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Research paper

A new one-step method for physical purification and organic modification of sepiolite

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ABSTRACT

Organo-sepiolite (OSep) is conventionally prepared by two main steps, including purification of sepiolite (Sep) and organic modification procedure. These two steps were completed independently by two factories or production lines. In order to save more water, energy, cost and decrease polluted water, a one-step method to purify and organically modify Sep was proposed. Orthogonal test was used to optimize the conditions. X-ray diffraction demonstrated three impurities, i.e., quartz, calcite and talc, were include in the raw ore. The mass content of Sep in raw ore was 30%. By this one-step method, the crystalline impurities were completely removed. Organic modification did not influence on the crystal structure and morphology of Sep. The organic surfactant was not only used as organic modifier, but also used as flocculant, making OSep was easier to be separated from the dispersion. Zeta potential results demonstrated that dispersant increased the negative charges of Sep surface, enhancing the repulsive force between Sep. And the surfactant destroyed the electrical double layers and decrease the surface negative charges. Surfactant cations were adsorbed on the surface of Sep, resulting in hydrophobic surface. Contact angles and gel volumes indicated the compatibility between OSep and oil. The one-step method could not only purify Sep, but also efficiently modified the surface properties. This procedure is simple, environmentally friendly and cost saving, with high efficiency.

1. Introduction

Sepiolite (Sep) is a hydrous magnesium silicate with the ideal formula of $(Mg_{8-y-z}R_y^{3+}\square_z)(Si_{12-x}R_x^{3+})O_{30}(OH)_4(OH_2)_4 \cdot R_{(x-y+2z)/2}^{2+}(H_2O)_4$ (Bailey, 1980). Like all ideal phyllosilicates containing 2:1 layers where there is an octahedral sheet between two opposing tetrahedral sheets, Sep has continuous planes tetrahedral basal oxygen atoms approximately 6.6 Å apart. However, unlike the ideal 2:1 phyllosilicates, the apical oxygen atoms point away from the basal oxygen plane in opposing direction to form ribbons of joined pyroxene-like chains. Because of the discontinuous octahedral sheets, many channels and tunnels occur in the Sep structure, with the size of 3.7 Å × 10.6 Å (Galan, 1996; Giustetto et al., 2011; Guggenheim and Krekeler, 2011). These structures, based on discontinuous sheets with parallel channels, result in a fibrous morphology for Sep. Fiber sizes vary widely but generally range from 0.2 μm to 5 μm in length, 100 nm to 300 nm in width and 50 nm to 100 nm in thickness (Galan, 1996; Wang et al., 2010; Álvarez et al., 2011; García-Romero and Suárez, 2013). Isomorphism substitution usually occurs in the structure of Sep, resulting in extra negative charges of the Sep framework. Hence, some exchangeable cations stay in the channels to balance the negative charges.

Due to its unique structure and morphology, Sep shows high special surface area (Sun et al., 1995; Rytwo et al., 2002; Álvarez et al., 2011), cation exchange capacity of 4–40 cmol/kg (Galan, 1996), rheological properties in polar solvents, adsorptive properties and microporous, etc. Therefore, Sep is usually used as catalyst carriers (Güngör et al., 2006; Núñez et al., 2014), adsorbents (Rytwo et al., 2002; Sabah et al., 2002; Özdemir et al., 2007). In addition, because of the fibrous morphology, Sep fibers can disperse well in high-polarity solvents and build network structure, resulting in excellent rheological properties. Sep was reported as a rheological additive in water-based drilling fluids (Guven, 1981; Murray, 1991; Galan, 1996; Razali and Zafirah, 2011; Altun et al., 2014). Recently, organo-sepiolite (OSep) attracts more attention because its special use in polymer/clay nanocomposites (Tartaglione et al., 2008; García et al., 2011; Garcia-Lopez et al., 2013; Mejía et al., 2014; Fernandez-Barranco et al., 2016) and removal of organic contaminants in water (Li et al., 2003; Rytwo et al., 2011). Thus, Sep is necessary to be organically modified before using in these fields.

However, Sep is naturally associated with other minerals, such as

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quartz, calcite, dolomite, talc and other clay minerals. To extend the utilization of Sep, purification is prerequisite for its all applications. Two steps have to be taken to obtain OSep products. The first step is to extract Sep from the raw ore; the second step is organic modification. Although details may be different, conventional procedures of purifying and organically modifying Sep are concluded as wet methods, including acid reaction, sedimentation, flotation and microwave-assisted method (Zhou et al., 2016). The organic modification of Sep is usually operated in aqueous solution (Li et al., 2003; Chen et al., 2012). Several disadvantages of two-step method can be concluded: (i) complex and detailed steps increase the cost, (ii) these two steps consume large amount of water and may result in more water pollution, (iii) Some repeated steps in both purification and organic modification processes, such as centrifugation, drying and smashing, cost more energy, resources and time, (iv) the flocculant is usually used to separate Sep from the dispersion but harmful for organic modification; the occupation of flocculant molecules on the Sep surface may decrease the loading level of organic modifiers. It will be better if these two steps can be combined into one.

Aiming to cut redundant steps, save more energy, resources and costs, and decrease the wasted water, a one-step method, which combined the purification and organic modification of Sep into a simple, economic and environmentally friendly procedure, is proposed and researched in this work.

2. Materials and methods

2.1. Materials

Raw ore, which contains sepiolite, was obtained from Xiangtan, Hunan, China. Sodium hexametaphosphate (SHMP, purity of 99%), used as a dispersant, was bought from Beijing Chemical works, China. Organic surfactant, benzyl dimethyl octadecyl ammonium chloride (C18) (purity of 99.9%) was bought from Shantou Xilong Chemical Co., Ltd., China. The white oil (No. 5) was bought from China National Petroleum Corporation.

2.2. One-step purification and organic modification of Sep

The one-step method for purification and organic modification of Sep is illustrated in Fig. 1. The raw ore was dried at 60 °C for 24 h; the dried ore was soaked in water (concentration of 150 kg/m^3) for 24 h and naturally disintegrated; SHMP (dispersant) was added into the mixture of ore and water, with the concentration of 1.5 kg/m^3, and the mixture was stirred for 1 h at the speed of 1000 rpm; after centrifugation at the speed of 2000 rpm for 5 min, the suspension was divided into upper dispersion (Sep/dispersant/water) and bottom sediments (impurities); organic surfactants were added into the dispersion and flocculation occurs; by centrifuging at the speed of 4000 rpm and drying at 60 °C, OSep was obtained. These conditions were optimized by orthogonal test (see Section 3.1). The amount of organic surfactant is 5%, 10%, 20% and 30% of the mass of Sep, and the corresponding OSep were marked as 5% C18-Sep, 10% C18-Sep, 20% C18-Sep and 30% C18-Sep. Sep samples were obtained by directly drying Sep dispersion at 60 °C for 24 h before the addition of organic surfactant.

2.3. Characterization

The X-ray diffraction (XRD) analysis was conducted on a Bruker D8 Advance X-ray powder diffractometer operating at Cu Kα radiation, 40 kV, 40 Ma, with a step size of 0.02°, a scan speed of 0.05 s per step and the range of 3 to 70°. The mineral contents of raw ore and purified Sep samples are calculated based on the Chinese standard SY/T 5163-2010 (Analysis method for clay minerals and ordinary non-clay minerals in sedimentary rocks by X-ray diffraction). The calculation follows the formula: $X_i = \left[\frac{I_i}{K_i} / \left(\sum \frac{I_i}{K_i}\right)\right] \times 100\%$, where X_i is the mass percent of phase i; K_i is the intensity ratio of phase i to corundum with the mass ratio i/corundum = 1:1. In this case, the K-value of minerals are listed in Table 1. The transmission electron microscope (TEM) analysis was conducted on a JEM 1200EX TEM equipment and operated at the voltage of 100 kV. Zeta potentials of sample dispersions were tested on a Malvern ZETASIZER Nano-ZS90 equipment. Contact angle tests were conducted on a contact angle measurement JC200D and the measurement was performed with distilled water. OMt samples for contact angle test were pressed to tablets under the pressure of 15 MPa for 1 min. Then a drop of distilled water dripped on the surface of OMt tablet and the picture was recorded simultaneously. The gel volume results were obtained by adding dispersion of sample in white oil (concentration of 0.03 kg/L) into a graduated cylinder (100 mL) with a stopper and standing for 24 h. The dispersion was stirred at 8000 rpm for 20 min before being added into the graduated cylinder.

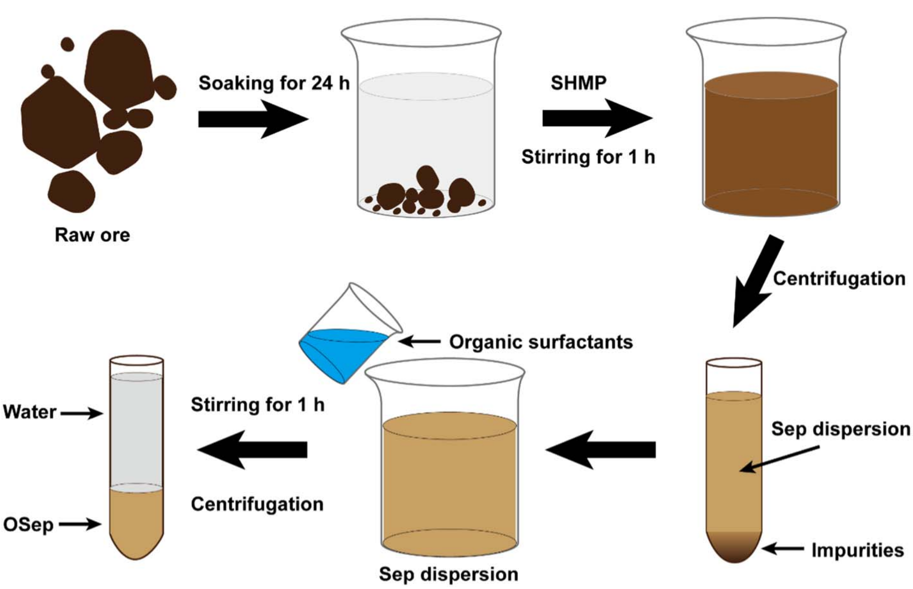

Fig. 1. Procedure of one-step purification and organic modification of sepiolite.