



Research paper

Facile batch synthesis of porous vaterite microspheres for high efficient and fast removal of toxic heavy metal ions



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ABSTRACT

The contamination of water by heavy metals has become one of the greatest threats to global ecological systems. Vaterite, in spite of the excellent performance to remove toxic metal ions, is difficult to be prepared with a large scale production, which limits its further industrial application. To this end, we developed a green and rapid approach to prepare in batch uniform porous vaterite/chitosan oligosaccharide (COS) hybrid microspheres (V-COS) at room temperature. Especially in the presence of 5 g L^{-1} COS, high vaterite content (nearly 100%) and large scale production of CaCO_3 microspheres were obtained within only 2 min without any other organic solvent. SEM images showed that an individual hybrid microsphere was composed of many nanoparticles, and TEM results demonstrated that these nanoparticles consisted of multiple nanocrystals. It was found that the concentration of COS and high shearing stirring were the key issues for the high production of V-COS. Based on the results the formation mechanism of V-COS was proposed. Their application for removal of lead and cadmium ions from aqueous solutions was investigated. The high and fast adsorption capacity for Pb^{2+} and Cd^{2+} ions were achieved with the adsorption amount up to 1884 and 156 mg/g within 6 min, respectively, which were much higher than that of rhombohedron CaCO_3 obtained without stirring (R-COS). The porous vaterite hybrid microspheres obtained with such large scale production has never been reported before, and this will lay foundation for its further wide applications.

1. Introduction

At present, the contamination of freshwater has become a worldwide problem and brings many detrimental effects on environment and human health. Among all kinds of water contaminants, heavy metals cannot be neglected because of their high toxicity to living organisms [1]. Calcium carbonate (CaCO_3), existing in the exoskeletons of mussel shells, egg shells and snail shell [2–5], has been widely investigated due to its highly regular arrangement structure and excellent mechanical properties. Moreover, CaCO_3 has already been applied in many industrial areas, such as heavy metal ion-removal, papermaking, plastics, paints, cosmetics, rubber industry, etc. [6,7]. However, the adsorption efficiency of natural and commercial calcite for heavy metal is very low because of its low stability and surface area [8]. Vaterite, commonly in the morphology of porous microspheres, has shown great potential in biomedical and industrial application due to its high surface area, solubility, and low specific gravity [9–11]. Recently, these porous vaterite

microspheres have been used to remove toxic heavy metal ions and show high adsorption capacity for Pb^{2+} and Cd^{2+} [12,13]. Usually vaterite can be prepared by the constant composition method using CaCl_2 and Na_2CO_3 as raw materials [14–19]. However, vaterite can easily transform to the thermodynamically stable calcite in aqueous solution, because it is the least stable phase among three common polymorphs of calcium carbonate. How to stabilize vaterite, therefore, has become an important issue.

It has been found that some organic substances containing amino and hydroxy group, such as protein, dopamine, peptides and carboxymethyl chitosan, can induce the nucleation and growth of vaterite crystals, because of the strong interaction between Ca^{2+} and the charged amino group [20–22]. In this way the stable vaterite-organic hybrid microspheres can be obtained. The most critical factor is the usage of water-soluble additives, which has been demonstrated to stabilize the amorphous calcium carbonate (ACC) and control the morphology and polymorphs of CaCO_3 crystals [4,5,23–26]. Kim et al.

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prepared the spherical vaterite crystals in the presence of dopamine [27]. At the same time, a number of proteins and synthetic substrates were used to induce the nucleation and growth of vaterite CaCO_3 crystals [20,21]. Recently, carboxymethyl chitosan was used to prepare calcium carbonate hybrid microspheres and nanospheres [28]. But the high cost of these organic substances containing amino group, harsh reaction conditions and low conversion yield still exist for these methods.

It is worth mentioning that the concentration and volume of CaCl_2 and Na_2CO_3 solutions used in above work is too low (0.33 M, for example) to prepare in large-scale vaterite microspheres, while increasing the concentration and volume may lead to the formation of more rhombohedron CaCO_3 or serious aggregation of spherical vaterite [29]. As reported by Ma [30], only 0.33 g product was obtained when mixing 10 mL of aqueous CaCl_2 and Na_2CO_3 solutions together at equal concentration (0.33 M). In addition, 0.125 g of CaCO_3 /carboxymethyl chitosan (CMC) hybrid microspheres were prepared by mixing with equal volumes (2.5 mL) and concentrations (0.5 M) of Na_2CO_3 and CaCl_2 solutions in the presence of carboxymethyl chitosan [28]. In addition, hierarchical CaCO_3 meso/macroporous hybrid materials can be obtained using a gas-diffusion method, whose production was even less than that obtained by the direct mixing method [12].

Therefore, in this study, a facile batch, green and rapid method to fabricate vaterite-organic hybrid microspheres is reported. Nearly 100% spherical vaterite was quickly obtained, even fixing the concentration of Na_2CO_3 and CaCl_2 solutions as high as 1.0 M, when choosing chitosan oligosaccharide (COS) as the crystal regulator for vaterite due to its good solubility in water, non-toxicity, low cost and biological activities [31]. Compared with carboxymethyl chitosan [28], COS doesn't need chemical modification and contains more amino and hydroxy groups, which will enhance the interaction with Ca^{2+} . The effect of the COS concentration, stirring speed as well as the reactant concentration on the morphology, size and surface properties of vaterite were investigated. A possible growth mechanism of vaterite with higher-order structure was proposed. The obtained vaterite/COS (V-COS) hybrid microspheres were used to remove Pb^{2+} and Cd^{2+} metal ions. These vaterite hybrid microspheres will be of great interest to polluted water treatment because of the easy synthesis, low cost, and non-toxicity.

2. Materials and methods

2.1. Materials

All the reagents employed here were commercially available and used as received. Chitosan oligosaccharide (COS, food grade, 95% degree of deacetylation, $M_w \leq 5000$ g/mol) was purchased from Golden-Shell Pharmaceutical Co., Ltd (Zhejiang, China). Lead nitrate ($\text{Pb}(\text{NO}_3)_2$, AR) and cadmium chloride (CdCl_2 , AR) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Calcium chloride (CaCl_2 , AR) and sodium carbonate (Na_2CO_3 , AR) were supplied by Kelong Chemical Industries Reagent Co. (Chengdu, China).

2.2. Preparation of V-COS hybrid microspheres

The V-COS hybrid microspheres were prepared by rapidly mixing solutions of CaCl_2 and Na_2CO_3 in the presence of COS. Briefly, 20 g L^{-1} of COS stock solution, 1.0 M of Na_2CO_3 solution and 1.0 M of CaCl_2 solution were prepared by dissolving the corresponding reagents in deionized water at room temperature. Subsequently, 1.0 M CaCl_2 aqueous solution was rapidly poured into the mixed solution of Na_2CO_3 and COS under stirring at the speed of 10,000, 20,000 rpm with a high-shear dispersion homogenizer (T18 digital ULTRA-TURRAX[®], Germany) for 2 min. The detail preparation conditions for different CaCO_3 microparticles are listed in Table S1. The hybrid microspheres were collected by filtration and washed three times with deionized water,

followed by lyophilization and storage in a vacuum desiccator at room temperature. The R-COS powder was obtained by the same procedure without stirring.

To increase the production yield of vaterite/COS hybrid microspheres, 250 mL mixed solution of Na_2CO_3 and CaCl_2 (1 M) containing COS (5 g L^{-1}) was used and the stirring speed was controlled at 10,000, 20,000 and 25,000 rpm. After drying, approximately 25 g of hybrid microspheres were obtained. The detailed preparation conditions of different CaCO_3 micro-particles are also shown in Table S1.

2.3. Removal of heavy metal ions

$\text{Pb}(\text{NO}_3)_2$ and CdCl_2 were used as the sources to prepare Pb^{2+} (3000 mg L^{-1}) and Cd^{2+} (1400 mg L^{-1}) solutions, respectively. As-prepared V-COS and R-COS powder (0.1 g) were added to 100 mL of the Pb^{2+} solution under stirring for 3 h. At different time intervals, the solids and liquids were separated by centrifugation and the concentration of Pb^{2+} remained in the solution was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (IRIS Advantage, TJA solution). The experiment of Cd^{2+} ion removal was conducted in the same way. The adsorption capacity (q_t) of CaCO_3 particles towards metal ions at time of t was calculated according to the follow equation:

$$q_t = \frac{C_0 - C_t}{W} \times V \quad (1)$$

Where C_0 and C_t (mg L^{-1}) are the initial concentrations of heavy metal ions and final concentrations after ion exchange, respectively; W is the mass of CaCO_3 used as the adsorbent (g) and V is the volume of the solution (L).

2.4. Characterization

The morphology of CaCO_3 particles was examined by a scanning electron microscope (SEM) (Philips XL-3, FEI, Bend, OR, USA) with an accelerating voltage of 20 kV. Samples were coated with a thin layer of gold before test. The crystal structure of V-COS was analyzed by X-ray diffraction (XRD) (DX-1000 CSC, Fangyuan, Dandong, China) within the range of 20°–70° at a scanning rate of 3.6° min^{-1} . The accelerating voltage and the applied current were 40 kV and 25 mA, respectively. Fourier transform infrared (FT-IR) analysis was conducted with a Thermo Nicolet 670 spectrometer from 4000 to 400 cm^{-1} . Thermogravimetric analysis (TGA) measurement was performed on a TG209 F1 (NETZSCH, Germany) with a heating rate of 10 °C min^{-1} under a steady flow of nitrogen (50 mL min^{-1}) within the temperature range from 40 to 800 °C. The specific surface area was measured by the Brunauer-Emmett-Teller (BET) method using a Quadrasorb SI specific surface area analyzer (Quantachrome, Boynton Beach, FL, USA). Transmission electron microscopy (TEM) techniques, such as high-resolution TEM (HRTEM), scanning TEM (STEM) and selective area electron diffraction (SAED), were conducted on a Philips CM 200 Transmission Electron Microscope with an accelerated voltage of 120 kV. The mean particle size and size distribution of as-prepared V-COS microspheres were measured by laser diffraction (Mastersizer 2000, Malvern). The zeta potential (ζ) of V-COS was dispersed in ethanol (50 mg mL^{-1}) and determined by a zeta potential instrument (Zetasizer Nano ZS90, Malvern).

3. Results and discussion

3.1. Effect of COS concentration on V-COS preparation

Just as outlined in the introduction, some organic substances containing amino groups play an important role in the formation of vaterite. Only rhombohedral calcium carbonate is obtained in the absence of COS without stirring (Fig. S1). Therefore, COS is chosen as a crystal

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