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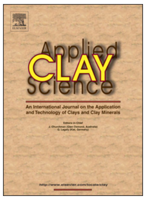

Research paper

Dispersion of kaolin particles with carboxymethylated xylan

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ABSTRACT

In this work, the performance of carboxymethylated xylan (CMX) as a dispersant for kaolin particles in an aqueous system (20 g/L) was systematically investigated. The influence of process parameters, such as pH and CMX dosage, on the kaolin dispersions was also determined. Adsorption studies revealed that CMX had a maximum adsorption of 2.48 mg/g on kaolin particles under the treatment conditions of pH 6, 15 mg/g CMX/kaolin, 30 °C and 30 min. The minimum zeta potential of −33 mV and the highest stability for the kaolin dispersions were found under the same treatment conditions using photometric dispersion, vertical scan analysis and turbidimetry. Isotherm and kinetic studies revealed that the adsorption of CMX on kaolin particles tended to significantly impact the zeta potential and relative turbidity of the kaolin dispersion, but the zeta potential did not necessarily predict the high stability of the kaolin dispersion. CMX improved the stability of the kaolin dispersions more than unmodified xylan (UX) and mechanical stirring.

1. Introduction

The stabilization of kaolin slurries is a crucial step in the production of cosmetics, ceramics, paints and coating formulas in order to obtain stable and homogenous colloidal systems (Brady et al., 1996; Zaman et al., 2002). Dispersants have been widely used in the stabilization of kaolin dispersions (Yuan et al., 1998). The surface of kaolin particles is usually heterogeneous consisting of positive charges at the edges and negative charges on the basal face, and the interaction of these charges with surrounding environment promotes the aggregation of particles (Nuntiya and Prasanphan, 2006). Dispersants prevent the aggregation of kaolin particles by inducing electrostatic/steric repulsion between them via adsorbing on their surface (Boisvert et al., 2001).

Numerous inorganic and synthetic dispersants are currently used in the stabilization of clay slurries. Sodium silicate (Amoros et al., 2010; Ma, 2011), sodium carbonate (Eygi and Atesok, 2008) and sodium pyrophosphate (Qin et al., 2012) have been used as dispersants for stabilizing clay minerals in the mining and oil industries. In one study, the sodium salt of poly acrylic acid (1 wt.%) improved the fluidity of highly concentrated (12–15 wt.%) kaolin dispersions by 30% (Loginov et al., 2008). Poly acrylic acid, poly methacrylic acid and sodium silicate mixtures were used as dispersants for the stabilization of porcelain dispersions (40 vol%) (Garcia et al., 2009). Similarly, a water soluble non-ionic polyethylene oxide (4000 g/mol) served as an effective dispersant for bentonite dispersions (Ece et al., 2002). Although synthetic dispersants are effective, there are concerns about their non-biodegradable nature and health impacts, and as such, there is a strong incentive for producing green dispersants.

In the past, the utilization of polysaccharide based dispersants in colloidal dispersions was reported (Conceicao et al., 2003; Laskowski et al., 2007). The addition of 0.8 wt.% carboxymethylated cellulose to a kaolin dispersion increased its stability by 20% at pH 6 (Penkavova et al., 2015). In another study on the stabilization of dolomite dispersions using carboxymethylated cellulose (CMC), an increase in the dosage of CMC from 8 to 100 mg/L increased the turbidity of the dolomite dispersion from 20 to 90% (Pawlik et al., 2003). The addition of starch (0.8 wt.%) to red kaolin based ceramic dispersions (at pH 7) increased the fluidity of dispersions by decreasing the kaolin particle size from 2.8 to 1.5 μm (Umaran and Menchavez, 2013). On the stabilization of coal dispersions, the addition of a lignin-based dispersant (1 wt.%) increased the turbidity of the dispersion by 68% (Li et al., 2009). However, starch is mainly used as a food product and cellulose is widely used in the paper production, thus they may have limited availability to be used for other purposes including dispersant production. On the other hand, xylan currently has limited industrial applications (e.g. xylitol, ethanol) but available in plentiful and can be produced in the hydrolysis stage of kraft-based dissolving pulp production process (Schild and Sixta, 2011). To widen the application of xylan-based products, carboxymethylated xylan (CMX) was produced in aqueous conditions via modifying xylan with sodium chloroacetate (Konduri and Fatehi, 2016). In the present study, the first objective was to evaluate the dispersion performance of CMX in a kaolin dispersion under varied process conditions.

The stability of kaolin particles in dispersions is affected by many factors. The behaviour of kaolin particles is affected by the chemistry of the

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dispersions, the properties of particles in the dispersions and process conditions, such as shear rates (Zaman and Mathur, 2004; Guillemet et al., 2006). These factors significantly influence the repulsive and attractive inter-particle forces, which should be controlled in order to stabilize kaolin particles in dispersions (Li and Li, 2008). The increase in repulsive/attraction force depends on the dielectric properties and compositions of kaolin particles and medium (Gregorova and Pabst, 2011). To overcome the attraction force and to have a well-stable dispersion, one approach is to introduce charges with sufficient magnitude on the surface of kaolin particles by adsorbing dispersants on them. Alternatively, the agglomeration of particles can be prevented by introducing shear rates (Papo et al., 2002; Konduri et al., 2015). In this study, the impact of CMX as a dispersant will also be compared with that of shear rates for stabilizing kaolin particles in a dispersion.

The main novelty of this work was the investigation on the dispersion performance of CMX in kaolin dispersions by monitoring the adsorption of CMX on kaolin particles and its resultant impacts on the properties of the dispersion. The impact of dispersant dosage, time and pH on the stability of kaolin particles was fundamentally studied. The effect of shear rates on the dispersion performance of CMX was also determined and compared with that of CMX treatment.

2. Experimental

2.1. Materials

Beechwood xylan, sodium chloride (97.0%), sodium hydroxide, sodium chloroacetate and kaolin were purchased from Sigma Aldrich Company and used as received. Potassium chloride and sulfuric acid (95–98%) were received from Fisher scientific, USA. All chemicals were analytical grades. Polydiallyldimethylammonium chloride (PDADMAC) was obtained from Sigma Aldrich Company and diluted to 0.005 M prior to use. Polyacrylic acid (PAA, 35 wt.%) used in the study was obtained from Sigma Aldrich. Potassium polyvinyl sulfate (PVSK) was obtained from Wako Pure Chemical Industries Ltd., Japan. Cellulose acetate dialysis membrane (molar mass cut-off of 1000 g/mol) was obtained from Spectrum Labs., USA. The TEGO trant A100 polymer was also received from Metrohm, Canada, and used as received.

2.2. Surface area analysis

The surface area of kaolin particles was determined by using Quantachrome surface area analyzer, Nova2200e. In this set of experiments, the samples were initially dried in an oven at 105 °C overnight and approximately 0.05 g of sample was pretreated for 4 h at 250 °C prior to analysis. The specific surface area of the samples was then analyzed according to Branuer-Emmett-Teller (BET) method via adsorption-desorption isotherms using nitrogen gas at −180 °C in the relative pressure range of 0.01 to 0.99 (Wang et al., 2016).

2.3. Charge density analysis

The surface charge density of kaolin was determined via a back titration method with a particle charge detector (Mutek, PCD 04, Germany). In this set of experiments, 0.2 g of kaolin was dispersed in 50 mL of PDADMAC (0.005 M) solution and incubated for 2 h at 150 rpm and 30 °C. After the incubation, the samples were filtered using Whatman#1 filter paper and the filtrates were titrated against PVSK (0.005 M) solution. In another experiment, 0.2 g of kaolin sample was dispersed in 50 mL of PVSK (0.0025 M) solution and incubated for 2 h at 150 rpm and 30 °C. After the incubation, the samples were filtered as described above and filtrates were titrated with 0.005 M PDADMAC solution. Similarly, the titration analysis was conducted for control sample (i.e. PDADMAC and PVSK solutions) and the difference was considered for quantifying the anionic and cationic surface charge densities of kaolin particles.

The charge density of unmodified xylan (UX), CMX and PAA was determined using the same particle charge detector via titrating with PDADMAC (0.005 M). In this set of experiments, the UX and CMX were initially dried in an oven at 105 °C overnight and 0.2 g of the samples was mixed with 20 mL of deionized water and incubated for 2 h at 30 °C and 150 rpm. After incubation, the samples were titrated with PDADMAC to determine the surface charge density.

2.4. Chemical and mineralogical analyses of kaolin

The chemical compositions of kaolin were determined using scanning electron microscopy (SEM), Hitachi Su-70, Schotty in tandem with energy dispersive X-ray spectroscopy (EDX) (Senoussi et al., 2016). In this set of experiments, approximately 0.2 g of kaolin was dispersed in 20 mL of acetone under ultrasonic vibrations for 5 min and allowed to air dry for 24 h. After drying, the sample was coated with carbon using Edward Auto 306 system (Edward International Corp, UK) under vacuum (3×10^{-5} mbar) for 10 min prior to SEM analysis.

The mineralogical analysis of kaolin was carried out using spinning stage PANalytical X'pert-PRO diffractometer (XRD), PW1050–3710 with a Cu Kα ($\lambda = 1.5405$ Å) radiation source (Senoussi et al., 2016). A 0.5 g of kaolin sample was air dried and loaded on the spinner of XRD. The sample was then scanned from 6 to 43° with a step of 0.02° per second for 2 min. The X'pert High Score software was used to determine the mineral compositions of kaolin as described previously (Mcintosh et al., 2015).

2.5. Carboxymethylated xylan (CMX) preparation and analysis

The CMX was synthesized according to the method described in the previous study under the conditions of 0.75 M NaOH concentration, 1.0 mol/mol sodium chloroacetate (SCA)/xylan ratio, 2 h reaction time, 70 °C and 15 g/L xylan concentration to obtain the CMX with the charge density of 1.6 mmol/g (Konduri and Fatehi, 2016). The properties of UX and CMX are reported in Table 1.

The carboxylate content of UX/CMX was measured using an automatic potentiometer, Metrohm, 905 Titrado, Switzerland. In this set of experiments, 1 g of UX/CMX sample was added to 100 mL of deionized water and the pH of the solution was adjusted to 10.5. The solution was then titrated with a cationic polymer, TEGO trant A100, in order to identify the carboxylate content of UX or CMX (Konduri and Fatehi, 2016).

The weight average molar mass (M_w), number average molar mass (M_n) and polydispersity (M_w/M_n) of UX, CMX and PAA samples were determined using a Malvern GPCmax VE2001 Module + Viscotek TDA305 (RI and viscometer detectors) with polyethylene oxide standards. About 100 mg of UX, CMX or PAA was dissolved in 10 mL of 0.1 mol/L $NaNO_3$ solutions and filtered with a nylon 0.2 μm filter (13 mm diameter). The filtered solutions were used for molar mass analysis by passing though PolyAnalytic columns, PAA206 and PAA203, at the column temperature of 35 °C. A 0.1 mol/L $NaNO_3$ solution was used as a solvent and eluent at a flow rate of 0.70 mL/min in this analysis.

Table 1
Properties of UX, CMX and PAA (Konduri and Fatehi, 2016).

Sample	UX	CMX	PAA
Charge density, mmol/g	0.38 (± 0.05)	1.62 (±0.02)	13.5 (±0.3)
Carboxylate content, mmol/g	0.36 (±0.05)	1.48 (±0.02)	–
M_w, g/mol	20,840	24,127	100,120
M_n, g/mol	15,852	19,254	30,253
M_w/M_n	1.31	1.25	3.3