Materials Chemistry and Physics 192 (2017) 72–77

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Polyacrylamide-based inorganic hybrid flocculants with self-degradable property

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HIGHLIGHTS

- A new polyacrylamide (PAM)-based inorganic hybrid flocculants with self-degradable property was developed.
- TiO_2 nanoparticles show a unique surface-initiated property under the condition of visible light.
- We designed a facile strategy for the synthesis of inorganic soil@TiO_2@PAM hybrid materials.

ARTICLE INFO

Article history:
Received 30 March 2016
Received in revised form
18 January 2017
Accepted 23 January 2017
Available online 27 January 2017

Keywords:
TiO_2 nanoparticles
Hybrid materials
Chemical synthesis
Surface properties
Nanostructures

ABSTRACT

Polyacrylamide (PAM)-based inorganic hybrid materials are of great potential as flocculants in soil-liquid separation. Herein, we reported the design of inorganic soil-TiO_2-PAM hybrid materials using a unique process, which involved coating of titanium dioxide (TiO_2) nanoparticles on the surface of inorganic soils and subsequent polymerization of acrylamide (AM) on these nanoparticles under visible light. Inorganic soils including kaolin, bentonite, montmorillonite and diatomaceous earth were used to control the volume and to reduce the cost, and the TiO_2 nanoparticles accelerated PAM degradation. The nanoparticles initiated AM polymerization directly under visible light, thus providing a facile strategy for the synthesis of new organic-inorganic hybrid flocculants. The obtained hybrid materials were characterized using Fourier transform infrared spectroscopy and transmission electron microscopy. The degradation of PAM initiated by UV irradiation exceeded 24% in 2 h, depending on its initial concentration.

1. Introduction

The reserves of the Canadian oil sand are at least 177 billion barrels of oil, which can be economically recovered using current technologies [1]. Large volumes of mature fine tailings (wastes) are produced during exploitation, 83% of which is water (by volume), leading to serious environmental problems. For example, the storage of the mature fine tailings has occupied a lot of land for several decades and a large amount of water has been wasted [1,2]. To this end, numerous dewatering technologies have been developed since 2000, most of which use commercial polyacrylamides (PAMs) as flocculants initially developed for other applications [3–5].

Generally, inorganic-PAM hybrid materials excel traditional PAM flocculants in sewage and oil sand tailing treatments [6]. Inorganic component, which is usually a carrier, is typically coated by organic compounds with high molecular weights, e.g. PAM. To obtain a material with strong ability of solid/liquid separation, hybrid flocculants, such as $CaCl_2$-PAM, $Al(OH)_3$-PAM and cationic

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http://dx.doi.org/10.1016/j.matchemphys.2017.01.064
0254-0584/

polymeric microparticles, have been synthesized in previous studies [7–9].

However, the development of inorganic-PAM hybrid flocculants remains challenging [10]. Firstly, the polymer concentration and configuration affect the adsorption of hybrid flocculants on the surface of model particles [11–13]. The efficiency of flocculation can be increased by coating inorganic particles with high-grafting-density PAM [1]. Given the barrier induced by low polymer concentration, the initial polymer layer deposited on the particle surface delays further polymer adsorption through electrostatic repulsion. As a result, the "grafting from" method has attracted particular attention, which needs a complicated technology including linkage of initiator onto particles and surface-initiated polymerization of monomer on the particle surface [14]. Therefore, researchers have endeavored to develop simpler processes to synthesize inorganic-PAM hybrid flocculants with high-grafting-density PAM [15].

Secondly, PAM on particle surface may degrade during a long time, and the resulting acrylamide (AM) may threaten the environment, water resource and even the health of human being [20]. Titanium dioxide (TiO_2) nanoparticles can accelerate the photocatalytic degradation of PAM effectively, but they are hardly dispersible in PAM solution [15–17].

To solve the above-mentioned problems, we reported the design of inorganic soil-TiO_2-PAM hybrid materials using an alternative process, which involved coating of TiO_2 nanoparticles on the surface of inorganic soils and subsequent polymerization of AM on these nanoparticles under visible light. Inorganic soils including kaolin, bentonite, montmorillonite and diatomaceous earth were used to control the volume and to reduce the cost, and the TiO_2 nanoparticles accelerated PAM degradation.

2. Experimental

2.1. Materials

AM (>99.0%), aqueous sodium formate, aqueous aluminum chloride, cadmium iodide and absolute ethanol were obtained from Tianjin Kermel Chemical Reagent Co., Ltd. Butyl titanate was purchased from Tianjin Fuchen Chemical Reagent Factory. Kaolin, bentonite, diatomaceous earth and montmorillonite were supplied by Shenzhen Haichengxingye Chemical Co., Ltd.

2.2. Synthesis of composites consisting of inorganic soil and TiO_2 nanoparticles

TiO_2-inorganic composites were prepared by the sol-gel method. In detail, 3 g of kaolin was mixed with 75 ml of absolute ethanol in a beaker (250 ml). Then 21 ml of butyl titanate was added. After 20 min of ultrasonic dispersion, the mixture was heated to 35 °C in water bath. Subsequently, a mixed solution comprising 75 ml of absolute ethanol, 6 ml of deionized water and 0.9 ml of diluted hydrochloric acid (12 mol/L) was added dropwise under vigorous stirring. After being heated at 35 °C for 30 min, the mixed liquid was reacted at 70 °C to fulfill gelification and ageing as dry powders. The as-prepared product was put in an oven at 60 °C for over 2 h until it was dry, and then calcined in a muffle furnace at 450 °C for 2 h to obtain the inorganic composites.

2.3. Synthesis of inorganic-organic hybrid polymers

For the synthesis of inorganic-organic hybrid polymers, 0.3 g of kaolin-TiO_2 composites were put into a quartz tube, to which AM (6 g) was added, followed by constant bubbling of nitrogen. Then, the chemical reaction was initiated under visible light at room temperature. After 2 h, the formed gel was dispersed into absolute ethanol to remove the residual monomer.

2.4. Degradation of PAM

Typically, the hybrid polymers were dissolved in 50 ml of 18 mM H_2O_2 solution, and then the reaction mixture was irradiated under UV light for 2 h and sampled (5 ml) every 20 min.

2.5. Determination of PAM concentration

A buffer solution was prepared by adding 25 g of $NaAc \cdot 3H_2O$ and 0.75 g of $AlCl_3 \cdot H_2O$ to 800 ml of distilled water, and the pH value was adjusted to 4 with acetic acid before the solution was diluted to 1000 ml. A standard starch-cadmium iodide solution was also prepared by dissolving 11 g of cadmium iodide in 400 ml of boiling distilled water. The solution was then diluted to 800 ml before 2.5 g of soluble starch was added. Suspending particles were filtrated and the filtrate was diluted to 1000 ml at last. During degradation, the 5 ml samples taken every 20 min were diluted to 35 ml with distilled water, to which 1 ml of saturated bromine water was introduced [21]. After 15 min, 5 ml of aqueous sodium formate solution (1%) was added, and 5 ml of standard starch-cadmium iodide solution was added after another 5 min. The mixture was left still for 15 min before UV–visible detection at 590 nm.

2.6. Instruments and characterizations

The chemical compositions of inorganic-organic hybrid polymers were analyzed with a Fourier transform infrared (FT-IR) spectrophotometer that was operated with a resolution of 4 cm^{-1} from the wavenumber of 4000 to 400 cm^{-1}. The structures of hybrid materials were determined using X-ray diffraction (XRD). The morphology of materials was observed using transmission electron microscopy (TEM).

2.7. Detection of flocculation performance

Briefly, 5 g of kaolin soil was added into a beaker (250 mL) and dissolved with water. The suspension was poured into a volumetric flask and diluted with water to 1000 ml. The suspension was ultrasonically agitated and fully stirred to make sure that kaolin was well dispersed. Afterwards, 1000 ml of suspension was equally divided into four conical flasks, to which different volumes of kaolin-TiO_2-PAM were introduced. The transmittance of the suspension was measured after 5 min, 10 min and 15 min to investigate the relationship between flocculating effect and flocculating time, as well as that between flocculating effect and volume of kaolin-TiO_2-PAM.

3. Results and discussion

3.1. Synthetic and degradation mechanisms

The synthetic process is schematized in Fig. 1, including coating of TiO_2 nanoparticles on the surface of inorganic soils, and subsequent polymerization of AM on these nanoparticles under visible light. The mechanism underlying the protocol proposed in this study is different from that of surface-initiated controlled polymerization, whereby the polymers are initiated on the surfaces of nanoparticles by using other initiators [18,19]. We found that the TiO_2 nanoparticles initiated the polymerization of AM directly under visible light, thus providing a facile strategy for the synthesis of new organic-inorganic hybrid flocculants.