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Adsorption of organic–inorganic hybrid polymers on kaolin from aqueous solutions

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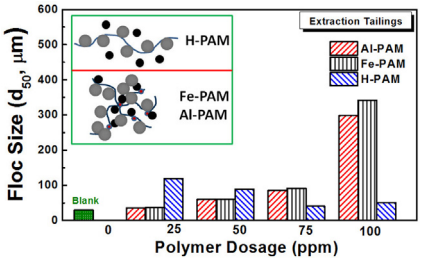
HIGHLIGHTS

- Flocculation by Al-PAM and Fe-PAM in comparison with partially hydrolyzed H-PAM.
- Adsorption kinetics of Al-PAM, Fe-PAM and H-PAM on silica and alumina surfaces.
- Role of electrostatic attraction and hydrogen bonding in polymer adsorption and flocculation.

GRAPHICAL ABSTRACT



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ABSTRACT

Adsorption of two in-house synthesized organic-inorganic hybrid polymers, $Al(OH)_3$-polyacrylamide (Al-PAM) and $Fe(OH)_3$-polyacrylamide (Fe-PAM) on kaolin and corresponding flocculation of fluid fine kaolin suspensions were investigated. For comparison, a commercial anionic flocculant (partially hydrolyzed polyacrylamide or known as H-PAM) was also examined. The flocculation dynamics of fine kaolin suspensions were determined using an on-line focused beam reflectance measurement (FBRM) probe. As an example of applications, flocculation of a laboratory oil sands extraction tailings sample was studied. A quartz crystal microbalance with dissipation (QCM-D) was used to determine adsorption kinetics of the polymers on silica and alumina as representative of T- and O-basal planes of kaolin.

Al-PAM, Fe-PAM and H-PAM were shown to be excellent flocculant of kaolin suspensions, with H-PAM being less effective and more sensitive to overdosing. The flocculation performance was greatly influenced by proper mixing. Strong flocculation of kaolin suspension by Al-PAM and Fe-PAM is attributed to their ability to adsorb on both basal planes of kaolin, in contrast to relatively weak flocculation of kaolin by H-PAM which adsorbs only on positively charged aluminum oxy-hydroxyl basal planes. The electrostatic attraction or repulsion is identified as a critical parameter in determining polymer adsorption and hence corresponding flocculation of kaolin suspensions.

1. Introduction

Controlling stability of colloidal clay suspensions is of great scientific and practical importance. For ceramic processing, for example, highly dispersed clay suspensions are desirable as it allows processing of high solid content suspensions and avoidance of defects in the produced products. On the other hand,

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solid–liquid separations are employed at many stages of mineral processing, ranging from product liquor recovery to tailings processing. Increasing the efficiency of these separations can contribute to enormous reductions in running cost and the volume of waste produced [1]. Flocculation of fine clays is highly desirable for solid–liquid separation or waste management. Rapid dewatering and consolidation of mining and oil sands processing wastes (fluid fine tailings) are becoming increasingly more important in the past few years [2]. Producing one barrel of oil from Athabasca oil sands by surface mining using the Clark hot water extraction (CHWE) technology, for example, generates approximately 0.25 m^3 of fluid fine waste of approximately 30 wt% fine solids [3]. Such mine wastes consisting mainly of fine clays could take centuries to see a further noticeable densification [4]. The fluid fine tailings known as mature fine tailings (MFT), trap a substantial amount of water and require safe containment [5,6]. Currently, tailings ponds from oil sands industry cover more than 170 km^2 of Alberta's oil sands region. Without further development of effective new treatment technologies, the tailings ponds from oil sands operations are predicted to increase to 250 km^2 by 2020 [7].

Producing stackable solids from fluid fine wastes by thickening and filtration for backfill of mined area and timely reclamation have been considered as one of most promising solutions to these wastes. Using filtration to produce stackable solids from fluid fine wastes would also reclaim the maximum amount of process-affected water for recycle. To achieve a desirable thickening and filtration performance that could be practiced for the management of fluid fine wastes, proper choice of flocculants to produce fine particle aggregates of sufficient hydraulic drainage with rapid filtration rate is of crucial importance. Despite effective particle flocculation and hence enhanced solids settling, the H-PAM was found ineffective in promoting fluid fine waste filtration [8]. The poor flocculation of ultrafine particles by H-PAM, as indicated by turbid supernatant of flocculated fluid fine wastes, was identified to be the blame as fines remaining suspended could quickly block the channels of the hydraulic drainage in the filter cake.

In our earlier studies, a cationic organic–inorganic hybrid polymer, $Al(OH)_3$-polyacrylamide (Al-PAM) was shown to be effective in flocculating properly diluted fluid fine wastes [9]. Al-PAM was able to flocculate ultrafine particles in fluid fine wastes as indicated by a clear supernatant. The enhanced flocculation performance could be attributed to two synergistic processes: effective adsorption of positively charged $Al(OH)_3$ colloids on the surfaces of negatively charged clay particles through charge neutralization mechanism, and reduction of particle–particle repulsion due to charge neutralization by adsorbed polymers to bring particles to close proximity for effective bridging of ultrafine particles by PAM chains. The removal of suspended ultrafine particles preserves open channels of the filter cake to allow for effective hydraulic drainage [8,9].

Alagha et al. [10] studied the adsorption kinetics of Al-PAM and H-PAM on differentiated tetrahedral silica (T) and octahedral aluminum oxy-hydroxyl (O) basal planes of kaolinite using a quartz crystal microbalance with dissipation (QCM-D). The results showed that Al-PAM has a higher affinity to negatively charged tetrahedral (T-) silica basal planes positively charged octahedral (O-) aluminum oxy-hydroxyl basal planes than to positively charged aluminum oxy-hydroxyl octahedral (O-) basal planes. In contrast, anionic H-PAM exhibits higher adsorption mass only on positively charged O-basal planes with unstable adsorption on negatively charged T-basal planes. Moreover, results obtained from an earlier study on alternate adsorption/deposition of silica nanoparticles (SNPs) on Al-PAM film suggested potential flocculation of 15 nm SNPs by Al-PAM molecules, which makes this type of hybrid polymers a promising solution to dealing with ultrafine clay suspensions in solid–liquid separation processes [11].

With the success of Al-PAM for treating fluid fine wastes using thickening and filtration technology, another novel organic–inorganic hybrid polymer, $Fe(OH)_3$-polyacrylamide (Fe-PAM) was recently synthesized and found to be as effective as Al-PAM in flocculating both kaolin suspensions and laboratory extraction oil sands tailings. However, Fe-PAM was shown to be more effective than Al-PAM in the filtration of laboratory extraction oil sands tailings [12]. It is hypothesized that this difference in performance is related to a higher adsorption mass of Fe-PAM than Al-PAM on residual bitumen remained in the tailings slurry after the extraction process, although in small quantities. The adsorption of Fe-PAM would result in hetero-flocculation of fine solids with fine bitumen droplets. The hetero-flocculation of fine bitumen droplets and fine solids prevents blinding of filter medium and pores of filter cake by viscous bitumen droplets, which in turn, preserves the filtration process and leads to a cleaner filter medium.

The objective of this study is to understand the adsorption characteristics of organic–inorganic hybrid polymeric flocculants on kaolin surfaces and to establish the relationship between polymer adsorption and flocculation dynamics. Adsorption kinetics and flocculation dynamics of H-PAM, a partially hydrolyzed, polyacryamide-based commercial flocculant, were also studied for comparison. A focused beam reflectance measurement (FBRM) probe and quartz crystal microbalance with dissipation (QCM-D) were used to study the flocculation dynamics and adsorption kinetics of polymer flocculants on solid surfaces from aqueous solutions. The floc size and stability of kaolin suspensions were determined under different polymer dosages and shear rates using FBRM probe. As an example of potential industrial applications, flocculation of a laboratory extraction oil sands tailings sample was also attempted using the hybrid polymers. Once the optimum flocculation dosage of each polymer was obtained, QCM-D tests were conducted to quantify the adsorption of polymers on silica and alumina as model basal plane surfaces of kaolin. To draw a better correlation, experiments in this work were performed using plant recycle process water that was also used in flocculation dynamics study by FBRM. The aim of using process-affected water is to obtain a more reliable model and to understand the effect of ions on the adsorption of polymers on kaolin surfaces.

2. Materials and methodology

2.1. Materials

Three water soluble polymers were used in flocculation and adsorption tests: H-PAM, Al-PAM and Fe-PAM. H-PAM was purchased from Ciba Chemicals (U.K.) and used without further purification. Al-PAM and Fe-PAM were synthesized in-house using procedures that were described elsewhere [11,12]. The metal content of Al-PAM or Fe-PAM was determined by atomic absorption spectroscopy (AAS). The molecular weights of polymers were determined using Mark–Houwink equation:

$$[\eta] = KM_V^{\alpha}$$

where M_v is the viscosity average molecular weight, while K and α are constant for a given polymer/solvent/temperature system [11,13]. The exponent α increases as coil expands in good solvent. General range for α is [0.5, 0.8] for flexible chains in good solvents. The values of K and α used in this study were 6.3×10^{-3} and 0.8, respectively [13,14]. A dual Huggins–Kraemer plot was used to evaluate intrinsic viscosity ($[\eta]$) of each polymer flocculant. The viscosity measurements were conducted using polymer solutions of five different concentrations. At each concentration, both the reduced and inherent viscosities were determined from