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Contributed Paper

Adsorption of Natural Product Compound, Goniothalamin, by Dodecyltrimethylammonium-Montmorillonite

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ABSTRACT

An organoclay (dodecyltrimethylammonium-montmorillonite) was prepared by the ion exchange reaction between quaternary ammonium surfactant, dodecyltrimethylammonium ion, and sodium ion in the interlayer space of montmorillonite. The modification changed the surface property of the clay mineral from hydrophilic to hydrophobic property and significantly increased the basal spacing of montmorillonite to be 1.72 nm. The adsorption of goniothalamin in dodecyltrimethylammonium-montmorillonite was carried out by solid-liquid reaction. The product was characterized by powder X-ray diffraction, infrared spectroscopy, thermal analysis and elemental (CHN) analysis. The presence of the alkylammonium ion and goniothalamin in the product suggested the adsorption of goniothalamin and dodecyltrimethylammonium ion into interlayer space of montmorillonite.

Keywords: montmorillonite, goniothalamin, dodecyltrimethylammonium, organoclay

1. INTRODUCTION

Hybrid materials based on organic or inorganic species and layer inorganic materials such as clay minerals have attracted much attention, because of the improvement of the physical and chemical properties of both organic and inorganic substrates by the host-guest interactions [1-3]. A 2:1 layered clay mineral including montmorillonite provides low toxicity, high adsorption ability as well as cation exchange, hydrophilic, and swelling properties [4]. The hydrophilic property can be converted to hydrophobic property by the ion exchange reaction between the interlayer cations and organic cations such as quaternary ammonium ions [5-8]. The organically modified montmorillonite is an ideal candidate for the selective intercalation of neutrally organic and inorganic species [9]. The hydrophobic montmorillonites have found various applications including adsorbents to remove organic pollutants such as *p*-nitrophenol, *p*-chlorophenol and

2,4,5-trichloronitrophenol [7, 10-11] and so on. As an example for biomedical application, it was recently reported that aripiprazole-montmorillonite coated with polyvinylacetate diethyl amino acetate was a promising delivery system for taste masking and enhancing the bioavailability of the drug, aripiprazole [12]. Thus, organophilic montmorillonites play an important role in the pharmaceutical health products and industries either as excipients or active reagents.

Goniothalamin (Figure 1) is an bioactive styryllactone, which shows the strong activity against *Plasmodium falciparum* and three human cancer cell lines including oral cavity cancer, breast cancer and small cell lung cancer. It can be isolated from the bark of *Goniothalamus elegans* Ast, a herbal plant that can be found in north east of Thailand [13]. The improving and/or controlling the property of goniothalamin is worth investigating.

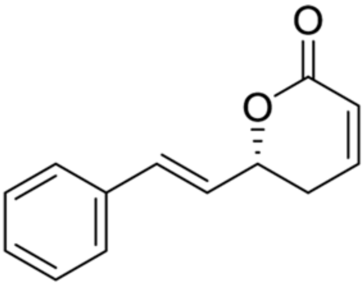


Figure 1. Structure of goniothalamin (GNT).

In this work, the adsorption of goniothalamin on dodecyltrimethyl ammonium-montmorillonite was investigated by liquid-solid reaction. The organization of goniothalamin within montmorillonite may achieve as novel medicinal hybrid material that might be suitable for using in biopharmaceutical and technological process [12, 14]. To the best of our knowledge, there is no adsorption of natural product compound, goniothalamin, on dodecyltrimethylammonium-montmorillonite. *Herein*, goniothalamin was intercalated in dodecyltrimethylammonium-montmorillonite by the reaction between dodecyltrimethylammonium-montmorillonite and goniothalamin. The clay mineral may potentially be used as a selective adsorbent of the natural product compounds from the crude extracts.

2. MATERIALS AND METHODS

2.1 Materials

Sodium-montmorillonite (subsequently referred to as Mt, the reference clay sample of the Clay Science Society of Japan, JCSS-3101, Kunipia F, obtained from Tsukinuno mine, Japan) was used as a host material. The cation exchange capacity (CEC) of the montmorillonite is 119 meq/100 g of the clay mineral. Dodecyltrimethylammonium bromide ($C_{15}H_{34}NBr$, DTAB) (Sigma-Aldrich Corporation, USA) was used as received. Goniothalamin (abbreviated as GNT) was isolated from the crude extracts of *Goniothalamus elegans* Ast bark as reported previously by Suchaichit et al. [13].

2.2 Preparation of Organoclay

The aqueous suspension of Mt was prepared by dispersing 0.5 g of Na- montmorillonite in 300 mL of deionized water under magnetic stirring for 30 min [11]. A stoichiometric amount of dodecyltrimethylammonium bromide was subsequently added into the clay suspension. The molar ratio of alkylammonium ion to the interlayer sodium cation was 1:1. The mixture was magnetically stirred for 24 h at 80°C. The resulting solid was separated by centrifugation, washed repeatedly with deionized water until a negative $AgNO_3$ test was obtained and dried at 60°C for 24 h. The dried solid was ground in an agate mortar and stored in a desiccator. The sample was denoted as DTA-Mt.

2.3 Adsorption of Goniothalamin

The adsorption of goniothalamin was carried out by adding the aqueous dispersion of 0.1 g of DTA-Mt in 100 mL aqueous solution of goniothalamin (400 mg/L). The pH of the mixture was adjusted from 4 to 5 by dropping diluted HCl (0.1 M) and then continuously agitated by magnetic stirrer at room temperature for 12 h [13]. The resulting solid was separated by centrifugation, washed several times with deionized water and dried at 60°C for 24 h. The product was ground in an agate mortar and stored in a desiccator and abbreviated as GNT-DTA-Mt.

2.4 Characterization

X-ray diffraction patterns were collected on a Bruker D8 ADVANCE diffractometer using monochromatic Cu Ka radiation. FT-IR spectra were recorded between 750-4000 cm^{-1} on a BRUKER TENSOR 27 FT-IR spectrophotometer. Thermal gravimetric analysis (TGA) was performed on a Perkin Elmer Pyris Diamond TG-DTA instrument at a heating rate of 10°C/min under a dry air atmosphere using a-alumina (a-Al_2O_3) as a standard material. Elemental analysis (CHN) data were obtained from a Perkin Elmer 2400 CHN/O Analyzer.

3. RESULTS AND DISCUSSION

The XRD pattern of the product is shown in Figure 2 together with those of Na-Mt and DTA-Mt. The basal spacings of Na-Mt and DTA-Mt were 1.21 and 1.72 nm, respectively. After the ion exchange reaction, the XRD pattern of DTA-Mt showed the increase in the basal spacing of *ca.* 0.72 nm, which was obtained by subtracting the thickness of the silicate layer of montmorillonite (*ca.* 1.0 nm) from the observed basal spacing (1.72 nm), indicating the successful intercalation of dodecyltrimethylammonium ion into the interlayer spaces of montmorillonite. From the observed basal spacing (1.72 nm), the dodecyltrimethylammonium ion was assumed to arrange as bilayer structure in between the silicate layers with the alkyl chain lied in horizontal position (Scheme 1a) [15]. After the adsorption of GNT, the interlayer space of the GNT-DTA-Mt did not increase further, indicating that the adsorbed GNT molecules did not expand the interlayer space more. Taking the expansion of the interlayer space (*ca.* 0.72 nm) and the size of DTA cation into account, it was thought that the adsorbed GNT molecules did not affect the bilayer structure of the DTA cation. Therefore, DTA cation was assumed to arrange in bilayer structure and the GNT molecule might be adopted in between the adjacent alkyl chain length of the DTA cation. The structure is proposed in Scheme 1b.

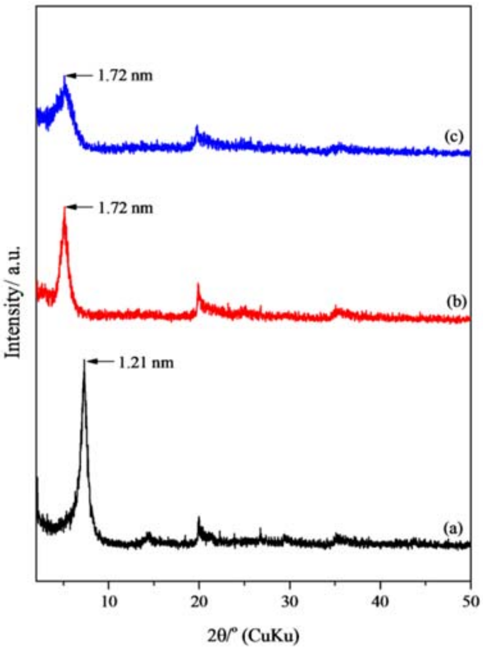
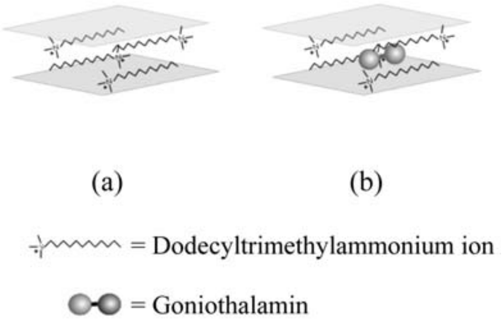


Figure 2. XRD patterns of (a) Na-Mt, (b) DTA-Mt and (c) GNT-DTA-Mt.



Scheme 1. Proposed structures of (a) DTA-Mt and (b) GNT-DTA-Mt.

The FT-IR spectrum of montmorillonite (Figure 3a) showed the characteristic bands at 3621, 3408, and 1636 cm^{-1} assigned to the inner OH groups within the montmorillonite structure and to water of hydration of the sodium cation. The FT-IR spectrum of goniothalamin (Figure 3c) showed the absorption bands for C-H stretching of carbon-carbon double bonds (3048 and 3026 cm^{-1}), C=O stretching (1701 cm^{-1}) and C-O stretching (1244 cm^{-1}) due to unsaturated ester and aromatic groups. The FT-IR spectrum of DTA-Mt (Figure 3d) showed the characteristic bands corresponding to inner OH groups of montmorillonite at 3623 cm^{-1} as well as CH_2 stretching vibrations at 2928 and 2850 cm^{-1} and CH_2 scissoring mode (1473 cm^{-1}) of alkylammonium ion. The bands slightly shifted from the frequencies that observed for DTAB (2919, 2852 and 1467 cm^{-1}, Figure 3b) due to the interactions with the clay mineral, suggesting the intercalation of dodecyltrimethylammonium ion in montmorillonite. The FT-IR spectrum of GNT-DTA-Mt (Figure 3e) exhibited the characteristic bands corresponding to the methylene groups of dodecyltrimethylammonium ion (2927, 2853 and 1473 cm^{-1}) and hydroxyl groups of montmorillonite (3624 and 1641 cm^{-1}) and the additional characteristic bands due to the ester group of goniothalamin (1704, 1382 and 1247 cm^{-1}). The bands slightly shifted to the higher frequencies, indicating the intercalation of GNT molecule with DTA-Mt [16, 17]. This resulted in the appearance of GNT in DTA-Mt.

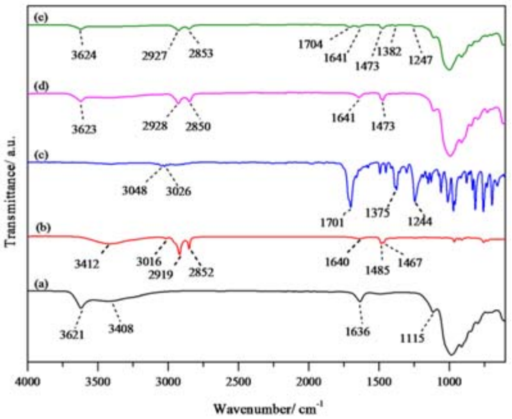


Figure 3. FT-IR spectra of (a) Na-Mt, (b) DTAB, (c) GNT, (d) DTA-Mt and (e) GNT-DTA-Mt.

Thermal stability of the organoclay and the product was investigated by the thermo-gravimetric analysis [18-20]. The TG-DTG curves of Na-Mt (Figure 4a) showed two steps of mass losses. The first mass loss step involved the dehydration of the adsorbed water observed from room temperature to at around 200°C. The second step of mass loss was interpreted to the dehydroxylation of the structural OH group observed at 450-900°C. While, the TG-DTG curves of DTA-Mt (Figure 4b) and GNT-DTA-Mt hybrid (Figure 4c) showed three steps of mass losses. The first step of mass loss involved the dehydration started from room temperature to at around 150°C. While, this process was found in lower temperature range (from room temperature to 100°C) for GNT-DAT-Mt, that might arise from the higher amount of organic species that replaced the adsorbed water on the surface of montmorillonite. The second mass loss step observed at 150-460°C for DTA-Mt and 100-510°C for GNT-DTA-Mt was assumed to the decomposition the adsorbed GNT molecule and/or the intercalated DTA cation. The last mass loss step related to the thermal decomposition of the structural OH group of montmorillonite and the partial decomposition of carbon residue in the different thermal reaction processes observed at 460-900°C for DTA-Mt and 510-900°C for GNT-DTA-Mt. These results confirmed the intercalation of DTA and/or GNT in montmorillonite. The percentage of mass loss in second step observed in the TG curves of DTA-Mt and GNT-DTA-Mt were 13.30 and 16.98, respectively, thus, 3.68% of mass loss observed at this step was thought to be arisen from the amount of goniothalamin that absorbed in DTA-Mt. This confirmed the presence of GNT in DTA-Mt.

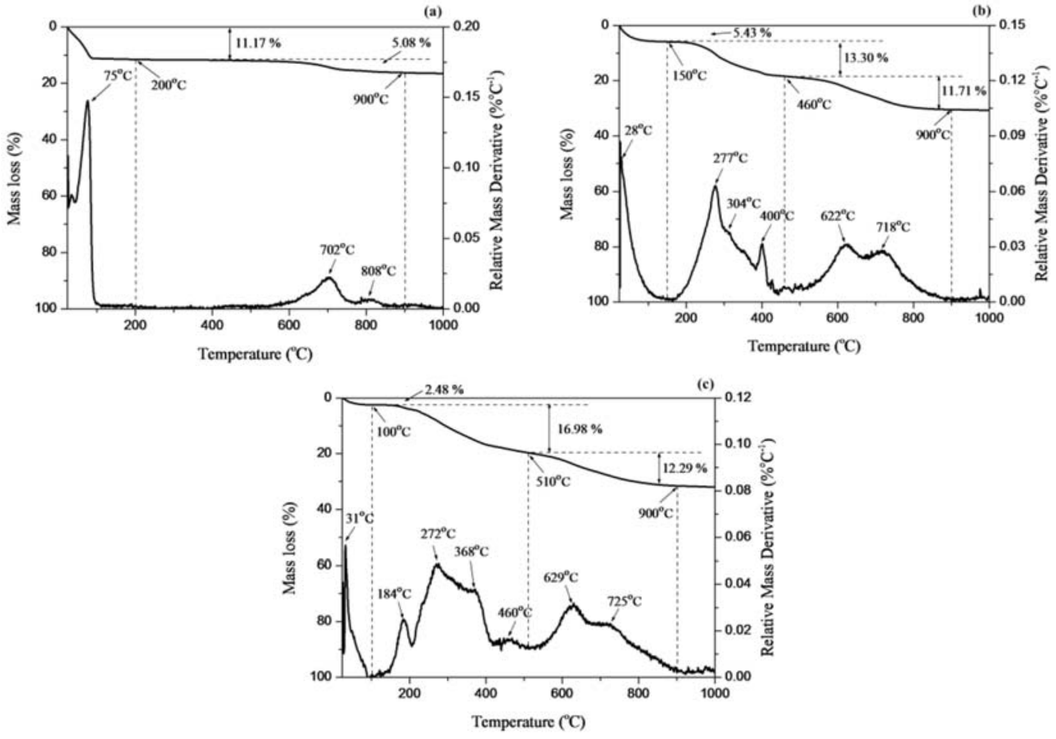


Figure 4. TG-DTG curves of (a) Na-Mt, (b) DTA-Mt and (c) GNT-DTA-Mt.

The CHN data of DTA-Mt showed the percentage of carbon and nitrogen contents of about 16.47% and 1.31%, respectively. The calculated empirical formula was $C_{15}N$, compatible with the chemical formula of DTA ion, suggesting the adsorption of DTA in the clay mineral. The CHN data of GNT-DTA-Mt hybrid showed the increasing of the percentage of carbon to be 18%. The higher amount of carbon content observed in GNT-DTA-Mt was assumed to the adsorption of goniothalamin in DTA-Mt. Which was consistent with the TG-DTG result mentioned above (17% of mass loss).

The introduction of quaternary ammonium ion in montmorillonite is a simple way to prepare the organophilic layered silicate for adsorbing neutral organic molecule from natural product. Further works on the modification of montmorillonite with various quaternary ammonium surfactants are being done in our laboratory in order to improve the biological activities of natural product compounds and/or possibly use as a selective adsorbent for isolating single compound from the crude extract.

4. CONCLUSIONS

The organophilic clay, dodecyltrimethyl ammonium-montmorillonite, was successfully investigated by the ion exchange reaction and used as the host for adsorbing goniothalamin molecule from the extract of *G. elegans*. The preparation of goniothalamin-dodecyltrimethyl ammonium-montmorillonite hybrid may initiate the chance for designing novel medical and pharmaceutical heath product with unique bioactive properties controlled by host-guest and guest-guest-intercalations.

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