

Intercalation of Anthraquinone-2-Sulphonate into Magnesium-Aluminum Layered Double Hydroxide and its Calcined Products by Ion Exchange and Memory Effect Properties

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Abstract

Layered double hydroxide of Mg-Al-nitrate system (LDH) was prepared and its heat-treated products (LDHTs) were obtained by calcining the LDH at 250 - 750°C, for 5 hours at atmospheric condition. The LDH and the LDHTs were used as an inorganic host for the intercalation of AQ2 via ion exchange or memory effect property by exposing the LDH and LDHTs in aqueous solution containing an anion, anthraquinone-2-sulfonate (AQ2) for the formation of an organic-inorganic layered nanohybrid materials. X-ray diffractograms showed that the layered structure of LDH collapsed when it was heated at around 350°C, and an oxide phase, MgAl₂O₄ appeared. Due to the memory effect property, the regeneration of LDH from LDHT was observed and at the same time the AQ2 was intercalated when LDHT was treated with the aqueous solution containing AQ2. As a result, formation of an organic-inorganic layered nanohybrid material was also observed. Similarly, the same material can be formed by ion exchange of LDH with AQ2. The basal spacing of LDH was found expanded from 8.1 Å to around 20 Å in the resulting nanohybrid. This is to accommodate a bigger size of the AQ2 moiety with specific orientation inside the interlamella of the inorganic layered structure that warrants the layer expansion. Incomplete intercalation and ion exchange process resulted in a mixed LDH and a nanohybrid phase as observed in the PXRD pattern of the resulting material.

Introduction

Layered double hydroxide (LDH) is a type of material known as anionic clay. This material is considered as antitypes of 2:1 (three-layer) clay mineral of cationic clay group, the common clays that can be found abundantly in nature such as montmorillonite, vermiculite, mica, etc. The charge of the layer and the interlayer ions of LDH are the reverse to that of cationic clay.

A general formula for LDH can be written as $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A^{n-}]_{x/n} \cdot mH_2O$, where M(II) is any divalent cation and M(III) is any trivalent ion, Aⁿ⁻ is any anion, such as carbonate, sulfate, chloride and *etc.* For LDH, the value of x can be in the range of 0.15-0.34 [1]. LDH is called hydrotalcite or manasseite if it has a specific formula of Mg₆Al₂(OH)₁₆CO₃·4H₂O with a symmetry of 3R and 2H, respectively [2]. Therefore, LDH is generally known as hydrotalcite-like

material.

Calcined LDHs have properties sometimes totally different from its precursors. Oxides and mixed oxides are the common resulting materials of calcined LDH and they have 4 main properties, namely basic properties, paracrystallinity, formation of non-stoichiometric spinels and memory effect [2].

Memory effect property of calcined hydrotalcite-like or layered double hydroxides materials has been exploited for various applications. For example, LDH and its calcined products were widely used as adsorbents for water treatment such as the removal of organic pollutants [3] and Cr (VI) [4], pesticide [5] and humic acid [6-8]. In addition, calcined LDH was also used as catalyst for hydrogenolysis of CCl₂F₂ [9], and as a starting material for the preparation of intercalation compounds of LDH or the so-called nanocomposite [10] materials.

Another property of LDH, which was widely exploited, is the ion exchange capability. This property

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is useful for water treatment and formation of new nanohybrid materials of organic-inorganic type. For example, removal of 2,4-dichlorophenoxy acetic acid [11] and the formation of the organic-inorganic hybrid of it [12] were done by the virtue of this property.

Here we report and discuss our work on the intercalation of anthraquinone-2-sulfonate, an organic moiety into an inorganic LDH lamellae of Mg-Al-nitrate system (LDH) and the heat-treated products, (LDHTs) by calcination of the LDH at 250-750°C. The intercalation was done by using the ion exchange and memory effect properties of the LDH.

Experimental

Synthesis and characterization of the absorbent materials

All the chemicals used in the synthesis of LDH were obtained from different chemical suppliers and used without further purification. LDH was synthesized according to the method of Reichle [13]. A solution containing salts of Mg and Al, with Mg/Al atomic ratio, $R = 4$ was titrated into a conical flask containing concentrated NaOH solution, while stirring with a magnetic stirrer at about 35°C. The resulting slurry was heated in an oil bath at about 70°C for 18 h with continuous agitation. The LDH formed was cooled, centrifuged, thoroughly washed and dried in an oven at 120°C, overnight and kept in a sample bottle for further use and characterizations. This sample was labeled as LDH. LDHTs were prepared by calcining the LDH at 250-750°C in an electric furnace for 5 hours, under atmospheric condition. The samples were kept in sample bottles for further use and characterisations.

Powder X-ray diffraction (PXRD) patterns of the samples were obtained on a Shimadzu Diffractometer D-6000 using filtered Cu K_{α} radiation. The FTIR spectra were recorded by a Perkin-Elmer 1750 spectrophotometer. KBr pellet containing 1% sample was used to obtain the FTIR spectra.

Intercalation of AQ2

Intercalation of AQ2 by virtue of ion exchange and memory effect properties of LDH was done by two different techniques, "direct" and "conditioned" methods.

In the direct method, ion exchange process was done by adding about 2.5 g of LDH into a conical

flask containing 250 cm³ of 0.5 M AQ2 aqueous solution. The solution was stirred for 18 h and the resulting material was washed several times with deionized water, dried in an oven overnight and kept in a sample bottle for further use and characterisations. A similar procedure was adopted for LDHTs.

Another method used in this study is by first stirring the LDH or the LDHTs in deionized water for 18 h, thereafter the LDH or LDHTs was put in contact with AQ2 solution for another 18 h as was mentioned earlier in the direct method. This method is called "conditioned method". At the end of the process, the samples were washed and dried in an oven overnight and kept in a sample bottle for further use and characterisations. The resulting samples were also subjected to X-ray diffraction and FTIR studies.

AQ2 uptake

The amount of AQ2 uptake (w/w) by LDH and LDHTs via ion exchange or intercalation process was studied by dissolving the resulting materials in 2 M HNO₃ and the resulting solution was subjected to absorbance measurements ($\lambda_{\max} = 289.3$ nm) using a Perkin-Elmer Lambda 20 UV-visible spectrophotometer. The amount of AQ2 was obtained from a calibration curve of absorbance against concentration.

In this work, the term "uptake" instead of amount of the dye adsorbed, was meant to refer to the amount of AQ2 taken by the LDH and LDHTs by ion exchange, intercalation, adsorption or absorption, or by any combination thereof. This is because the mechanism involve in this particular study was not limited to adsorption only. As a result we refer the LDH and LDHTs as absorbents instead of adsorbents.

Results and discussion

Properties of LDH and its calcined products

PXRD patterns for LDH and LDHTs calcined at various temperatures is given in Fig. 1. Shown in Fig. 1 (at the bottom) is the as synthesized LDH, showing high intensity of the 001 reflection and other associated reflections, indicating a good crystallinity of the material. The LDH has a basal spacing of 8.1 Å (Table 1).

Part of the LDH sample was subsequently heated at 250-750°C, for 5 hours at atmospheric condition to prepare the LDHTs. The PXRD pattern for the LDHTs (Fig. 1) showed that the layered structure of

Table 1

Properties of AQ2-intercalated LDH and LDHTs via ion exchange and memory effect properties.

Calcination temperature, °C	Direct method			Conditioned method		
	Basal spacing, Å	Phase observed	AQ2 ^a uptake, %	Basal spacing, Å	Phase observed	AQ2 ^a uptake, %
LDH	8.1	LDH	-	8.1	LDH	-
LDH (ion exchanged)	20.1	LDH+NC	25.7	20.3	LDH+NC	31.6
250	19.9	LDH+NC	26.7	20.9	LDH+NC	28.5
350	19.4	LDH+NC	26.6	19.1	LDH+NC	28.5
500	19.7	LDH+NC	26.2	19.7	LDH+NC	29.7
750	20.6	LDH+NC	26.3	20.8	LDH+NC	30.6

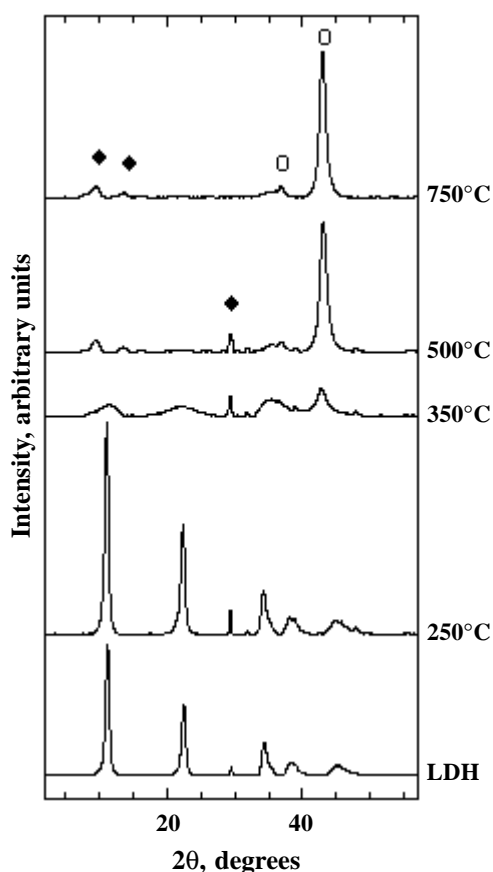
^aAQ2 uptake, % (w/w), NC = nanocomposite

Fig. 1. PXRD pattern of LDH and its calcined products calcined at various temperatures, 250 – 750°C (○ = $MgAl_2O_4$ phase, ♦ = unknown phase).

LDH collapsed when LDH was calcined at around 350°C, resulting in the formation of a new oxide phase, $MgAl_2O_4$. This phase become dominant as the calcination temperatures increased form 350 to 750°C.

FTIR spectra of the samples are shown in Fig. 2. The FTIR spectrum of LDH is shown at the bottom

of the figure, showing bands associated with functional groups belonging to LDH. Similar features of the FTIR spectra were observed for the LDHTs calcined at 250-500°C, however the features is different for the sample calcined at 750°C, in which the intensity of the bands in the 1400-2000 cm^{-1} region were reduced substantially. Since the bands in this region are associated with the presence of nitrate and hydroxyl groups in LDH, the reduced in intensity is parallel with the decomposition of these groups and the formation of the oxide. The observation of the absorption band belonging to the nitrate group when LDH was heated up to 500°C indicates that nitrate is still present in the resulting LDHT and decomposed only when the LDH was heated at 750°C.

Ion exchange and intercalation of AQ2

Direct method

Figure 3 shows the PXRD patterns of AQ2-intercalated by ion exchange and memory effect property of LDH and LDHTs, respectively by direct method. An AQ2 intercalated by ion exchange shows expansion of the LDH inorganic lamella from 8.1 to 20.1 Å (Table 1), indicating that the nitrate in the inorganic lamella was exchanged with the AQ2 in the aqueous solution, resulting in the formation of a new nano-hybrid layered materials. Expansion is attributed to the accommodation of the AQ2 of bigger size than nitrate together with its orientation in the inorganic LDH lamella. The presence of the LDH phase was also observed, giving rise to in a mixed phase of the resulting material, due to the incomplete ion exchange process.

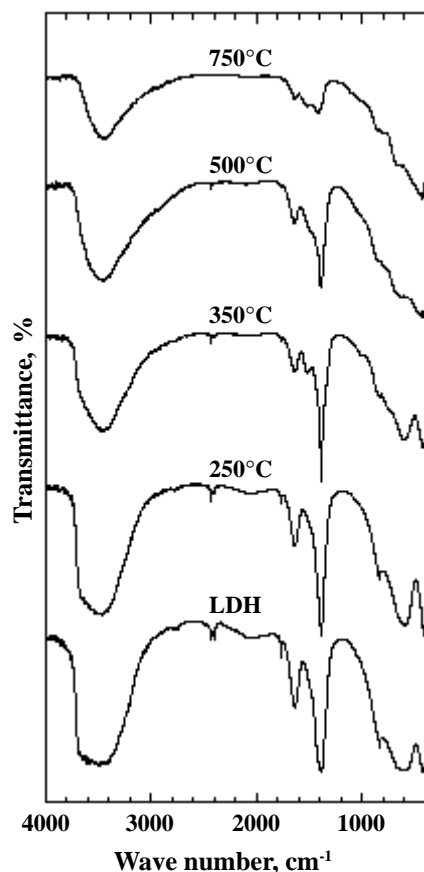


Fig. 2. FTIR spectra of LDH and its calcined products calcined at various temperatures, 250 – 750°C.

Similarly, expansions of the inorganic LDH layered structure to around 19.4–20.6 Å (Table 1) were observed when LDHTs calcined at 250–750°C were exposed to AQ2 in the aqueous solution, resulting in the formation of the organic-inorganic nanohybrid material. This shows that LDHTs prepared at temperature 250–750°C afford the formation of the organic-inorganic nanohybrid when they were put in contact with the AQ2 in the aqueous solution. However, the LDH phase was also present with slightly different basal spacing, indicating a mixed phase of the resulting materials, due to incomplete process of the intercalation by reconstruction of LDH from LDHTs at the experimental condition set in our study. The expansion of the basal spacing indicates that the LDH calcined at 250–750°C resulted in the reconstruction of LDH phase with AQ2 intercalated in the interlamella as a counter ion. Previous study showed that an intercalation of humic acid had occurred when the layered structure of the original compound was decomposed and reconstructed in the solution of the humic acid [7].

In general, the result shows that LDH and LDHT

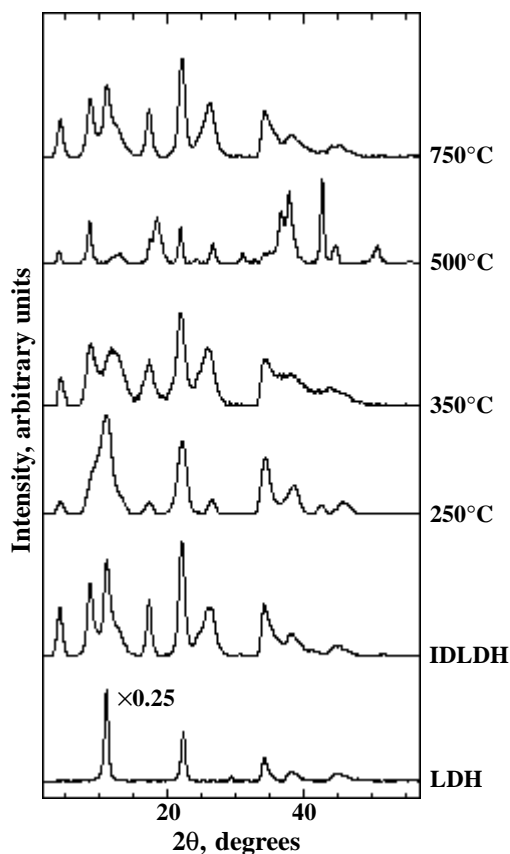


Fig. 3. PXRD patterns of LDH (for intensity comparison), AQ2-ion exchanged LDH (IDLDH) and AQ2-intercalated LDH from LDHTs calcined at various temperatures, 250 – 750°C done by direct method.

were capable of removing the AQ2 from the aqueous solution by intercalation via ion exchange or memory effect property. Optimization can be done depending on the requirements. For example, if a single pure phase or nanohybrid material is desired, parameters such as LDH or LDHTs to AQ2 ratio, pH and contact time can be optimized. On the other hand if only uptake of AQ2 is important, then calcination temperature together with the parameters previously mentioned have to be considered. In addition, the method of pretreatment of the absorbents should be taken into account and this will be further discussed in the following section.

Figure 4 shows the FTIR spectra for AQ2 and LDH-ion exchanged AQ2 and LDHTs calcined at 250–750°C and intercalated with AQ2 by reconstruction via memory effect property. The spectra of the latter show the presence of the AQ2 species together with the LDH phase, indicating simultaneous presence of both in the LDHTs intercalated with AQ2. This observation is parallel with the expansion of the basal spacing of the corresponding PXRD pattern

shown in Figure 3, indicating that the resulting materials contain the intercalated AQ2.

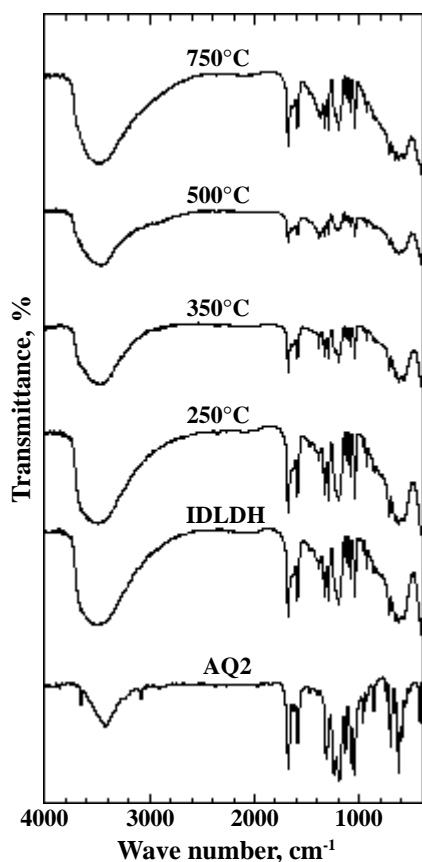


Fig. 4. FTIR spectra of AQ2, AQ2-ion exchanged LDH (IDLDH) and AQ2-intercalated LDH from LDHTs calcined at various temperatures, 250 – 750°C C done by direct method.

Conditioned method

Apart from intercalation by direct ion exchange or memory effect property, pretreatment of the LDH or LDHTs can be used to enhance the AQ2 uptake. As mentioned earlier, in the conditioned method, the LDH and LDHTs were first conditioned by stirring the samples in decarbonated deionized water for 18 h, thereafter, a similar treatment as in the direct method was adopted.

Figure 5 shows the PXRD patterns of AQ2-intercalated by ion exchange and memory effect property of LDH and LDHTs, respectively. The PXRD of the samples show essentially similar patterns to that of the direct method. The basal spacing is essentially similar, in a range of 19.1–20.9 Å (Table 1). However, a close look on the uptake of AQ2 by both methods shows that it is different and this will be further discussed in the following section.

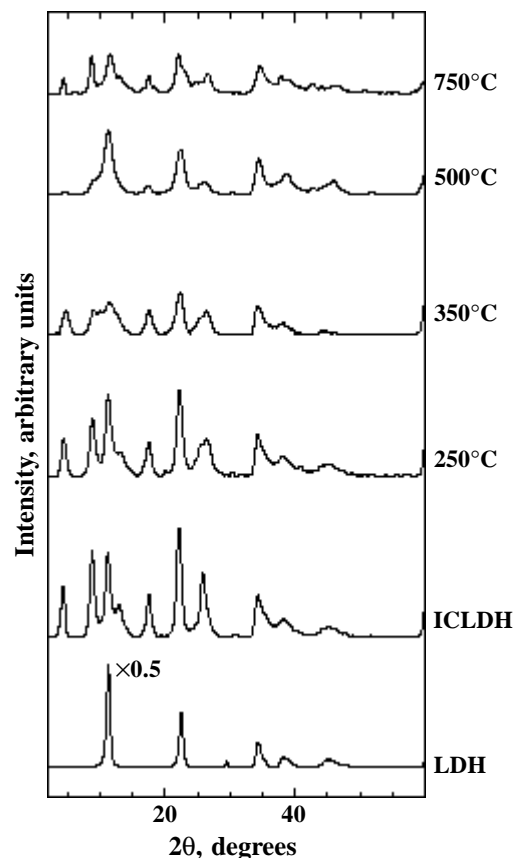


Fig. 5. PXRD patterns of LDH (for intensity comparison), AQ2-ion exchanged LDH (ICLDH) and AQ2-intercalated LDH from LDHTs calcined at various temperatures, 250 – 750°C done by conditioned method.

Again the FTIR spectra (Figure 6) of the resulting samples obtained by this methods show similar features to that of the direct method. Therefore, similar interpretation can be offered.

Uptake of AQ2

Figure 7 compares the uptake of AQ2 by intercalation via ion exchange or by memory effect property. For the ion exchange process in which AQ2 from the aqueous solution was ion exchanged with nitrate ion in the LDH, the conditioned method shows higher uptake than the direct method, 31 and 25% (w/w), respectively.

Similarly, it was found that conditioned method was also more effective compared to the direct method in the uptake of the AQ2 from the aqueous solution on LDHTs. As mentioned earlier, the uptake was by intercalation via memory effect property, *i.e.* the ability of the component species of the calcined LDH (LDHTs) for the reconstruction of the LDH inorganic layers and the AQ2 in the aqueous solution as a

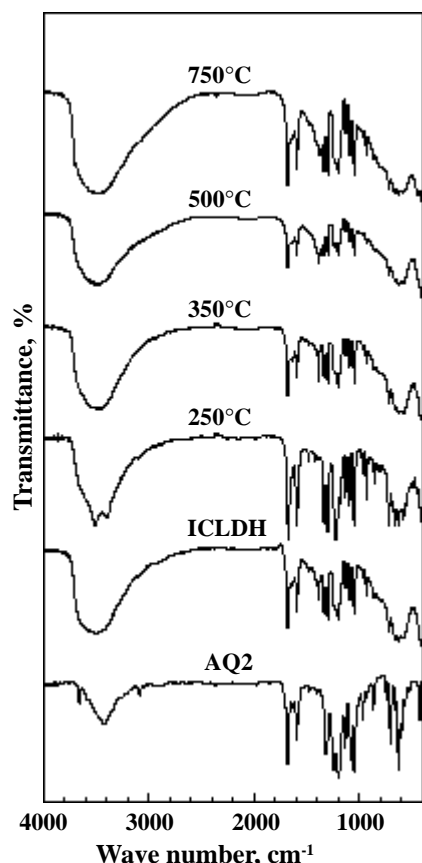


Fig. 6. FTIR spectra of AQ2, AQ2-ion exchanged LDH (ICLDH) and AQ2-intercalated LDH from LDHTs calcined at various temperatures, 250 – 750°C done by conditioned method.

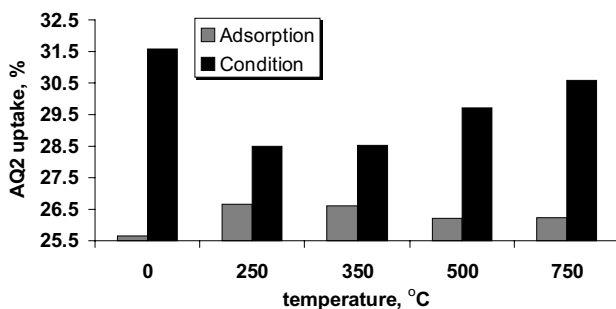


Fig. 7. Comparison of AQ2 uptake on LDH and LDHTs by direct method (opened) and conditioned method (striped).

counter ion for the formation of the nanolayered hybrid material. It was also found that the percent uptake of AQ2 increased with the calcining temperature of the LDHTs in the conditioned method compared to a decreasing trend in the direct method. This shows that pretreatment of the LDH and LDHTs by leaving them for 18 h in deionized water prior to the ion exchange and reconstruction process improved the AQ2 uptake. LDH was found to be more sensitive than LDHTs for this treatment. For LDHTs, the

uptake increased with calcination temperature in the conditioned method. On the other hand, temperature increase of calcination resulted in slightly decrease in AQ2 uptake in the direct method.

Conclusion

This study shows that synthetic LDH and its calcined products could be used as an absorbent for anthraquinone-2-sulphonate removal. Regeneration of LDH from its calcined LDH occurred when the LDHTs was put in contact with AQ2 in aqueous medium indicating the “memory effect” property of LDH. At the same time the AQ2 anion was intercalated as a counter ion in the regenerated LDH inorganic lamella and both of these phenomena were observed in this study. When LDH was used, expansion of the basal spacing was observed, indicating that ion-exchange process has occurred in which the nitrate from the inorganic lamella was ion exchanged with AQ2 from the solution and AQ2 is the preferred counter ion compared to nitrate in the inorganic interlamella. An expansion of the basal spacing indicates that the intercalation of the anthraquinone-2-sulphonate moiety with a specific orientation occurred, which warrants the expansion of the inorganic LDH interlayers.

Another important aspect in the intercalation by ion exchange or memory effect properties is the method of pretreatment of the precursors, LDH or LDHTs. Pretreatment by first conditioning the precursors in deionized distilled water improved the amount of AQ2 uptake by intercalation or ion exchange. However, the AQ2 uptake decreased slightly with calcination temperature of the LDHTs if direct method was adopted, but improved if the conditioned method was adopted.

Acknowledgement

The support of this research by Ministry of Science, Technology and Environment, Malaysia under IRPA Grant No. 09-02-04-0325-EA001 and UPM for MZH sabbatical leave is gratefully acknowledged.

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Received 12 April 2002.