UNIVERSITI PUTRA MALAYSIA

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By

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INTERCALATION AND ADSORPTION OF ORGANIC DYES ON LAYERED DOUBLE HYDROXIDES

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September 2003

Chairman: Professor Mohd Zobir bin Hussein, Ph.D.

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Nanostructured material of layered organic-inorganic hybrid nanocomposites can be generated by encapsulation of an organic moiety into an inorganic lamella in which the open lamellar systems such as layered double hydroxides (LDHs) can be used as the host. For this study, synthesis of nanocomposite materials was carried out by using Mg/Al LDH as a host of inorganic layers and naphthol blue black (NBB), fast green (FG) and methyl orange (MO), organic dyes, as a guest. It was found that the concentrations of the organic moiety and pH are critical for the formation of the well-ordered nanolayered hybrid materials. The optimum concentration of NBB at 1.50 x 10^{-3} M, FG of 2.50 x 10^{-2} M and 3.00 x 10^{-2} M of MO at pH 10 resulted a well-ordered nanolayered organic-inorganic hybrid nanocomposites. FTIR spectrum of each nanocomposites resembled a mixture of each spectrum of the organic and inorganic species, indicating the presence of both in the resulting materials. Surface morphology of Mg/Al-LDH and its nanocomposites show agglomerates of compact

and non-porous structure, a typical surface morphology for LDH and its nanocomposites

For the adsorption studies, the hydrotalcite-like compounds of Mg-Al-carbonate system (MAC) were prepared and their heat-treated products were obtained by calcination of MAC under atmospheric condition for 5 hours at 300 °C (MAC300) and 500 °C (MAC500), respectively Each of the materials was used as an adsorbent for color removal of naphthol blue black (NBB) Batch kinetic study showed that these materials are efficient adsorbents for the anionic dye The adsorption data were fitted to the Langmuir adsorption isotherm and the adsorption capacity of MAC500 and MAC300 were found to be higher than MAC The adsorbent was subsequently recovered and the resulting properties were characterized There was no significant differences in FTIR and surface morphology between the adsorbents and their NBB adsorbed species, except for Powder X-Ray Diffractogram in which they resembled the LDH diffractogram indicating the memory effect property of the calcined LDH

The formation of Mg/Al-FG (MAF) with and without microwave-assisted aging was done and the properties of the resulting material were compared For both methods, the results showed that the FG anion was successfully intercalated into the Mg/Al-layered double hydroxide lamella However, the microwave-assisted method did not accelerate the formation of MAF but the aging period played an important role in the production of better-ordered layer structure of MAF The PXRD pattern showed that as the aging time for the synthesis of MAF increased the intensity of the (003) peak increased, indicating a better order of the nanolayered structure of the resulting material.

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

INTERKALASI DAN PENJERAPAN BAHAN PERWARNA ORGANIK KE ATAS LAPISAN BERGANDA HIDROKSIDA

Oleh

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Bahan nanostruktur dari lapisan hibrid organik-tak organik nanokomposit boleh dihasilkan dengan pengkapsulan bahan organik ke dalam lamella tak organik melalui sistem terbuka lamella contohnya lapisan berganda hidroksida. Sinthesis bahan nanokomposit ini boleh dihasilkan dengan menggunakan Mg/Al hidroksida berlapis ganda sebagai lapisan tak organik dimana naphthol blue black (NBB), fast green (FG) dan methyl orange (MO) bahan perwarna organik, terinterkalasi di celahnya. Didapati bahawa kepekatan bahan organik serta pH adalah penting dalam pembentukan bahan hibrid nano lapisan yang sempurna. Kepekatan NBB adalah 0.0015M, FG adalah 0.025M dan 0.03M bagi MO pada pH 10 menghasilkan bahan lapisan nanohibrid organik-tak organik nanokomposit yang sempurna. Spektrum FTIR bagi nanokomposit menyerupai campuran setiap spektrum spesies organik dan tak organik menunjukkan kewujudan kedua-dua bahan di dalam bahan yang terhasil. Morphologi permukaan Mg/Al hidroksida berlapis ganda dan nanokomposit yang lain

menunjukkan penggumpalan secara kelompok yang padat serta struktur tidak berliang, struktur yang biasa dikaitkan dengan morphologi permukaan bahan hidroksida berlapis ganda serta nanokompositnya

Selain dari itu, kajian terhadap serapan juga dijalankan, dimana bahan Mg-Al sistem karbonat (MAC) disediakan dan bahan terawat haba (MAC300 dan MAC500) diperolehi melalui pemanasan MAC dibawah tekanan atmosfera selama 5 jam pada suhu 300 °C dan 500 °C Bahan yang terbentuk digunakan sebagai penjerap dalam proses penyahwarna naphthol blue black (NBB) Keputusan kajian kinetik menunjukkan bahawa bahan ini merupakan penjerap yang efisen bagi pewarna anionik Di samping itu, didapati proses serapan mematuhi model isoterma Langmuir dimana kapasiti jerapan MAC500 dan MAC300 didapati lebih tinggi berbanding dengan MAC Penjerap yang telah digunakan diproses semula dan proses pencirian dijalankan terhadap bahan tersebut Tiada perbezaan ketara yang dapat dilihat dari bahan yang terjerap serta bahan yang menyerap dalam analisis FTIR dan analisis mikroskop pengimbasan elektron, kecuali spektrum PXRD dimana ia menyerupai spektrum lapisan hidroksida berganda menunjukkan kesan memori ke atas bahan lapisan hidroksida berganda terawat haba

Pembentukan MAF telah disintesis dengan atau tanpa bantuan gelombang mikro telah dikaji di mana ciri-ciri bahan yang terbentuk dibandingkan Bagi kedua-dua kaedah, didapati proses interkalasi berlaku dimana anion FG, masuk ke dalam lamella Mg/Al lapisan hidroksida berganda Tetapi bantuan gelombang mikro tidak dapat mempercepatkan proses pembentukan MAF Namun demikian, proses penuan memainkan peranan penting dalam pembentukan struktur lapisan MAF yang sempurna Spektra PXRD menunjukkan bahawa jika proses penuan bagi MAF meningkat maka, keamatan puncak (003) juga meningkat, membuktikan kewujudan struktur lapisan nano yang lebih baik

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I certify that an Examination Committee met on 23 Septemjber 2003 to conduct the final examination of Azira Abd Aziz on her Master of Science thesis entitled "Intercalation and Adsorption of Organic Dyes on Layered Double Hydroxides" 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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This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as the fulfilment of the requirements for the degree of Master of Science The members of the Supervisory Committee are as follows

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions

AZIRA ABD AZIZ

Date 8 JAN 2004

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LIST OF ABBREVIATIONS

AMAC	adsorbed material with NBB solution for MAC
AMAC300	adsorbed material with NBB solution for MAC300
AMAC500	adsorbed material with NBB solution for MAC500
ASAP	Accelerated Surface Area and Porosimetry
BET	Brenauer, Emmett and Teller
CAM	Cu/Al-MO
FG	Fast Green
LDH	Layered Double Hydroxide
MAC	Mg/Al-LDH
MAF	Mg/Al-FG
MAF60min	Mg/Al-FG (60min)
MAM	Mg/Al-MO
MAN	Mg/Al-NBB
MO	Methyl Orange
NBB	Naphthol Blue Black
NC	Nanocomposite
PXRD	Powder X-Ray Diffraction
R	Ratio of Mg^{2+} to Al^{3+}
SEM	Scanning Electron Microscopy

TGA/DTG — Thermogravimetric (TGA) and Differential Thermo Gravimetry (DTG) Analyse

ZAM — Zn/Al-MO

CHAPTER 1

INTRODUCTION

Nanocomposite Materials

Nanosized and/or nanostructured materials have dimensions, as their names imply, in the scale range of 1 – 100 nanometer (1nm = 10^{-9} m, *i.e.*, one billionth of a meter) thick layers (sheets) range.

Nanostructured materials are becoming of major significance and the technology of the production is rapidly growing into a powerful industry. These fascinating materials include nanofilms, nanocrystal, nanoparticle, nanotubes, alloys, nanocomposite and semiconductors. Exploitation of the nanoparticles or nanostructured materials is expected to lead to 'breakthrough in areas such as materials and manufacturing, nanoelectronics, medicine and environment' (Fendler, 2001).

The syntheses of organic-inorganic hybrid materials, especially in the area of composite in a nanoscale regime, or the so-called nanocomposite materials have received considerable attention lately. Nanocomposite are particularly of interest because the electrical, mechanical, optical, and other physicochemical properties of the materials can be favorably modified due to nanometer level interphase interactions and quantum effects (Komarneni, 1992; Ozin 1992).

Layered double hydroxide commonly used for the formation of nanocomposite material with their crystal lattice consists of two-dimensional layers where a central octahedral sheets of alumina or magnesia is fused to external layer of tetrahedron by tips so that the oxygen ions of the octahedral sheets also belong to the tetrahedral sheets. These layers organize themselves to form stacks with a regular Van der Waals gap in between them called the interlayer gallery. Morphological descriptors such as intercalation and exfoliation are commonly used to describe the state of aggregation of the individual sheets of the layer. A variety of anionic species can be inserted as guests into the interlayer spaces of the LDH, resulting in an expansion of the interlayer distance to a nanometer sized dimension to form a new nanocomposite material (Moore and Reynold, 1997).

Layered Double Hydroxides (LDHs)

In recent years, research on layered double hydroxides (LDHs) also known as anionic clays has become an active field in material research in layered solids. Among these interesting layered materials, hydrotalcite-like compounds (HTlcs), in particular have attracted great attention because of their intercalation ability and other important physiochemical properties for technological applications (Xu and Zeng, 2001, Carja *et al*., 2001 and Olanrewaju *et al*., 2000)

The structure of most of them corresponds to that of hydrotalcite, a natural magnesium-aluminium hydroxycarbonate, discovered in Sweden around 1842, which occurs in nature in foliated and contorned plates and/or fibrous masses. Its formula is $Mg_6A_2(OH)_{16}CO_3.4H_2O$, although due to the relationship between the structure and that of brucite, $Mg(OH)_2$, it is usually formulated as $[Mg_{0\ 75}Al_{0\ 25}(OH)_2](CO_3)_{0\ 025}.0.5H_2O$. Brucite shows the well known CdI_2-type structure, i.e. an hexagonal close-packing of hydroxy ions, with all octahedral sites every two interlayers occupied by Mg^{2+} ions. Partial substitution of Mg^{2+}/Al^{3+} gives 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 *et al*., 1999)