analisis PXRD menunjukkan bahawa penyisipan HEDTA ke dalam ruang lapisan Mg/Al-NO<sub>3</sub><sup>-</sup> dan Co/Al-NO<sub>3</sub><sup>-</sup> pada nisbah Mg/Al dan Co/Al=5 telah berjaya dilakukan, di mana terbentuknya Mg/Al-HEDTA (MATA5) dan Co/Al-HEDTA (COATA5) dengan masing-masing sebatian mengalami pengembangan jarak basal daripada 8.0 Å kepada 14.8 Å dan 8.9 Å kepada 15.3 Å. Pengembangan jarak saiz antara ruang lapisan adalah disebabkan oleh saiz HEDTA yang lebih besar berbanding dengan anion nitrat. Spektrum-spektrum FTIR bagi MATA5 dan COATA5 menunjukkan kehadiran corak gabungan antara spektrum HEDTA dan MAL5 serta COAL5. Analisis unsur telah membuktikan kehadiran unsur Mg, Al, C dan Co di

dalam bahan-bahan yang berkaitan. Analisis terma menunjukkan bahawa MAL5 dan COAL5 runtuh secara perlahan-lahan apabila mula dipanaskan pada suhu sekitar 600 °C. Kajian mikroskopi imbasan electron (SEM) menunjukkan tiada perbezaan ketara diantara morfologi permukaan MAL5, COAL5, MATA5 dan COATA5.

Pertukaran anion nitrat dengan anthraquinon-2-sulfonat (AQ2) dalam ruang lapisan Zn/Al-LDH (ZAL), telah dilakukan dalam keadaan akues pada pelbagai kepekatan, suhu dan masa. Kaedah penukaran anion telah menyebabkan pengembangan jarak ruang antara lapisan hidoksida daripada 9.2 Å kepada 20 Å. Ini kerana saiz dan orientasi anion AQ2 dalam ruang yang terdapat dalam struktur antara lapisan tak organik ZAL. Apabila proses pertukaran anion dilakukan dengan kepekatan AQ2 di antara 0.01-0.025 M selama 18 jam dan suhu 70 °C (ZALAQ2S), struktur fasa tulen telah diperolehi. Ini bermakna pertukaran anion telah berlaku dengan lengkap. Walaubagaimanapun, fasa tidak tulen boleh dilihat ketika proses berlaku pada suhu sekitar 25-50 °C dengan kepekatan 0.025 M selama 18 jam. Proses penukaran anion jelas berlaku pada suhu bilik dengan kepekatan AQ2 0.025 M walaupun hanya selepas 10 minit, tetapi keadaan ini masih tidak memberikan fasa tulen sepenuhnya selepas 48 jam. Pertukaran anion ini berlaku dengan pantas sehingga 200 minit pertama dan menjadi perlahan pada masa berikutnya, dan seterusnya mendatar pada 1000 minit. Spektrum FTIR bagi ZALAQ2S menunjukkan sifat gabungan diantara spektrum FTIR ZAL dan AQ2. Analisis unsur telah membuktikan kehadiran unsur Zn, Al dan C dalam ZAL dan ZALAQ2S. Morfologi permukaan bagi ZAL pada pembesaran 5000 x adalah lebih padat berbanding dengan ZALAQ2S.

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I certify that an Examination Committee met on 9<sup>th</sup> December 2005 to conduct the final examination of Mazlina Musa on her Master of Science thesis entitled “Synthesis of Layered Double Hydroxide-Nanocomposites Using N-(2-Hydroxyethyl)-Enthylenediamine Triacetic Acid and Anthraquinone-2-Sulphonic Acid as Guest Anions” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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## LIST OF ABBREVIATIONS

Å	Amstrong
ASAP	Accelerated Surface Area and Porosity
AQ2	Anthraquinone-2-sulphonic acid
BDDT	Brunauer, Deming, Deming and Teller
BET	Brenaeur, Emmett and Teller
BJH	Barret, Johner and Halenda
CHNS	Carbon, hydrogen, nitrogen and sulphur analysis
COAL	Co/Al-NO <sub>3</sub> <sup>-</sup> - layered double hydroxides
COAL5	Co/Al-NO <sub>3</sub> <sup>-</sup> - layered double hydroxide prepared at ratio 5 and pH 7
COATA	Co/Al-HEDTA-nanocomposites
COATA5	Co/Al-HEDTA-nanocomposites prepared at ratio 5 and pH 7
EDX	Energy Dispersive X-ray analysis
FTIR	Fourier Transform-Infrared Spectroscopy
HEDTA	<i>N</i> -(2-hydroxyethyl)-ethylenediamine triacetic acid
HTLCs	Hydrotalcites
ICP-AES	Inductive Coupled Plasma-atomic Emission Spectromerty
MAL	Mg/Al-NO <sub>3</sub> <sup>-</sup> - layered double hydroxides
MAL5	Mg/Al-NO <sub>3</sub> <sup>-</sup> - layered double hydroxide prepared at ratio 5 and pH 10
MATA	Mg/Al-HEDTA-nanocomposites
MATA5	Mg/Al-HEDTA-nanocomposite prepared at ratio 5 and pH 10
M <sub>fc</sub>	Mole fraction
PXRD	Powder X-Ray Diffraction



R	Ratio of $M^{2+}$ to $Al^{3+}$
$R_{form}$	Ratio of $M^{2+}$ to $M^{3+}$ formed
SEM	Scanning Electron Microscopy
TGA-DTG	Thermogravimetric and Differential Thermal Gravimetric Analyses
x	Fraction of $Al^{3+}$ in brucite-like layer, $x = Al^{3+}/(Al^{3+}+Mg^{2+})$
ZAL	Zn/Al- $NO_3^-$ - layered double hydroxide
ZALAQ2	Zn/Al-AQ2-nanocomposites
ZALAQ2S	Zn/Al-AQ2-nanocomposite prepared at 70 °C and 18 hour with concentration of AQ2 0.025 M.

## CHAPTER I

### INTRODUCTION

#### Layered Double Hydroxide (LDH)

Hydrotalcite-like compound are layered solids having positively charged layers and interlayer charge-compensating anions or counter anion. This type of material is called layered double hydroxide (LDH) or anionic clay. They are less well known and diffuse in nature than cationic clays. Hydrotalcite belongs to a large class of anionic clay and will be taken reference name for many other isomorphous and polytype compound (Cavani *et al.*, 1991). The common clays can be found abundantly in nature such as montmorillonite, vermiculite, etc. The charges of the layer and the interlayer ion of the LDH are opposite to that of cationic clay.

The chemical composition of the LDH is generally expressed as  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{n-}_{x/n} \cdot YH_2O]^{x-}$ .  $M^{2+}$  is a metal by such  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$  and  $Mn^{2+}$ .  $M^{3+}$  a trivalent metal ion such as  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$ ,  $Ga^{3+}$  and  $V^{3+}$  (Labajos *et al.*, 1996).  $A^{n-}$  is an interlayer anion such as  $CO_3^{2-}$ ,  $NO_3^-$ ,  $SO_4^{2-}$  or  $Cl^-$ .

#### Characteristic of cations and anions of LDH

In LDH, the  $M^{2+}$  and  $M^{3+}$  ions that can be accommodated in the holes of the close packed configuration of OH groups in the brucite-like layers with the ionic radius is similar to  $Mg^{2+}$  in order to form HTLcs. All the bivalent cations from  $Mg^{2+}$  to  $Mn^{2+}$  form HTLc, except for  $Cu^{2+}$ , which form HTLc only when another bivalent cation in Table 1.1 is



present. The deviant behaviors of  $\text{Cu}^{2+}$  compared with other divalent cations can be attributed to the nature of the cation itself; ions like  $\text{Cu}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Ni}^{3+}$  form compounds characterized by the presence of the cooperative Jahn-Teller effect: energy is gained when the distortion in the octahedral coordination structure, occurred.

All the trivalent ion with the atomic diameters ranging from 0.5 Å to 0.8 Å form LDH except  $\text{V}^{3+}$  and  $\text{Ti}^{3+}$  which is not stable in the air (Cavani *et al.*, 1991).

There is no limitation to the nature of the anion. Suitability of an anion depends on selectivity (accounted charge, size), A-OH bond strength and chemical composition. The only problem that arises is the crystallinity and purity of the compound. This is because of the most stable anion interlayer space is carbonate ion. Hence it is very difficult to avoid contamination of carbon dioxide in the aqueous solution.

Basically, LDH containing four types of anions, three are inorganic anions, heteropolyacids, organic acids and layered compound (Table 1.2). Ion selectivity of anion determined what kind of the anion to be intercalated inside the inorganic lamella. The number, size, orientation and the strength of bond between the anion and the hydroxyl group of brucite-like layers determined the height of the gallery (Cavani *et al.*, 1991).

Table 1.1: Ionic radius of some cations (Cavani *et al.*, 1991)

Metal Cations	Examples and Ionic Radius (Å)									
Bivalent, $M^{2+}$	Be	Mg	Cu	Ni	Co	Zn	Fe	Mn	Cd	
	0.3	0.65	0.69	0.72	0.74	0.74	0.76	0.8	0.97	
Trivalent, $M^{3+}$	Al	Ga	Ni	Co	Fe	Mn	Cd	V	Ti	
	0.5	0.62	0.62	0.63	0.64	0.66	0.69	0.74	0.76	

Table 1.2: Examples of anions for the chemical composition of LDHs (Cavani *et al.*, 1991).

Anions [ $A^{n-}$ ]	Examples
Inorganic Anions	$F^-$ , $Cl^-$ , $Br^-$ , $I^-$ , $ClO_4^-$ , $IO_3^-$ , $OH^-$ , $CO_3^{2-}$ , $S_2O_3^{2-}$ , $WO_4^{2-}$ , $CrO_4^{2-}$ , $[Fe(CN)_6]^{3-}$ , $[Fe(CN)_6]^{4-}$ , $[SiO(OH)]^{3-}$
Heteopopolyacids	$(PMo_{12}O_{40})^{3-}$ , $(PW_{12}O_{40})^{3-}$
Organic Acids	Ethylenediamine-triacetic acid, 5-fluorouacil, 2,4-dichlorophenoxyacetic acid, 1-naphthaleneacetic acid, 1,12-dodecanedicarboxylic acid, anthraquinone-2-sulphinic acid and metallorganic complexes.
Layered Compounds	As in the mineral chlorite: $[Mg_2Al(OH)_6]^+$ , $[Mg_3(OH)_2/Si_3AlO_{10}]^-$

### The value of x

The value of mole fraction, x generally for hydrotalcite structure can exist in the range of 0.1-0.5. Many indications show that it is possible to obtain pure HTLC only for  $0.2 < x < 0.33$ . If x value is lower than 0.33, the  $M^{3+}$  octahedral are not neighboring and for higher value of x, the increased number of  $M^{3+}$ , octahedral in the brucite-like sheet, acting as nuclei for the formation of  $M(OH)_2$  (Cavani *et al.* 1991).

The value of x can be calculated by using the following formula:

$$x = [M^{3+} / M^{2+} + M^{3+}]$$

For the synthetic LDH, the value of x can be in the range of 0.15-0.34 (Miyata *et al.*, 1983). The maximum molar amount of interlayer water that can be structurally incorporated as a monolayer in the hydrotalcite is  $1 - (x/n)$ . The  $M^{2+}/M^{3+}$  structural cation ratio generally varies from 1 to 5 (You *et al.*, 2001). Recently, it has been shown that tetravalent cations, such as  $Zr^{4+}$  and  $Sr^{4+}$  could also be incorporated in the brucite-like layers (Velu *et al.*, 1998).

### The Structure of Hydrotalcite

Hydrotalcite was first discovered in Sweden around 1842 as natural mineral clay that can be easily crushed into white powder. E. Manasse, Professor of Mineralogy at university of Florence, Italy, was the first to recognize that carbonate ions were essential for this

type of structure (Manasse, 1915) with the formula  $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}]$ . However, the structure of LDH was only determined in 1970 by Allman (Ehisissen et al., 1993). The formula derived from the structure of brucite,  $\text{Mg}(\text{OH})_2$  and is usually formulated as  $[\text{Mg}_{0.75}\text{Al}_{0.25}(\text{OH})_2](\text{CO}_3)_{0.025} \cdot 0.5\text{H}_2\text{O}$ .

Brucite shows the well known CdI<sub>2</sub>-type structure, i.e. an hexagonal close-packing of hydroxy ions, with all octahedral sites every two interlayers occupied by  $\text{Mg}^{2+}$  ions. Partial substitution gives of  $\text{Mg}^{2+}/\text{Al}^{3+}$  rise to positively charged layers, thus leading to location of anions in the unoccupied interlayers. In natural hydrotalcite, these interlayer anions are carbonate, and water molecules also exist in the interlayer space (Rives and Ullibari 1999). Figures 1.1 and 1.2 show the structure of brucite lattice for LDH.

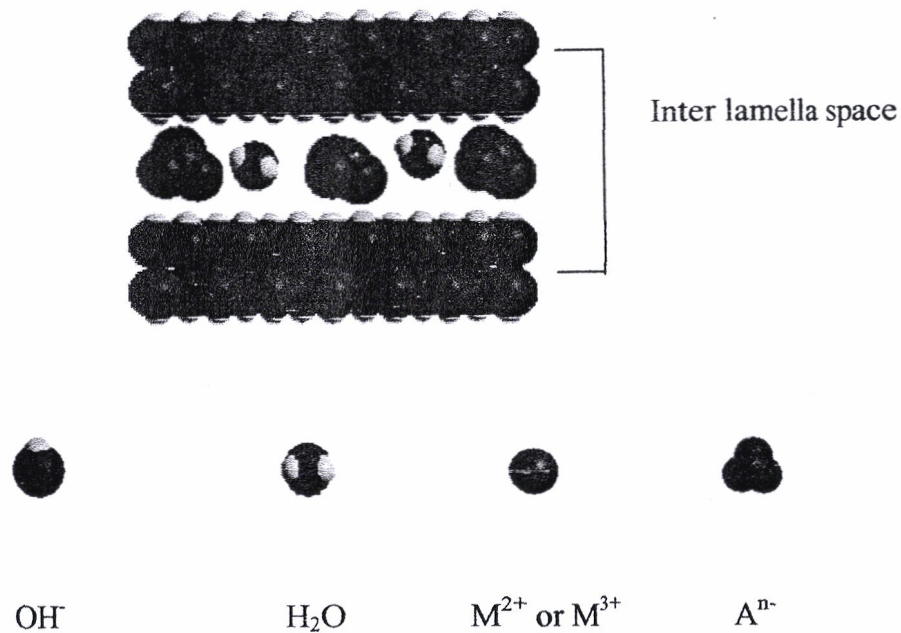


Figure 1.1: Structure of LDH



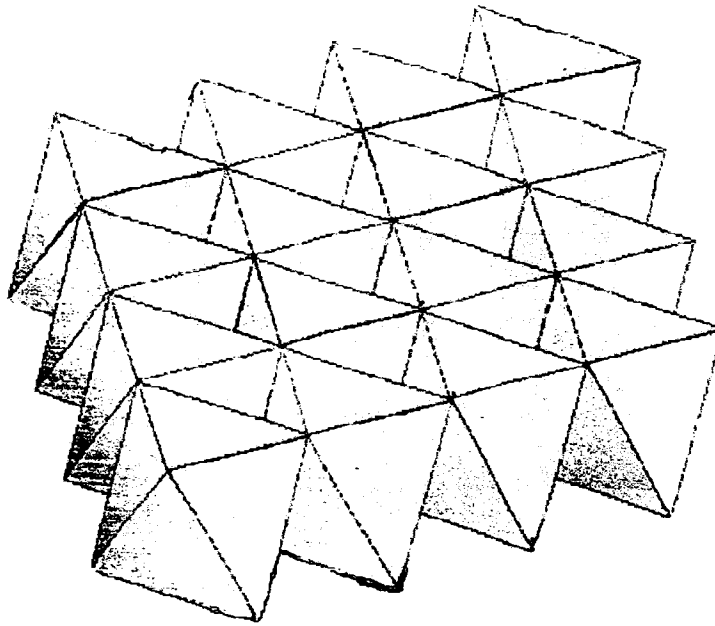


Figure 1.2: Brucite lattice for LDH (Cavani *et al.*, 1991)

### **Nanocomposite material**

Composite materials are mixture of two or more phases. Composite materials have acquired a leading position in the development of new materials because of the realization that with judicious choice of combination of materials starting new combination of properties can be obtained. Composite materials have certain features in common including the following:

- a) Contain two or more distinct but closely related phases, which maybe continuous or discontinuous.
- b) These phases are related to each other depending upon the adhesive mechanism at the interface of two or more phases.