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Preparation of polyacrylamide/silica composite capsules by inverse Pickering emulsion polymerization

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ABSTRACT

Polyacrylamide/silica (PAM/SiO_2) composite capsules were synthesized by inverse Pickering emulsion polymerization. Silica nanoparticles modified with methacryloxypropyltrimethoxysilane (MPS) were used as a stabilizer. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, and thermal gravimetric analysis (TGA) were used to characterize the morphology and composition of the composite capsules. SEM and TEM images showed that capsules consisted of a particle shell and a polymer inner layer. The capsule size depends on the nanoparticle concentration in the continuous phase. The composite rigidity largely depends on the acrylamide concentration. FTIR and TGA results indicated the existence of polyacrylamide and SiO_2 in the composite particles. Aqueous Hg(II) removal testing by the PAM/SiO_2 composite capsules indicated promising potential for removing heavy metal ions from wastewater.

1. Introduction

Pickering emulsions stabilized by solid particles have attracted much recent attention. In Pickering emulsion processes, solid particles are irreversibly anchored on droplet surfaces (Cameron, 1992). After polymerization, solid particles form an inorganic shell, while the polymer forms an organic core. In this way, the favourable properties of inorganic nanoparticles and polymers can be combined.

Chen, Colver, and Bon (2007) used Pickering emulsion droplets as polymerization vessels for preparing TiO_2 organic/inorganic hollow microcapsules. Bon, Cauvin, and Colver (2007) synthesized raspberry-shaped interpenetrating polymer network reinforced microcapsules by a radical polymerization inside the colloidosomes and imparted the raspberry core–shell morphology. Duan, Chen, Zhou, and Wu (2009) synthesized poly(*N*-isopropylacrylamide)/silica composite microspheres via inverse Pickering suspension polymerization, using a silica particle stabilizer. The release properties of the synthesized microspheres could be controlled by temperature. The combination of monomer droplet, water, and solid particles in such Pickering emulsion processes allows various inorganic coated polymer microspheres to be prepared, including polyaniline/modified silica (He & Yu, 2007), polystyrene/clay (Voorn, Ming, & van Herk, 2006), poly(vinyl acetate)/SiO_2 (Wen, Tang, Chen, & Wu, 2008), polystyrene/ZnO (Chen, Liu, Liu, & Kim, 2010), polystyrene/SiO_2 (Yin, Zhang, Zhang, & Yin, 2010; Zhang, Fan, Tian, & Fan, 2012), polyaniline/clay (Palaniappan & John, 2008), and polyaniline/nano-Fe_3O_4 (Zhang, Wu, Guo, Chen, & Zhang, 2009; Zhang, Wu, Meng, Guo, & Chen, 2009) nanoparticles.

Polyacrylamide (PAM) is water-soluble and an efficient adsorbent and flocculent. It has been extensively investigated for wastewater treatment and sludge dewatering applications (Babel & Kurniawan, 2003; Sreedhar & Anirudhan, 2000; Liu & Guo, 2006). PAM is susceptible to swelling and has poor mechanical properties (Vallés, Durando, Katime, Mendizábal, & Puig, 1999; El-Rehim, 2005), so more efficient adsorbents are required. Silica is a commonly used supporting material, and SiO_2 can provide a hard porous inorganic matrix and mechanically control the swelling without affecting PAM adsorption. Ramadan, Ghanem, and El-Rassy (2010) compared the mercury removal efficiency from aqueous solutions using silica, PAM, and silica-PAM aerogels. The hybrid aerogel exhibited favourable adsorption capacity after regeneration, and did not swell. Fabrication of PAM/SiO_2 composite capsules has been proposed using sol–gel (Jang & Park, 2002), step by step grafting (An, Feng, & Gao, 2009), inverse micro-emulsion polymerization (Bhardwaj, Singh, Singh, & Aggarwal, 2008) and

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dispersion polymerization (Cao, Shi, Cao, & Zhou, 2008) methods. To the best of our knowledge, Pickering emulsion polymerization has not yet been used for its preparation. PAM/SiO_2 composite capsules are expected to exhibit better adsorption properties than their composite particle analogues because of their porous hollow structure.

Our previous study investigated the preparation of inorganic–organic composite particles by Pickering emulsion polymerization. Polystyrene/nano-SiO_2 composite microspheres were prepared using modified SiO_2 nanoparticles as stabilizers (Zhang, Wu, Guo et al., 2009; Zhang, Wu, Meng et al., 2009). The particle concentration and wettability, and dispersion pH affected the morphology of the synthesized composite particles. Temperature-responsive poly(*N*-isopropylacrylamide)/poly(methyl methacrylate)/silica hybrid capsules were also prepared by inverse Pickering emulsion polymerization (Zhang, Wu, Guo, Chen, & Zhang, 2010). It is a promising method for preparing organic/inorganic hybrid materials, and is worthy of further investigation for preparing dispersed well-defined microspheres.

In this study, PAM/SiO_2 composite capsules with a PAM inner layer and SiO_2 shell were prepared by inverse Pickering emulsion polymerization. The products were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy and thermal gravimetric analysis (TGA). Sorption properties for the removal of aqueous Hg(II) were also investigated.

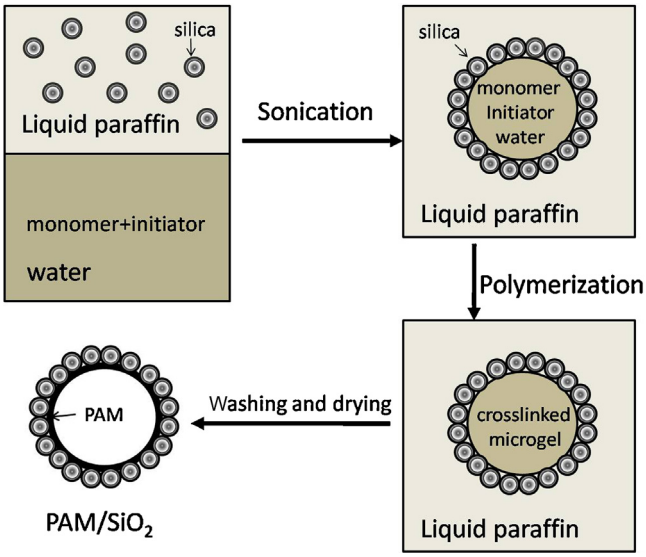
2. Experimental

2.1. Surface modification of SiO_2 nanoparticles

A total of 5 g of 20 nm diameter SiO_2 nanoparticles (Beijing Spaceflight Saide Corp., China) was added to 230 mL of cyclohexane/water (v/v, 12/1) (cyclohexane, Beijing Chemical Reagent Corporation, China; purity >99%; deionized water, self product of Beijing University of Chemical Technology) under ultrasonic agitation. Methacryloxypropyltrimethoxysilane (MPS, Beijing Chemical Reagent Corporation, China; purity 99%) in 20 mL of cyclohexane was added dropwise to the silica dispersion, and the reaction heated at 65 °C for 24 h. The reaction mixture was centrifuged and the SiO_2 particles were thoroughly washed with deionized water and ethanol (Beijing Chemical Reagent Corporation, China; purity >99.7%). The resulting modified SiO_2 nanoparticles were dried under vacuum at 60 °C for 12 h.

2.2. Synthesis of PAM/SiO_2 composite capsules

The preparation process is shown in Scheme 1. In a typical procedure, 0.4 g of acrylamide (AM, Beijing Beihua Fine Chemical Products Co Ltd., China; purity 99.9%), 0.004 g of *N*,*N*-methylenebisacrylamide (NMBAM, Beijing Chemical Reagent Corporation, China; purity >99.7%) and 0.02 g of ammonium persulfate (APS, Beijing Chemical Reagent Corporation, China; purity >98%) were dissolved in 5 g of deionized water to form a monomer solution. Modified SiO_2 nanoparticles (0.3 g) dispersed in 10 g of liquid paraffin were mixed with the monomer solution. A stable Pickering emulsion was generated via digital sonication for 20 min, at 70% amplitude with a 40 s pause for every 1 min of sonication. The resulting Pickering emulsion was transferred to a 100 mL three-necked flask equipped with a nitrogen inlet and reflux condenser. The emulsion was polymerized at 72 °C for 24 h. The product was filtrated, alternatively washed with deionized water and ethanol three times, and dried at 60 °C in vacuum for 12 h. PAM hydrogel was prepared similarly, but without the addition of SiO_2 nanoparticles.



Scheme 1. Fabrication process of the PAM/SiO_2 composite capsules.

2.3. Characterization

An optical microscope (Olympus BX41TF, Japan) fitted with a digital camera was used to observe the Pickering emulsion. Microsphere structure and morphology were characterized using TEM (JEM-3010, JEOL Technics Co. Ltd., Japan) and SEM (Hitachi S-4700, Tokyo, Japan). FTIR spectra were recorded as KBr pellets using a FTIR spectrometer (Nicolet-8700, Thermo Electron Corporation, America), over the range 4000–300 cm^{-1} from 32 scans. TGA was conducted using a thermal analysis instrument (STA-449C, NETZSCH Corporation, Germany) under a nitrogen gas flow rate of 25 cm^3/min and scanning rate of 10 °C/min. Contact angles were measured using tensiometer machine (Krüss K100, KRüSS GmbH, Germany).

2.4. Hg(II) adsorption experiments

Experiments were performed in a 500 mL flask in a shaking thermostatic bath (SHZ-B, China) at 170 rpm and 40 °C. In each experiment, 100 mg of SiO_2, PAM, or PAM/SiO_2 composite capsules was added to 150 mL of aqueous $HgSO_4$ solution (Hg concentration of 20 mg/L). After adsorption, 4 mL of solution was removed and centrifuged. The separated upper clear liquid was mixed with a given amount of ethylenediaminetetraacetic acid, NaOH, TritonX-100, and dithizone solution in a 25 mL flask, and then diluted with deionized water. Absorbance was measured using a UV spectrophotometer (UV-2501, Japan) at 556.5 nm, with a solvent blank as a reference. The Hg(II) concentration was calculated according to the as-obtained function relationship.

3. Results and discussion

3.1. Formation of Pickering emulsion

Particle wettability is quantified by the contact angle θ, and is an important parameter influencing particle location in the emulsion formation (Binks & Fletcher, 2001). A particle is held