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INTERCALATION STUDY OF CURCUMIN INTO ZINC LAYERED HYDROXIDE

(Kajian Mengenai Penyisipan Kurkumin ke dalam Zink Hidroksida Berlapis)

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Abstract

Zinc layered hydroxide (ZLH) intercalated with curcumin was successfully prepared by ion exchange method. The synthesised nanocomposite was characterised by Powder X-ray diffraction (PXRD) and Fourier transform infrared spectroscopy (FTIR). The obtained intercalation compound, ZLH-curcumin nanocomposite (ZiCUR), showed a basal spacing of 10.0 Å when 0.01M of curcumin solution was used in the synthesis. The shifting in the stretching frequency of the curcumin anion provides strong evidence that the anion is bonded to the ZLH through electrostatic force. In FTIR, after intercalation, there is a noticeable shift of the O-H stretching vibrational bands. This is due to the formation of strong hydrogen bonds between curcumin and –OH groups in ZLH. Thus, this indicates that curcumin anions are present in the sample and were intercalated between positively charged ZLH layers, as indicated by the characteristics of PXRD pattern.

Keywords: zinc layered hydroxide, curcumin, ion exchange method

Abstrak

Zink hidroksida berlapis (ZHB) disisip bersama kurkumin telah berjaya disediakan menggunakan kaedah pertukaran ion. Komposit nano yang telah di sintesis dicirikan menggunakan X-ray Serbuk Pembelauan dan Spektroskopi Infra Merah Transformasi Fourier. Sebatian interkalasi yang diperoleh iaitu komposit nano zink hidrosida berlapis-kurkumin, menunjukkan jarak basal sebanyak 10.0 Å apabila kepekatan 0.01M larutan kurkumin digunakan semasa proses sintesis. Perubahan pada frekuensi anion kurkumin menunjukkan bukti yang kukuh di mana anion telah dilekatkan kepada ZHB menggunakan daya elektrostatik. Melalui Spektroskopi Infra Merah Transformasi Fourier, selepas interkalasi, perubahan yang ketara pada O-H regangan jalur getaran dapat di lihat. Hal ini kerana, pembentukan ikatan hidrogen yang kuat antara kurkumin dan kumpulan -OH di dalam ZHB. Maka, ia menunjukkan bahawa anion kurkumin hadir di dalam sampel dan telah disisipkan antara lapisan ZHB yang bercas positif, seperti mana yang ditunjukkan oleh ciri – ciri corak Spektroskopi Infra Merah Transformasi Fourier.

Kata kunci: zink hidroksida berlapis, kurkumin, kaedah pertukaran ion

Introduction

According to the World Health Organization, open injuries have the potential for serious bacterial wound infections, including gas gangrene and tetanus, and these, in turn, may lead to long term disabilities, chronic wound or bone infection, and death [1]. Wound infection is particularly of concern when injured patients are presented late for definitive care. Problems, such as lack of **knowledge** about how to diagnose and treat wounds and **lack of** funding to proper therapies, medical technologies and trained wound-care professionals, will lead to millions of untreated and mistreated patients each year.

Turmeric, (*Curcuma longa* L.), has been used in traditional medical applications since ancient times. The principal curcuminoid in turmeric is curcumin [2], which was extensively studied as antibacterial compound. The wound healing ability of curcumin, involving the mechanisms of reduced inflammation, granulation, and remodelling of the tissue, was intensively examined in rats and guinea pigs. The recent studies have highlighted that punch wounds in curcumin-treated animals healed much faster than curcumin untreated animals [3] [4]. However, the curcumin molecule is unstable and therefore, demonstrates limited biological activity and practical applications. In this study, in order to stabilize the curcumin, attempts were made by intercalating curcumin into layered metal hydroxide.

Layered metal hydroxide can be classified as layered double hydroxide (LDH) and layered hydroxide salt (LHS). Layered double hydroxide (LDH) nanocomposite is a class of inorganic material with a chemical composition represented by the general formula, $[M^{2+}{}_{1-x}\ M^{3+}{}_{x}\ (OH)_2]^{\ x+}\ [A^{n-}{}_{x/n}.mH_2O]$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, respectively [5]. Previous studies have shown that curcumin intercalated into Mg/Al LDH exhibited excellent wound healing properties [6]. However, to the best of our knowledge, the application of a Zinc layered hydroxide salt (LHS) as a host has yet to be explored.

Zinc layered hydroxide (ZLH) is represented by the general formula of $M^{2+}(OH)_{2-x}(A^{m-})_{x/m}.nH_2O$, where M^{2+} in this case is the metal cation Zn^{2+} and A^{m-} is the counter ion [7]. The ZLH structure consists of positively charged layers that can expand or contract depending on the nature of the interlayer anions. In this current investigation, we study the intercalation of curcumin into interlayer galleries of ZLH via ion exchange method, as well as properties of the resulting ZLH-curcumin intercalation compound. This direct method involved a direct reaction between the curcumin solution and the zinc oxide (ZnO) precursor. Compared with other LHS synthesis methods, like urea hydrolysis [8], structural memory effects [9], co-precipitation [10] and solid state reactions [11], ion exchange method was chosen as the best method because it is simple, environmentally friendly, and economical as it involves fewer chemicals and fewer steps.

Materials and Methods

Materials

Zinc oxide, 99%, curcumin ($C_{21}H_{20}O_6$ molecular weight 368.3799 g/mol), 98%, and sodium hydroxide, 99% purity, were purchased from Acros Organics (Geel, Belgium) and Merck (Darmstadt, Germany), respectively. Chemicals were used without further purification. Deionized water was used throughout the experiment.

Synthesis of zinc layered hydroxide intercalated with curcumin

The curcumin-intercalated ZLH was prepared using the ion-exchange method [12,13,14]. An amount of 100 mL of Curcumin at 0.01 M was added to the aqueous solution containing 1.0 g ZnO. The mixture was stirred vigorously for 2 hours at room temperature. The reaction mixture was aged at 70 °C for 18 hours before the resulting slurry was centrifuged, washed with water, dried in an oven at 70 °C, and kept for further characterisation.

Characterisation

Powder X-ray diffraction (PXRD) patterns were recorded with a XRD-6000 (Shimazdu, Kyoto, Japan) using CuKα radiation (λ = 1.5418 Å) at 30 kV and 30mA. Fourier transform infrared (FTIR) spectra were recorded over the range of 400 – 4000 cm^{-1} on a Perkin-Elmer Spectrum 100 (Perkin-Elmer, Waltham, Massachusetts, USA) equipped with a universal attenuated total reflectance (ATR) accessory.

Results and Discussion

Powder X-ray diffraction analysis

Figure 1 shows the PXRD patterns of ZnO and ZLH-curcumin nanocomposite (ZiCUR). The PXRD pattern of ZnO showed characteristics of high crystallinity peaks. However, in ZiCUR, the peak of ZnO phase still dominated the PXRD pattern, which is due to an incomplete reaction. The intercalation occurred when the ZnO was transformed to ZLH and the curcumin anion was intercalated between the layers. This can be observed by the presence of peaks at a lower 2θ value, as shown in the diffraction patterns of ZiCUR. The expansion of the basal spacing recorded at

10.0 Å was caused by a larger molecular size of curcumin, as well as the spatial arrangement of the anion in the interlayer space. From previous studies, it was proposed that the formation of ZiCUR from ZnO occurred in three steps through a dissociation-deposition mechanism [15,16,17]. The first step described in Eq. 1 involves hydrolysis of ZnO in water. When ZnO particles are immersed in the water, the surface of ZnO hydrolyses to form a layer of $Zn(OH)_2$. The layer of $Zn(OH)_2$ that is formed then becomes more soluble than ZnO in the presence of acid to become Zn^{2+} and OH^- (Eq. 2). Finally, the Zn^{2+} species, hydroxyls, H_2O, and curcumin anions (CA^-) in the solution react to generate the layered intercalation compound (Eq. 3). The process is repeated until all the ZnO phase and the $Zn(OH)_2$ phase has completely converted to the layered compound. ZiCUR is formed from the host-guest interactions, namely electrostatic attraction, hydrogen bonding, and van der Walls forces [18]. The mechanism of dissociation-deposition is described in the equations below:

$$ZnO + H_2O \text{ -> } Zn(OH)_2 \quad (1)$$
$$Zn(OH)_2 \text{ -> } Zn^{2+} + 2OH^- \quad (2)$$
$$Zn^{2+} + 2OH^- + CA^- + H_2O \text{ -> } Zn^{2+} (OH)_{2-x} (CA^-)_x nH_2O \quad (3)$$

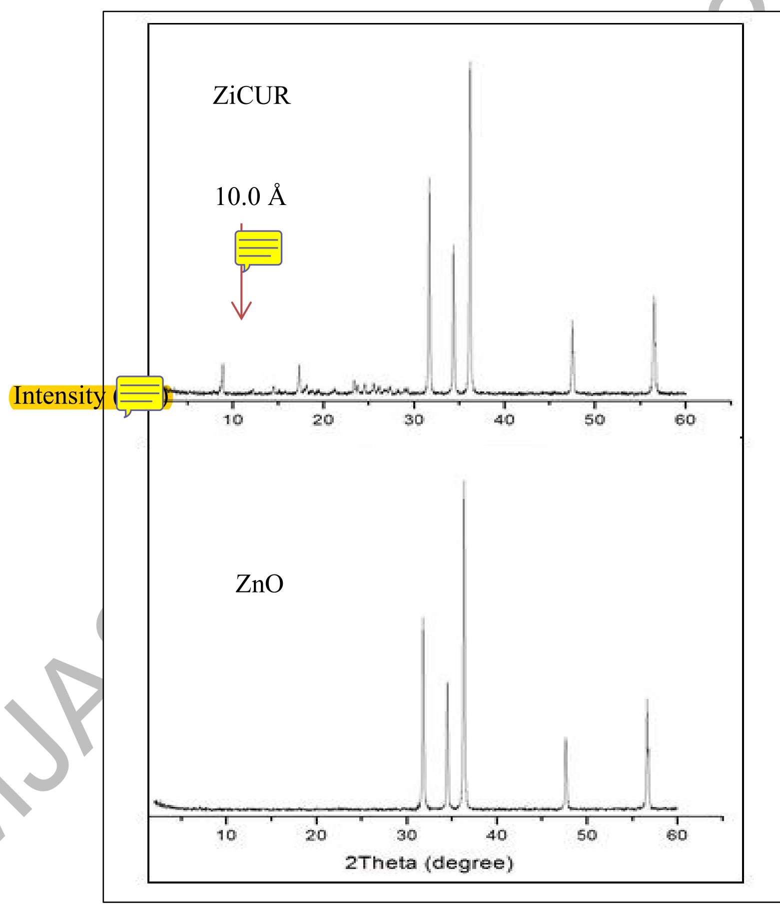

Figure 1. PXRD patterns of ZnO and ZiCUR compounds

Fourier transform infrared analysis

The presence of the curcumin in the ZLH interlayers was also elucidated by FTIR spectroscopy, which supported the PXRD results [19]. Figure 2 exhibited the FTIR spectrum of pure ZnO, curcumin, and ZiCUR. The sharp and intense peak of ZnO at the lower wavenumber range, 400 cm^{-1} is due to the Zn-O sublattice stretching vibration

[20]. Similar absorption bands could also be observed for the ZiCUR, as it possesses the same functional group. The FTIR spectra of curcumin showed strong characteristic vibrations at 1592 cm^{-1} attributed to C=C bending and 1270 cm^{-1} to C-O stretching. Trans-C-H out-of-plane bend for curcumin was detected at 960 cm^{-1}. The C-H monosubstitution band for phenyl group could be detected at 720 cm^{-1}, 809 cm^{-1}, and 856 cm^{-1}.

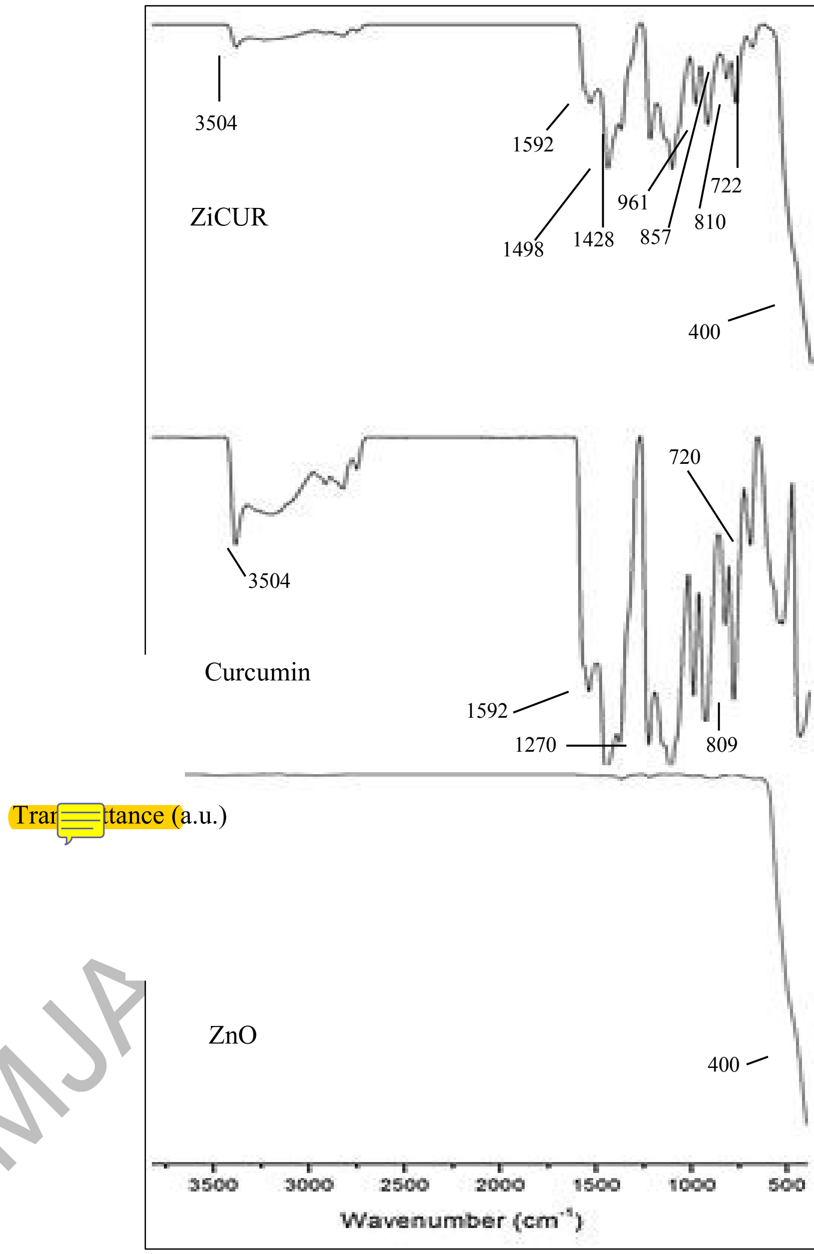

Figure 2. FTIR spectra of ZnO, Curcumin and ZiCUR compounds

On the other hand, the intercalation compound exhibited most of the vibrations assigned of curcumin, although several vibrations shifted due to the interaction between the curcumin anion and the interlayer. In particular,

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vibrations were due to trans-C-H out of plane bend at 961 cm^{-1} and C-H monosubstitution band at 722 cm^{-1}, 810 cm^{-1} and 857 cm^{-1}. COO^- stretching of intercalated curcumin anion overlapped and appeared at 1498 cm^{-1} and 1428 cm^{-1}. The C=C stretch in intercalated ZLH also overlapped at 1592 cm^{-1}. The broad band at 3504 cm^{-1} was assigned to the O-H stretching of vibration of interlayer water molecules. These results indicate that both curcumin and ZnO functional groups were present in the compound and further confirmed the intercalation of curcumin between positively charged ZLH layers, as indicated by the characteristics of PXRD pattern.

Conclusion

The curcumin anion was successfully intercalated into the Zn layered hydroxide by the ion exchange method. The interlayer spacing of ZiCUR obtained by PXRD characterization suggests the successful intercalation reactions between ZLH nanolayers and curcumin. The FTIR spectra further confirmed the presence of curcumin in the ZLH. The product, therefore, is hoped to demonstrate future potential as wound dressings for human skin.

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