



Stable formamide/palygorskite nanostructure hybrid material fortified by high-pressure homogenization



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ABSTRACT

High-pressure homogenization was employed to incorporate formamide (FM) in palygorskite (Pal) for the fabrication of aminated hybrid materials. The interactions of FM molecules with Pal and the positions of FM molecules inside the structure of Pal after hybridization and heat treatments were investigated. It was found that high-pressure homogenization could improve the dispersion of Pal bundles and facilitate the additional incorporation of FM molecules into the tunnels or channels of Pal and that supported the formation of stable FM/Pal hybrid materials. Spectroscopic and thermal analysis results confirmed that FM molecules could attach to Pal via H-bonds. The tunnel of Pal remained perfect after calcination at 380 °C owing to the incorporated FM molecules. The adsorption capacity of the homogenized FM/Pal hybrid material towards Pb(II) (58.4 mg·g⁻¹) was improved in comparison with the raw Pal (32.2 mg·g⁻¹) after calcination at 380 °C. The enhanced interactions between the organic species and Pal structure via high-pressure homogenization provided an alternative strategy to design new stable hybrid materials.

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1. Introduction

Hybrid materials of organic and inorganic natures attracted many attentions due to their excellent chemical-physical properties and high stability. For instance, Maya Blue is an unprecedented stable hybrid blue-pigment used since the Maya's ancient time [1–5]. Conventionally, Maya Blue is composed of two main ingredients, which are an organic color dye and the palygorskite (Pal) or sepiolite [3]. In order to underpin the chemical stability of Maya Blue, the researchers located the dyes inside the structure of Pal or sepiolite and the results indicated several scenarios: the organic indigo molecules could adsorb on the external channels of Pal [3], or be incorporated inside the tunnels of Pal or sepiolite [6,7].

Chiari et al. demonstrated that the organic molecules formed H-bonds inside the tunnels and edges of Pal's channels [8]; whereas other studies revealed that the dye molecules inserted inside the silanol groups present in the clay minerals or coordinated water molecules [6, 9–11]. Evidences highlighted superficial interactions between the C=O groups of the organic dye and the Mg or Al atoms of the clay's structure

[7,12,13]. Recently, many other organic dyes such as methyl red and alizarin [14], eosin Y [15] and thioindigo [7] were used to prepare Maya Blue analogues. These studies corroborated the fact that the stability of the dye/Pal hybrids stemmed from the strong host/guest interactions between the organic dye and the Pal allowed by its specific crystal structure.

Pal likes sepiolite but differentiates from the other clay minerals (i.e., kaolinite [16], montmorillonite [17]) by presenting a rod-like morphology [18,19]. The structure is formed by continuous tetrahedral sheets intercalated by discontinuous octahedral sheets and tunnels (presenting the dimension of 0.37 nm × 0.64 nm) that are elongated in the [001] direction, and filled with zeolitic water molecules or exchangeable cations under ambient conditions. Indeed, it was observed that terminal Mg²⁺ ions that are located at the edges of the octahedral sheets could complete their coordination order by bonding to two water molecules, which are in turn H-bonded to zeolitic water [20]. The crystalline structure presented adequate pore and surface features that rendered the absorption of organic dyes by Pal to form stable composites [14,21–28]. Moreover, polar molecules such as ethanol [29], acetone [30], methanol [31], or pyridine [32] were also access to the tunnels of the Pal's structure either by displacement of the zeolitic water or even fully coordinated water or filling the free space after removal of the zeolitic water by heating or by application of dynamic vacuum. Although a growing number of stable hybrid are being developed, strengthening

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the interactions between the organic molecules and Pal remains challenging and the change of “host/guest” interactions is still at the exploratory stage.

The interactions between the organic molecule and Pal could be strengthened by selecting structural feature of the Pal. Indeed, high-pressure homogenization is a highly effective dispersion/emulsion technology that can disassociate bulk aggregates and transform them into small-size particles [33,34]. It has been confirmed that high-pressure homogenization can generate cavity effect to disaggregate the crystal bundles of Pal as individual rods [35,36]. In addition, high-pressure homogenization could also support the migration and attachment of organic molecules into Pal *via* shear, impact and cavitation forces [36–38]. It is a feasible approach to strengthen the interactions between organic molecules and the Pal for the fabrication of strongly robust hybrid-material. In order to further understand the role of these specific chemical groups, we selected formamide (FM) presenting the $-NH_2$ group and incorporated them into Pal *via* high-pressure homogenization. The interactions of FM molecules with Pal and the positions of FM molecules inside the structure of Pal after hybridization and heat treatment were investigated. The adsorption capability of FM/Pal materials was also studied using Pb(II) as the model ion.

2. Experimental

2.1. Materials

Pal, presenting a chemical composition of 51.72% (w/w) SiO_2 , 10.47% Al_2O_3 , 20.41% MgO, 0.87% Fe_2O_3 , 1.29% CaO, 1.52% Na_2O , and 0.13% K_2O , as well as the bulk density of $750 \text{ kg}\cdot\text{m}^{-3}$ was taken from the Huangnishan Mine located in the Xuyi county of the Jiangsu Province in China. Formamide (FM, analytical reagent grade) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without prior purification. All suspensions and solutions were prepared using deionized water.

2.2. Preparation of the FM/Pal hybrid materials

An amount of Pal (40.0 g) was dispersed in FM (400 mL) under mechanical stirring at 400 rpm for 24 h. Pal suspension was then collected and treated with a high-pressure homogenizer (GYB-3004, Shanghai Donghua High Pressure Homogenizer Factory, Shanghai, China) at 20 MPa. The resultant homogenized suspension was centrifuged at 4500 rpm for 10 min to separate the solid from the solution. The collected solid was then dried in an oven at $150 \text{ }^\circ\text{C}$ for 4 h until a constant weight. Finally, the dried product was grinded and passed through a 200 mesh screen ($<74 \mu\text{m}$) for further experiments. The bulk density of obtained product is $480 \text{ kg}\cdot\text{m}^{-3}$. FM-treated Pal with or without homogenization were named H-FMPalx and uH-FMPalx (with x representing the calcining temperature), respectively.

2.3. Characterization

The X-ray diffraction (XRD) data was collected using an X'Pert PRO diffractometer equipped with a $\text{Cu K}\alpha$ radiation source (40 kV, 40 mA). The EDS spectra were observed using a field emission scanning electron microscope (FESEM, Sigma ULTRA55, Germany). High-resolution transmission electron microscopy (HRTEM) images were obtained using a high-resolution transmission electron microscope (Tecnai G^2 F30). The C, H and N elemental composition was determined using an Elementar Vario EL Elemental Analyzer (Germany). The Infrared (IR) spectra were recorded on a Thermo Nicolet NEXUS TM spectrophotometer (USA). Band fitting was done using a Lorentz-Gauss function with the minimum number of component bands used for the fitting process by the software Peakfit v. 4.0. The fitting was undertaken until reproducible results were obtained with squared correlations of $R^2 > 0.99$. N_2 adsorption-desorption isotherm was recorded using a

Micromeritics ASAP 2020 instrument at 77 K (Micromeritics, Norcross, GA, USA). The specific surface area (S_{BET}) was calculated by the BET method. The micropore volumes (V_{micro}) were estimated by the *t*-plot method. The thermogravimetric (TG) analysis were performed on a Diamond TG-DTA 6300 thermoanalyzer under a nitrogen atmosphere from ambient temperature to $800 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. X-ray photoelectron spectra (XPS) were recorded using an X-ray photoelectron spectrometer (Thermo Scientific, K-Alpha). Single-pulse ^1H magic-angle spinning (MAS) NMR spectra were recorded on an Agilent DD2 600 spectrometer operating at a Larmor frequency of 600.25 MHz for ^1H . These experiments employed a 6.0 mm double resonance 1H-X MAS probe (Agilent) and a spinning frequency of 8.0 kHz. Single-pulse ^{29}Si Dipolar-Decoupling Magic Angle Spinning (DD/MAS) experiments were carried out on an Agilent DD2 600 spectrometer operating at a Larmor frequency of 119.13 MHz for ^{29}Si . These experiments used a 6.0 mm double-resonance 1H-X MAS probe with a MAS frequency of 8.0 kHz and proton decoupling (TPPM) during acquisition.

3. Results and discussion

3.1. XRD analysis

The crystal structures of the prepared materials were determined by XRD and the obtained profiles are presented in Fig. 1. The patterns of raw Pal exhibited the characteristic reflections of Pal at $2\theta = 8.35^\circ$ (110 plane), 19.8° (040 plane), 27.5° (400 plane) and 35.0° (161 plane) [20]. The position and intensity of the reflections did not strongly change in comparison with the XRD pattern of raw Pal after treating with FM followed by high-pressure homogenization (Fig. 1c) or not (Fig. 1b). These results indicated that the crystal structure of Pal remained intact even after high-pressure homogenization and that the incorporation of FM inside Pal did not affect the octahedral and tetrahedral frameworks of Pal.

3.2. Elemental analysis

In order to determine the content of FM incorporated inside Pal, we determined the nitrogen content (mass%) of the samples by elemental analysis. As shown in Table 1, a content of 0.023% N was preserved in raw Pal and the value increased to 3.193% after the incorporation of FM (H-FMPal150). However, the nitrogen content decreased to 1.348% and 0.626% after calcination the H-FMPal150 at 240 and $380 \text{ }^\circ\text{C}$, respectively. A lower nitrogen content of 2.443% was found for FM/Pal without homogenization and more FM were removed after calcination the uH-FMPal150 at $240 \text{ }^\circ\text{C}$ (0.996%) and $380 \text{ }^\circ\text{C}$ (0.610%). These results

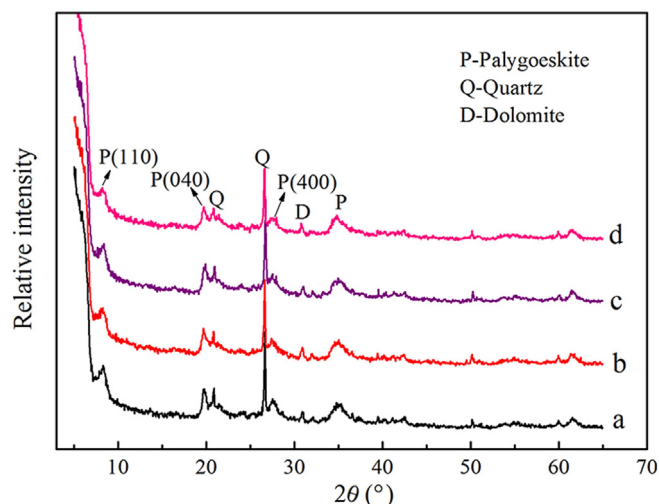


Fig. 1. XRD patterns of (a) raw Pal, (b) uH-FMPal150, (c) H-FMPal150, (d) H-FMPal380.

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