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Nanoscale dispersion crystal bundles of palygorskite by associated modification with phytic acid and high-pressure homogenization for enhanced colloidal properties

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ABSTRACT

The nanoscale dispersion of rod-like crystal bundles or aggregates of natural palygorskite (PAL) is not only significant in practical application but is also a challenge. In this paper, phytic acid (PA) was introduced during high-pressure homogenization (HPH) process to simultaneously disperse PAL crystal bundles and restrain the re-aggregation of the dispersed nanorods. SEM, TEM, XRD, FTIR and N_2 adsorption–desorption analyses confirmed that the crystal bundles or aggregates of PAL were highly disaggregated and dispersed to individual nanorod with no disruption to the aspect ratio of rods after being homogenized at 30 MPa, and PA molecules are favorable to dispersion and restrain the re-aggregation of nanorods. The nanoscale dispersion of PAL rods increased the BET specific surface area and Zeta potentials, and effectively improved the colloidal properties. The colloidal viscosity of modified PAL was sharply increased by 110.4% (from 1728 mPa·s to 3636 mPa·s) at the optimal dosage of PA (0.1 wt.%) and the homogenization pressure of 30 MPa, and the suspension stability was clearly enhanced by 71%. This simple disaggregation process provides a new industrial approach to produce nanoscale PAL and extend its application in modern industry.

1. Introduction

Over the past decades, clay minerals as the materials of "greening 21st century material world" have been extensively concerned by virtue of their excellent properties and eco-friendly advantages [1–3]. Palygorskite (PAL) is a naturally available Mg-rich silicate mineral with nanorod-like crystal morphology and theoretical formula of $(Al_2Mg_2)Si_8O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$ [4]. The intrinsic microstructure of PAL endows it with the features of one-dimensional nanomaterials, and so PAL has found potential applications in many fields such as nanocomposites [5–7], catalyst supporters [8–10], crystalline film [11], adsorbents [12,13], colloidal agents [14,15] and pigment [16].

The performance of the materials derived from PAL is highly dependent on the dispersion scale of PAL nanorods [17–19]. However, the rods in natural PAL existed as bundles or "woodpile-like" aggregates because the strong hydrogen bonding and van der Waals interactions existed among rods [20]. These bulk bundles or aggregates are hardly to be dispersed into nanoscale rods by a common treatment method, and so raw PAL is only a precursor of nanomaterials, instead of a real nanomaterial. In that case, the colloidal, adsorption and reinforcing properties of natural PAL are extremely limited, and the derived materials hardly reach a satisfactory performance. Therefore, to disaggregate the crystal bundles of PAL and disperse them into nanoscale becomes the key to develop high-performance PAL-based materials.

Generally, the effective dispersion of PAL rods could be achieved by two processes: (i) using moderate mechanical treatment to take apart the crystal bundles [21]; (ii) introducing chemicals to adjust the surface character and restrain the re-aggregation of dispersed nanorods [22]. Thus far, many methods (i.e., extrusion, high-speed shearing, ultrasound, freezing and grinding) have been used to disaggregate the crystal bundles. However, these methods are subject to two contradictory problems: the disaggregation efficiency is not enough at lower shearing strength, but the excessive mechanical action may break the nanorods and decrease the aspect ratio. From the aggregation state of nanorods in natural PAL [20], it can be noticed that the aggregates or crystal bundles can be disaggregated when the external force can overcome the hydrogen-bonding or van der Waals forces existed among rods. However, in the methods described above, the imposed mechanical forces (i.e., squeezing, shearing, rub) mainly act on the rigid PAL rods, and so they have larger contribution to break rods than to disaggregate them. Furthermore, many of these methods are not suitable for large-scale industrial production.

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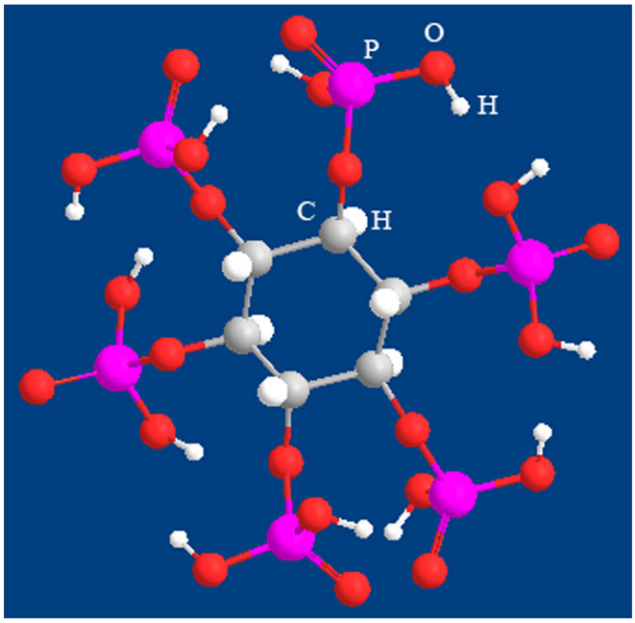
Different from the conventional mechanical treatment methods, high-pressure homogenization (HPH) is a technology designed on the basis of the "Bernoulli principle", and is used for large-scale industrial refinement and dispersion [23]. In the process of homogenization, the dispersion liquids firstly pass through a pressure-adjustable homogenization valve, and the "cavitation effect" was generated due to the sudden release of pressure. The mechanical forces generated from "cavitation effect" mainly act on the gaps among the crystal bundles, and mildly "burst through" the closely intertwined nanorods. So, the crystal bundles can be disaggregated effectively without disrupting the inherent aspect ratio of nanorods [24]. In addition, the dispersants or modifiers can be easily introduced in the process of high-pressure homogenization to realize the simultaneous disaggregation of crystal bundles and the surface modification by a one-step process [22,25]. This is very significant to the large-scale industrial production.

After disaggregation, the highly dispersed nanorods may be re-aggregated during drying due to the higher surface energy of free-standing nanorods, and so moderate modifier is required to restrain the re-aggregation process. Phytic acid (PA) is a saturated cyclic acid with six $-H_2PO_3$ groups (Scheme 1), and is the principal storage form of phosphorus in many plant tissues, especially in bran and seeds [26]. PA is an innoxious, biocompatible and environment friendly organic molecule, and is usually used as corrosion resistant inhibitor of metal materials for the paint or pigment [27]. Besides, PA can interact with the silicate (SiO_2) nanoparticles (with 7.94% of P loading) to form a new material with excellent functional properties [28], and it exhibits a stronger infinity with silicates. It was expected that PA can be attached on the surface of PAL nanorod to adjust its surface properties, decreasing the re-aggregation of nanorods during drying. In addition, it may contribute to alter the self-assembly and "face-to-edge" association capability of PAL nanorods in aqueous solution to improve the colloidal properties. However, there are no researches on the combination of PA with HPH process to improve the dispersion or other performance up to now.

In order to effectively disaggregate crystal bundles of PAL, disperse them into nanoscale rods and improve its colloidal properties, in this paper, natural PAL was modified with PA under high-pressure homogenization to obtain nanoscale PAL. It was expected that the "physical" homogenization action may disaggregate the crystal bundle, and the "chemical" modification with PA may restrain the re-aggregation of PAL nanorods. The effect of nanoscale dispersion treatment on the structure and physico-chemical properties was investigated by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electronic microscopy (SEM), BET specific surface area, and Zeta potential analyses, and the colloidal viscosity, stability and rheological properties were systematically evaluated.



Scheme 1. Molecular structure of phytic acid.

2. Experimental

2.1. Materials

PAL clay mineral was obtained from Guanshan Mine (Anhui, China), and was three-rolled for one time before use. The main chemical composition is Al_2O_3 (10.318%), MgO (14.474%), CaO (0.694%), SiO_2 (69.264%), K_2O (0.985%), and Fe_2O_3 (5.023%). PA (biochemical reagents, BR) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All aqueous solution was prepared with deionized water.

2.2. Dispersion and modification of PAL

Natural PAL was simultaneously dispersed and modified by introducing PA in the HPH process. Typically, PAL was dispersed in the solution of PA (0.1 wt.%) at the solid/liquid ratio of 7/100 under continuous mechanical stirring (800 rpm, 4 h), and then filtered through a 300-mesh sieve to remove the undesirable quartz. The filtered suspension was divided into six equal parts, and then homogenized under different pressures (0 MPa, 10 MPa, 20 MPa, 30 MPa, 40 MPa and 50 MPa) using the high-pressure homogenizer (GYB-3004, Shanghai Donghua High Pressure Homogenizer Factory, Shanghai, China). Finally, the solid product was separated by centrifugation at 4500 rpm, dried at 105 °C for 4 h, ground, and passed through a 200-mesh screen for use. The PA-modified PAL samples under different pressures were marked as pPAL-0, pPAL-10, pPAL-20, pPAL-30, pPAL-40 and pPAL-50, and the PAL sample that is only homogenized at 30 MPa (without adding PA) was marked as PAL-30.

2.3. Measurement of rotation viscosity

The homogeneous dispersion for viscosity test was prepared as the following procedure: 7.0 g of PAL samples was dispersed in 93 mL of deionized water by a high-speed stirring at 11 000 rpm for 20 min. Then, the rotary viscosity of the suspension at different shear times was measured on a ZNN-D6 rotational viscosimeter (Qingdao Camera Factory, China) at 30 rpm, using spindle 3#.

2.4. Measurement of colloidal stability

The colloidal stability of the suspension was evaluated using the conventional sedimentation method in a graduated cylinder. Generally, 2.0 g of PAL sample was dispersed in 120 mL of deionized water, and then high-speed stirring at 11 000 rpm for 10 min to form a uniform dispersion. The dispersion was transferred to a 100 mL graduated cylinder, and it was allowed to stand undisturbed for a certain time. The sedimentation volume was read directly from the graduated cylinder at a set time interval.

2.5. Measurement of rheological property

Shear rheological properties were measured on an Anton Paar Physica MCR301 Rheometer at 25 °C. For steady shear measurements, the shear rate ranged from 0.1 to 200 1/s. A cone-plate with water bath was used for all measurements. The concentration of the PAL suspension for measurement is 7.0 wt.% (mass fraction).