UNIVERSITI PUTRA MALAYSIA

SYNTHESIS AND CHARACTERIZATION OF NANOCOMPOSITE: 2-4-DICHLOROPHENOXY ACETATE-ZINC-ALUMINIUM HYDROTALCITELIKE LAYERS

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By

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

Faculty: **Science and Environmental Study**

A direct intercalation of 2,4-dichlorophenoxyacetate (2,4-D) into Zn-Al-layered double hydroxide (ZAL) was carried out by spontaneous self-assembly technique to produce Zn-Al-2,4-D nanocomposite (ZAD). The aging process was done by conventional and microwave-assisted methods. For both methods, the results showed that the intercalation process resulted in the expansion of the interlayer spacing from 10.7 Å in ZAL to around 19.0 - 24.6 Å in ZAD. Sharp and intense peaks for 003 and 006 reflections indicate well-ordered layered structure which exhibit some common features of layered materials, e.g. narrow, symmetrical and strong peaks at low 2θ values and weaker, less symmetric peaks at higher 2θ values. Further characterization of the resulting materials including organic-inorganic content, surface area and porosity, thermal analysis and morphology, were also carried out.

Both ZAL and ZAD have the capacity to neutralize aqueous solutions at different initial pH values. Deintercalation of 2,4-D from the interlayer of ZAD was achieved with sodium carbonate, buffer phosphate, sodium dihydrogen phosphate and sodium acetate solutions. In general, the release percentage of 2,4-D increased with time. Thermal decomposition on ZAL and ZAD was carried out by calcination of the resulting materials for 5 hours at different temperatures. Thermal decomposition of ZAL resulted in the formation ZnO phase. The LDH phase was no longer detected at temperature 300 ^{o}C. The surface area was found to increase as the temperature increased. This feature indicated that the layered clay-like structure was destroyed due to the formation of new a phase (ZnO phase). For ZADs, the layered structure was retained to at least 400 ^{o}C. However, at 450 ^{o}C, the layered structure completely collapsed due to the removal of the structural water and CO_2 from the interlayer together with the decomposition of the organic moiety of ZAD. The ZnO phase which was already observed in unheated ZAD became more prominent at 225 ^{o}C. The intensity of the peaks increased as the temperature was increased thereafter. The $ZnAl_2O_4$ spinel phase was also observed at 750 ^{o}C and became more prominent at 1000 ^{o}C. The surface area was found to decrease around 150 ^{o}C, constant at around 225 – 400 ^{o}C and increase at around 450 – 1000 ^{o}C. ZAD supplemented in the liquid culture media contributed to the multiplication of cultured cells.

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

PENYEDIAAN DAN PENCIRIAN NANOKOMPOSIT: LAPISAN SEAKAN HIDROTALSIT BAGI 2-4-DIKLOROFENOKSIASETAT–ZINK-ALUMINIUM

Oleh

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September 2003

Pengerusi: **Profesor Mohd Zobir bin Hussein, Ph.D.**

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Penyisipan terus 2,4-diklorofenoksiasetat ke dalam Zn-Al-hidroksida berlapis ganda (ZAL) telah dilakukan dengan kaedah pembentukan sendiri untuk membentuk nanokomposit Zn-Al-2,4-D (ZAD). Proses penuaan dilakukan dengan cara konvensional dan bantuan gelombang mikro. Melalui kedua-dua cara ini, nanokomposit yang terbentuk mengalami pengembangan jarak antara ruang untuk hidroksida berlapis ganda tersebut daripada 10.7 Å kepada 19.0-24.6 Å. Puncak yang tajam dan bersimetri pada puncak 003 dan 006 dalam corak pembelauan sinar-X menunjukkan bahawa nanokomposit yang diperolehi mempunyai struktur lapisan nano yang lebih tersusun, puncak yang tajam dan bersimetri pada nilai 2θ yang tinggi. Pencirian yang lain seperti kandungan organik-tak organik, luas permukaan dan keliangan, analisis terma dan morfologi permukaan juga telah dilakukan. Kedua-dua ZAL dan ZAD menunjukkan kuasa peneutralan dan penimbalan yang baik terhadap larutan akues pada pH awal yang berbeza. Deinterkalasi

anion 2,4-D daripada ruang antara lapisan ZAD telah dilakukan dalam larutan akues natrium karbonat, penimbal fosfat, natrium dihidrogen fosfat dan natrium asetat. Pada umumnya, peratus pembebasan 2,4-D bertambah dengan masa. Penguraian terma juga telah dikaji dengan memanaskan ZAL dan ZAD selam 5 jam pada suhu-suhu tertentu dan pencirian juga telah dilakukan. Penguraian terma ke atas ZAL membawa kepada pembentukan fasa ZnO. Fasa LDH tidak lagi kelihatan pada suhu 300 °C. Luas permukaannya didapati bertambah dengan kenaikan suhu. Ini menunjukkan bahawa struktur seakan tanah liat berlapis telah runtuh kerana wujudnya fasa baru (fasa ZnO). Bagi ZAD pula, struktur berlapis kelihatan hanya pada suhu sekurang-kurangnya 400 °C. Walaubagaimanapun, pada suhu 450 °C, struktur berlapis runtuh dengan sempurna disebabkan oleh kehilangan air, karbon dioksida serta penguraian sebahagian komponen organik ZAD. Fasa ZnO yang sudah sedia ada pada ZAD yang tidak dipanaskan menjadi lebih jelas pada suhu 225 °C. Keamatan puncaknya bertambah dengan kenaikan suhu pemanasan. Fasa spinal $ZnAl_2O_4$ juga telah dapat dilihat dengan lebih jelas pada suhu 750 °C dan 1000 °C. Luas permukaannya pula berkurang pada suhu sekitar 150 °C, tetap pada 225 – 400 °C dan bertambah pada suhu sekitar 450 – 1000 °C. ZAD yang digunakan dalam media kultura menunjukkan ia membantu multiplikasinya.

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Å	Angstrom
ASAP	Accelerated Surface Area and Porosity
BDDT	Brunaeur, Demming, Demming and Teller
BET	Brenaeur, Emmett and Teller
BJH	Barret, Johner and Halenda
CHNS	Carbon, Hydrogen, Nitrogen and Sulfur analysis
CRF	Controlled release formulation
HT	Hydrotalcite
ICP-AES	Inductive Couple Plasma-Atomic Emission Spectroscopy
LDH	Layered double Hydroxide
MS	Murashige and Skoog Medium
NAA	Naphtaleneacetic acid
PVC	Polyvinylchloride
PXRD	Powder X-Ray Diffraction
R	Ratio of Zn^{2+} to Al^{3+}
R_f	Ratio of Zn^{2+} to Al^{3+} formed
R_i	Ratio of Zn^{2+} to Al^{3+} initial
SEM	Scanning Electron Microscopy
STP	Standard Temperature and Pressure
TGA-DTG	Thermogravimetry Analysis – Derivative Themorgravimetry Analysis
x	Fraction of Al^{3+} in brucite-like layer, x = Al/(Al+Mg)

ZAL	Zn^{2+}-Al^{3+}-NO^{-}_{3}-Layered Double Hydroxide
ZAD	Zn^{2+}-Al^{3+}-2,4-dichlorophenoxyacetate
ZALMIC60	ZAL microwave 60
ZADMIC15	ZAD microwave 15
ZADMIC30	ZAD microwave 30
ZADMIC45	ZAD microwave 45
ZADMIC60	ZAD microwave 60
ZALOB60	ZAL oil bath 60
ZADOB15	ZAD oil bath 15
ZADOB30	ZAD oil bath 30
ZADOB45	ZAD oil bath 45
ZADOB60	ZAD oil bath 60
1 ppm C	MS liquid medium with 1ppm 2,4-D commercial
5 ppm C	MS liquid medium with 5ppm 2,4-D commercial
10 ppm C	MS liquid medium with 10ppm 2,4-D commercial
1 ppm C + 0.1 ppm NAA	MS liquid medium with 1ppm 2,4-D commercial + 0.1 ppm NAA
1 ppm Z	MS liquid medium with 1ppm 2,4-D ZAD
5 ppm Z	MS liquid medium with 5ppm 2,4-D ZAD
10 ppm Z	MS liquid medium with 10ppm 2,4-D ZAD
1 ppm Z + 0.1 ppm NAA	MS liquid medium with 1ppm 2,4-D ZAD + 0.1 ppm NAA

1 ppm ZND	MS liquid medium with 1ppm 2,4-D ZAD non-dissolved
5 ppm ZND	MS liquid medium with 5ppm 2,4-D ZAD non-dissolved
10 ppm ZND	MS liquid medium with 10ppm 2,4-D ZAD non-dissolved
1 ppm ZND + 0.1 ppm NAA	MS liquid medium with 1ppm 2,4-D ZAD non- dissolved + 0.1 ppm NAA
2,4-D	2,4-dichlorophenoxyacetate
θ	X-ray diffraction angle