



Research paper

Adsorption characteristics of chitosan *grafted* copolymer on kaolin

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ABSTRACT

Efficient destabilization of colloidal dispersions is the top challenge facing solid-liquid separation processes. In this study, an in-house synthesized environmentally friendly graft copolymer, chitosan-*graft*-polyacrylamide (chi-g-PAM), was investigated as a potential flocculant of fine kaolin dispersions. Chi-g-PAM was successfully prepared by combining the properties of synthetic monomer (acrylamide) and natural polymer (chitosan) using ceric ammonium nitrate as an initiator. The physical and chemical characteristics of the copolymer were analyzed using Fourier-transform infrared (FTIR), scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and Zetasizer Nano ZS in order to identify the active adsorption sites in the polymer structure. The performance of chi-g-PAM as a flocculant was evaluated by treating 5 wt% kaolin dispersion (d_{50} and mean diameter of 6.63 and 9.24 μm , respectively) with different dosages of the polymer and calculating the initial settling rates (ISR). The flocculation mechanism and the adsorption capacity were investigated using zeta potential and total organic carbon (TOC) measurements. Results showed that ISR increased with increasing chi-g-PAM dosages before reaching maximum values at corresponding optimal ones; then, the settling rate slightly decreased. Chi-g-PAM showed a better flocculation and settling behavior (ISR 24.84 m/h) as compared to chitosan (ISR of 7.2 m/h) at optimum dosages and performed similar to commercial PAM (ISR of 25.92 m/h). Reliable correlation of zeta potential measurement and adsorption isotherms obtained from TOC measurements demonstrated that bridging and charge neutralization were the dominant adsorption mechanisms involved. The experimental adsorption data were analyzed using Langmuir and Freundlich models. The best fit was obtained using the Langmuir isotherm model with a correlation coefficient value of 0.991 as compared with 0.895 for the Freundlich model. The TOC method has proven to be suitable and feasible for explaining the adsorption mechanism and determination of the adsorbed amount of chi-g-PAM on kaolin.

1. Introduction

Controlling the stability of colloidal dispersions is critical from an application perspective. For example, fully dispersed solid particles are needed for heterogeneous catalysis and heat transfer fluids, while controlled aggregation is needed for gel formation in sensitized solar cells (Wang et al., 2014a,b). However, full destabilization of colloidal particles and consequent sedimentation is considered the top challenge facing solid-liquid separation processes such as sludge dewatering and fine mineral tailings management (Koohestanian et al., 2008). Dewatering of tailings streams using flocculation technology has thus become one of the more promising approaches to solving problems related to tailing disposal and water recycling due to its simplicity and cost effectiveness (Wang et al., 2010; Kumar et al., 2014; Khodakarami and Alagha, 2017). In recent years, much research has been devoted to developing water soluble grafted flocculants made of natural based polymers and synthetic polymers (Wang et al., 2014a,b). These include

graft copolymerization of chitosan (natural polymer) with synthetic monomer (acrylamide), which has been acclaimed as a promising solution (Wang et al., 2008; Renault et al., 2009) due to abundant amino groups and hydroxyl groups in the chitosan backbone that could react with acrylamide monomers under mild conditions. Because of their novel properties, these copolymers are believed to be highly efficient, inexpensive, biocompatible, and environmentally friendly compared to synthetic polymers (Xu et al., 1996). In addition, grafting of acrylamide onto chitosan backbone has been acclaimed to improve the solubility of the polymer and thus its flocculation efficiency by increasing the probability of the flocculant approaching the solid particles (Renault et al., 2009; Wang et al., 2012). Many studies have tested the flocculation of clay dispersions in the presence of chitosan grafted polyacrylamide based flocculants (chi-g-PAM) (Wang et al., 2007, 2015; Ma et al., 2016). However, the underlying mechanism behind the adsorption of chi-g-PAM on fine and ultrafine kaolin particles has not been fully explored yet. In recent years, many versatile analytical techniques

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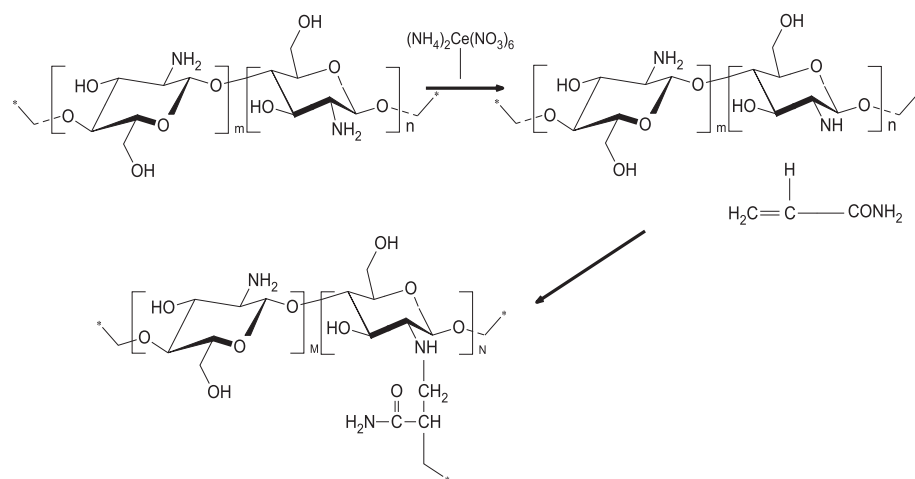


Fig. 1. Synthetic scheme of chitosan-grafted-polyacrylamide copolymer (chi-g-PAM).

have been developed such as total organic carbon analysis (TOC) and Zetasizer Nano measurements that can precisely measure the adsorption capacity and clarify the adsorption mechanism of polymers on colloidal and ultrafine clay dispersions at the nanometer scale. The TOC method has made it possible to determine rapidly and precisely small quantities of organic matter in dilute solutions. TOC analytical results are free of the interference of salts since the organic matter in the solution is converted to carbon dioxide gas in a combustion furnace and detected by the appropriate analyzers (Kokufuta et al., 1982). For this reason, the TOC method is thought to be feasible and suitable for elucidating the adsorption behavior of chi-g-PAM on kaolin. Despite of the quality work that has been done to study the adsorption of similar polymers on kaolin, to the best of the authors' knowledge, no previous literature is available on the use of TOC to investigate and quantify the adsorption of chi-g-PAM on fine and ultrafine kaolin particles.

This study investigates the potential of in-house synthesized chi-g-PAM as a biocompatible flocculant of fine kaolin dispersions. Extensive characterization of the copolymer was conducted using a variety of analytical techniques including Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), X-ray powder diffraction (XRD), and Zetasizer Nano ZS. The characterization of the chi-g-PAM was of crucial importance in identifying the different functional groups and to getting insights into the active adsorption sites in the polymer structure. The flocculation performance was evaluated by calculating the initial settling rate of 5 wt% kaolin dispersion at different polymer dosages. Investigations on the adsorption mechanism, electrical characteristics at solid-liquid interface and the adsorption capacity were performed using both electrokinetic measurements (zeta potential) and TOC analysis. For comparison purposes, the flocculation performance of polyacrylamide and chitosan polymers was also investigated.

2. Experimental

2.1. Materials

Three different polymers were used as flocculants in this study. These include commercial polyacrylamide (PAM) and chitosan polymers and in-house synthesized chitosan-grafted-polyacrylamide (chi-g-PAM) copolymer. Chitosan (molar mass 600,000–800,000 g/mol) was purchased from ACROS ORGANICS (part of Thermo Fisher Scientific, New Jersey, USA). Commercial PAM (PAA; 2-Propenamide homopolymer), a water soluble white to off-white powder with a molecular weight of 5,000,000 g/mol was purchased from Pfaltz & Bauer Rare and Fine Chemical Company (Waterbury, CT USA). Ceric ammonium nitrate (which was used as initiator in the polymerization reaction), acrylamide (C.P. grade) with a molar mass of 71.08 g/mol and acetic acid

(36 wt%), were purchased from Fisher Scientific, USA. Reagent grade hydrochloric acid and sodium hydroxide (used as pH modifiers), ethanol and acetone (> 99.5%) used to purify the synthesized chi-g-PAM copolymer were also purchased from Fisher Scientific, USA. All reagents used in this study were of analytical grade and used directly without any further purification. Acid-washed kaolin clay used in the adsorption tests was purchased from Thermo Fisher Scientific, USA.

2.2. Synthesis of chitosan-grafted-polyacrylamide

Chitosan-grafted-polyacrylamide (chi-g-PAM) was prepared by combining the properties of synthetic and natural polymer via the 'grafting to' method, which involved three stages. The first stage involved preparation of the chitosan stock solution (used as a backbone for graft copolymerization) followed by grafting acrylamide monomer into chitosan using a redox initiating system (Joshi and Sinha, 2007) with the final stage of purification and drying the chi-g-PAM. In a 250 mL three-necked round-bottom flask, about 3 g of chitosan powder was added to 150 mL of 1 w/v% acetic acid in aqueous solution. The addition was done under magnetic stirring at 40 rpm. To avoid oxidation and chain termination during polymerization, the whole system was purged with nitrogen gas from the beginning to the end of the experiment. A constant temperature of 40 °C was maintained throughout the experiment using an oil bath. The flask was also covered with aluminum foil to protect from the exposure to light. After 30 min of stirring, 1 mL of a 0.058 mM ceric ammonium nitrate initiator was added to the solution to generate the primary radicals on the chitosan backbone for further acrylamide (AM) grafting. The solution was allowed to stir for another 30 min before 9 g of AM monomer was added. The ratio of chitosan and acrylamide was 1:3. The reaction was run for 3 h. The formed gel was dissolved in MilliQ water at 10 wt%. The aqueous polymer colloidal dispersion was then precipitated in a mixed solution of acetone and ethanol with a volume ratio of 2:1, then filtered and washed to remove impurities. Finally, the purified solid product was transferred to a Teflon dish, and the dish was placed at 60 °C in a vacuum oven for overnight. The reaction scheme involved in the synthesis of chi-g-PAM was drawn (Fig. 1). The grafting ratio (G%) of Chitosan-grafted-polyacrylamide (chi-g-PAM) was determined by the percentage weight as follows. (Eq. (1))

$$G\% = \frac{W_{\text{chi-g-PAM}} - W_{\text{chitosan}}}{W_{\text{chitosan}}} \quad (1)$$

$W_{\text{chi-g-PAM}}$ and W_{chitosan} were the weight of chi-g-PAM copolymer and chitosan, respectively. The grafting ration was found to be 225%.

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