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Water dispersible avermectin-layered double hydroxide nanocomposites modified with sodium dodecyl sulfate

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ABSTRACT

Sodium dodecyl sulfate was utilized to modify the avermectin-layered double hydroxide nanohybrids for the preparation of water dispersible nanocomposites, resulting in the successful conversion of hydrophobic surfactant monolayer structure on the solid surface to hydrophilic bilayer. Concentrations of SDS and NaCl had important effects on the bilayer formation, and the highest suspensibility of the obtained nanocomposites reached 97.6%. All the samples were characterized using Fourier transform-infrared spectroscopy, X-ray diffraction, transmission electron microscopy, element analysis, zeta potential and contact angle measurements. It was found that the prepared materials could well control the release of avermectin, and the prepared nanocomposite would be a promising candidate for water dispersible controlled release formulation.

1. Introduction

Layered double hydroxides (LDHs), also known as anionic clays, have recently attracted considerable attention because of their useful properties as catalysts (Gerardin et al., 2008; Tong, et al., 2010), magnetic materials (Coronado et al., 2008), drug containers (Zhang et al., 2006; Liu et al., 2008; Li et al., 2009), DNA or biomolecules carriers (Choy et al., 2000; Darder et al., 2005; Desigaux et al., 2006; Costantino et al., 2008) and supports for agrochemicals (Bin-Hussein et al., 2002; Cardoso et al., 2006). LDHs consist of layers, containing the hydroxides of different kinds of metal cations and possessing an overall positive charge, which is balanced by intercalation of anions in the hydrated interlayer space (Evans and Duan, 2006). LDHs can be represented by the general formula (Khan and O'Hare, 2002; Leroux and Taviot-Gueho, 2005; Williams and O'Hare, 2006) $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\bullet mH_2O$, where M^{II} and M^{III} are divalent and trivalent metal ions, respectively, A^{n-} is an interchangeable compensating anion entrapped in the interlayer space, m is the number of mol of cointercalated water per formula weight of the compound, and x is defined as the $M^{III}/(M^{II}+M^{III})$ ratio.

The anionic exchange capability of LDHs can be utilized to incorporate surfactant organic anions into the interlayer space for preparing organo-LDHs (Clearfield et al., 1991; Newman and Jones, 1998; Xu and Braterman, 2003; Mohanambe and Vasudevan, 2006; Moyo et al., 2008). Converting of LDH hydrophilic surface to hydrophobic and accessibility of the interlayer region make organo-LDHs promising candidates for pollutants adsorbents (You et al., 2002a, 2002b; Zhao and Nagy, 2004; Chuang et al., 2008), nanocomposites (Tseng et al., 1996; Costa et al., 2008; Costantino et al., 2009b), corrosion resistance coatings (Zhang et al., 2008), emulsifier (Wang et al., 2008), flame retardant (Zhang et al., 2010), and pesticide carriers for controlled release formulations of charge neutral or poor water soluble organic species (Celis et al., 2000; Wang et al., 2005; Costantino et al., 2009a; Qiu et al., 2009).

Pesticide formulations developing should meet the requirements of high efficiency, low toxity, prolonged protections and lower impact on environment. At present, many effective and important pesticides are charge neutral and poor water soluble. It is preferable to prepare controlled release formulations for tuning their release rate. By now, many hydrophobic pesticides have been successfully intercalated into organo-LDHs interlayer regions, including triadimefon (Celis et al., 2000), chlorpyrifs (Wang et al., 2005), avermectin (AVM) (Qiu et al., 2009). However, most studies are limited to altering the intrinsic hydrophilic property of LDHs to hydrophobic for adsorbing or intercalating hydrophobic organic compounds. There are few reports involving changing the hydrophobic surface of organo-LDHs intercalated with poor water soluble pesticides to hydrophilic surface, which is of significant importance for improving the water dispersity of pesticide formulations.

In spite of the evident progress made in the pesticide hybrid preparation, it would be more effective and widely applicable if stable

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uniform water dispersions of hybrids could be obtained easily, which is a pivotal prerequisite for successful development of wettable powder, an environment friendly formulation without using any toxic organic solvent. In the present work, AVM, a charge neutral and poor water soluble pesticide (Qiu et al., 2009), was selected as a model molecule, which was initially intercalated into SDS modified LDHs (SDS-LDH, SL) to form nanohybrids (AVM-SDS-LDH, ASL). Then, additional SDS was uptaken in the presence of NaCl to modify the nanohybrid outer-surface to obtain water dispersible nanocomposites (AVM-SDS-LDH@SDS, ASLS). Effects of SDS and NaCl concentrations and treating time on the suspensibility of the composites were investigated. The properties, chemical compositions and structural aspects of the obtained wettable powder were investigated by zeta potential and contact angle measurements, element analysis, Fourier transform-infrared spectroscopy, X-ray diffraction and transmission electron microscopy. The release behavior of AVM from the composites was also explored.

2. Experimental

2.1. Materials

Avermectin sample (technical grade, white powder crystalline) was provided by Hebei Voke Biochemical Co. Ltd, China. It is a complex of avermectin B1a and B1b, and its total weight content is 94.2%. Analytical-grade sodium dodecyl sulfate (>97.0%) was supplied by Tianjin Bodi Chemical Co. Ltd. The metal chloride salts, ammonia solution, absolute ethanol and sodium hydroxide, obtained from Sinopharm Chemical Reagent Co. Ltd. China, were of analytical purity and used as received. All experiments were conducted with deionized water that was passed through an AFZ-1000-U purification system (Aquaplus), with a resistivity of 18.2 MΩ cm.

2.2. Preparation of the pristine LDHs, SDS modified LDHs and AVM-SDS-LDH nanohybrids

Samples of LDH, SL and ASL were synthesized using a procedure that was modified from our previous report (Qiu et al., 2009). The pristine LDHs sample was synthesized by the coprecipitation method under a N_2 atmosphere. The mixed salt solution of $MgCl_2 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$ at a molar ratio of 2:1 was prepared with a total metal ion concentration of 0.5 mol/L. Then diluted ammonia solution (3.5 mol/L) was added to the mixed salt solution under stirring at a speed of 25 mL/min until the final pH value reached 9.5. The precipitate was aged for 1.5 h in the mother solution at room temperature and then filtered and washed with pure water. The filter cake held in a glass bottle was peptized at a constant temperature of 80 °C in an oven for 24 h, to obtain pristine LDHs sol sample. The solid content and density of the sol sample were 12.2 wt.% and 1.05 g/ml respectively.

SL samples were synthesized by an ion-exchange method. A certain amount of the pristine LDHs sol samples were added in a desired volume of 0.09 mol/L SDS solution under stirring to form SDS/LDH suspensions with molar ratio of SDS to Al^{3+} fixed at 0.5. The pH values of the suspensions were adjusted to 10 ± 0.2 by 1 mol/L NaOH solution. The suspensions were kept under stirring for 2 d at room temperature, then they were filtrated and washed with deionized water for three times. The prepared SL samples were collected as filter cake and stored in a ground-glass bottle, avoiding the crystalline aggregation by direct drying. The solid content of SL sample was measured to be 50.6 wt.%.

Evaporating solvent enhanced intercalation method was used to synthesize ASL nanohybrids. After 2000 mL of 7.8 g/L AVM ethanol solutions was prepared, 65.9 g of wet SL samples was added, and the solid content of the system was 2.0 g/120 mL. The suspension was heated and distilled to remove about 1500 mL of ethanol under stirring at about 50 °C within 3 d. Then, the ASL nanohybrids were filtered with absolute ethanol for three times and used directly for the fabrication of ASLS. For the benefit of keeping the nanohybrids dispersible, drying process is omitted. The measured solid content of ASL was 51.8 wt.%.

2.3. Fabrication of AVM-SDS-LDH@SDS nanocomposites

5.79 g of ASL nanohybrids filter cake, with net solid mass of about 3.0 g, was mixed with 100 mL water under stirring at 60 °C, then weighted SDS (from 0.3456 g to 1.4688 g) was added, and a suitable amount of sodium chloride was put in the mixture slurry to promote the SDS adsorption on the hybrid surface. The salt concentration was varied in the range of 0–0.20 mol/L in the experiments. After 2–4 h of stirring time, the suspensions were filtrated and washed with deionized water and the ASLS nanocomposites were obtained. The products were dried at 40 °C, ground, and stored in sealing bag before use.

2.4. Characterization methods

2.4.1. Measurements of suspensibility, zeta potential and contact angle

The suspensibility was measured according to CIPAC (Collaborative International Pesticides Analytical Council) MT 15.1 (Katayama et al., 1992). In brief, 1 g of ASLS nanocomposite was added to 250 mL of CIPAC Standard Water D (342 ppm hardness) in a 250 mL stoppered graduated measuring cylinder. Suspension was made through 30-times inversion of the cylinder. After the cylinder was kept standing without disturbance in a water bath (20 ± 1 °C) for 30 min, the top 9/10ths of this dispersion was drawn off with an aspirator, then the rest was transferred into a preweighted beaker to evaporate the water completely, and the content of ASLS in the bottom 1/10th was determined. The suspensibility was calculated from the following equation:

$$\textit{suspensibility}(\%) = \frac{(m_1 - m_2)}{m_1} \times \frac{10}{9} \times 100$$

where m_1 is the mass of ASLS in the initial sample taken to prepare the suspension (g), m_2 is the mass of ASLS in the retained one-tenth of the suspension (g).

Zeta potentials of the pristine LDH particles and corresponding derivatives were measured with a JS94J2 microelectrophoresis instrument at pH value of 7.2. Static contact angles were measured through the compressed disk method using JC2000C8 contact angle measurer. The sample powder was compressed into circular disk with a Carver press (4350.L model) at a pressure of 16 MPa (Wang et al., 2008), and the disk thickness was about 1 mm. Deionized water drops were used in the measurement.

All tests were made in triplicate and the final values were an average of measurements.

2.4.2. Chemical composition and AVM loading amounts analysis

Compositional analysis for Mg^{2+} and Al^{3+} ions were performed by inductively coupled plasma emission spectroscopy (ICP) using a Leeman Prodigy XP instrument. C, H, S, O microanalysis were carried out using a Vario EL III elementary analyzer. The AVM loading amounts (A_{AVM}) in ASL nanohybrids and ASLS nanocomposites might be evaluated by using the elemental analysis data; at the same time, those were also measured by a TU-1901 model UV–Vis spectroscope using the method described in our previous report (Qiu et al., 2009).

2.4.3. Infrared spectrum, X-ray diffraction and transmission electron microscope investigations

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet iS10 spectrometer in air at room temperature using a KBr disc technique between 400 and 4000 cm^{-1}. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku D/MAX-2500/PC diffractometer, using a Cu Kα irradiation source (λ 1.54050 Å, 40 kV and