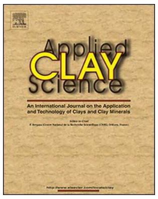
Applied Clay Science 158 (2018) 46–54

Contents lists available at ScienceDirect

Applied Clay Science

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



Research paper

Effect of electrolytes on electrokinetics and flocculation behavior of bentonite-polyacrylamide dispersions

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ARTICLE INFO

Keywords:
Bentonite
Flocculation
Polyelectrolyte
Electrolyte
Polyacrylamide
Charge density
Zeta potential
Floc size
Ionic strength

ABSTRACT

In this study, the influence of electrolytes on bentonite dispersions flocculated with different polyacrylamides varying in charge type, density and molecular weights has been investigated. The presence of electrolytes was found to induce profound impact on the flocculation behavior of bentonite-polyacrylamide dispersions, which was analyzed by means of residual turbidity, zeta potential and floc size distribution tests. Electrolytes enhanced the adsorption of anionic polyacrylamide chains on negative bentonite surface, while hindering adsorption of cationic polyacrylamides. Electric double layer compression and mediated flocculation by metal cations were the principle mechanisms involved in the improvement of flocculation behavior. High molecular weight and charge density variants greatly reduced the turbidity and negative zeta potential of dispersions for anionic polyacrylamides. Furthermore, charge density of metal ions was found to be a determining factor. Divalent salts were more efficient for flocculating dispersions using anionic polyacrylamides, while monovalent salts were preferable for cationic polyacrylamides owing to electrostatic repulsions. Amphoteric polyacrylamides displayed similar results based on their anionic/cationic nature. Similar observations were recorded for floc size measurements. High charge density variants of anionic polyacrylamides in the presence of divalent salts like $CaCl_2$ produced large flocs. On the other hand, no significant changes in floc sizes were observed for cationic polyacrylamides in the presence of salts. Overall, this study successfully determines the effect of electrolytes on the flocculation behavior of bentonite dispersions.

1. Introduction

Treatment of colloidal dispersions is an integral aspect of wastewater treatment technologies. Complex energy-intensive treatment processes are often involved to remove a myriad of stable contaminants in wastewaters, mainly colloidal organic matter, clay minerals and adsorbed heavy metals (Nasser and James, 2008; Nasser et al., 2013a, 2013b; López-Maldonado et al., 2014). Such challenges are often encountered when dealing with effluents released from mineral processing industries. Clay minerals like kaolinites and various montmorillonites released in effluents from various industries form stable dispersions in large amounts of water. Bentonite, a montmorillonite based material, is a particularly common colloidal contaminant found in wastewaters due to its industrial applications in large quantities as functional fillers (Murray, 2000; El-Nashar et al., 2012; Nasser et al., 2013a, 2013b; Wong et al., 2013).

The physical properties of bentonite pave the way for various applications in industries such as water treatment, environmental remediation, dyes and paints, pharmaceuticals, cosmetics, dyes, papermaking, and drilling fluids (Cara et al., 2000; Viseras et al., 2010; Zhang et al., 2013a, 2013b; de Figueirêdo et al., 2014; Vipulanandan and Mohammed, 2014; Wang et al., 2014; Zhuang et al., 2015). The mineral composition of bentonite largely dominated by montmorillonite, along with the abundance of interlayer exchangeable cations imparts versatility to its application. A large negatively charged surface area and the presence of exchangeable cations result in excellent adsorption and ion exchange properties in dispersions (Karimi and Salem, 2011). Bentonite dispersions are highly stable due to characteristic physical and chemical properties exhibited by bentonite particles. While montmorillonite clay mineral comprises a major portion of bentonite, there may be considerable variations in their mineralogical properties owing to the remaining composition of accessory minerals. The presence of quartz, illite, pyrite, feldspars, calcite, gypsum, various iron oxides/hydroxides, biotite and other minerals impart characteristic

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https://doi.org/10.1016/j.clay.2018.03.017
Received 9 December 2017; Received in revised form 7 March 2018; Accepted 11 March 2018
0169-1317/

properties to bentonite. Some bentonite clays may also contain amorphous and organic compounds in considerable proportions. Such variations are primarily characterized by the geochemical conditions of bentonite formation (Karnland, 2010). Montmorillonite, the dominant constituent in bentonite, is represented by the general formula:

$$(\mathrm{M}_{\mathrm{y}}^{+} \times \mathrm{nH_2O})(\mathrm{Al}_{2-\mathrm{y}}^{3}\mathrm{Mg}_{\mathrm{y}}^{2+})\mathrm{Si}_{4}^{4+}\mathrm{O}_{10}(\mathrm{OH})_{2}$$

where, *M* represents interlayer cations and *y* represents the layer charges (typically 0.2 per half unit cell) developing from isomorphic substitutions in tetrahedral and octahedral sites (Brigatti et al., 2006). Montmorillonite has a layered structure with two tetrahedral silica (SiO_2) layers bearing an octahedral alumina (Al_2O_3) layer in the middle. Its hexagonal plates bear a net negative surface charge, owing to isomorphic substitution on Al^{3+} metal centers in the layers by lower valence metal ions such as Fe^{2+} and Mg^{2+}, and is largely surrounded by exchangeable cations like Na^+, H^+, K^+ and Ca^{2+} balancing the net charge (Van Olphen, 1964; Duman and Tunç, 2009).

The surface chemistry of bentonite is largely influenced by the amphoteric characteristics of the structure. Adsorption on bentonite particles essentially occur on two sites – the faces and the edges of the clay platelets. The facial sites of generally bear negative charges, while the edges may bear positive charges according to the dispersion pH. The extent of adsorption on these sites is chiefly determined by dispersion pH and the presence of electrolytes that alter the structural and rheological properties of bentonite dispersions. Association between bentonite plates may occur in three ways - edge-to-face, face-to-face, and edge-to-edge. The excess H^+ ions in an acidic dispersion bind to the hydroxyl groups present on the crystal edges of bentonite rendering positively charged edges. Oppositely charged faces and edges render inter-particle attractions between bentonite particles in the form of face-edge interactions. The resulting aggregate structure is called the "card-house" arrangement. Similarly, the presence of electrolytes induces electrostatic attraction between bentonite particles by compressing the electric double layer around bentonite particles, thereby decreasing the repulsive forces between negatively charged bentonite particles and inducing aggregation. Agglomeration occurring from face-to-face interactions result in thick and dense aggregates. On the other hand, the "card-house" arrangement from edge-to-face and edge-to-edge associations result in large but less dense aggregates (Nasser and James, 2009; Padilla-Ortega et al., 2014).

Electrolytes also significantly govern the macroscopic behavior of clay dispersions flocculated with polyelectrolytes. Metal cations greatly improve the flocculation efficiency of polyelectrolytes, particularly anionic, in clay dispersions. This occurs through the phenomena of electric double layer compression or mediated flocculation, reducing the electrostatic repulsions between negatively charged bentonite particles as well as negatively charged polyelectrolyte and bentonite particles. Apart from this, cations also anchor to the negatively charged groups on polyelectrolytes and bridge between the particles and polyelectrolyte chains. This enhances polymer adsorption on bentonite rendering large and strong flocs. Further, the valency of metal ion is also a crucial factor in determining the electrolyte behavior. Divalent ions like Ca^{2+} and Mg^{2+} are far more effective in enhancing polymer adsorption on bentonite. This is due to stronger electrostatic interactions with polymer and bentonite particles in comparison to monovalent ions. The concentration of divalent salts required in flocculated systems is also less than monovalent salts. This is in accordance with the Schulze-Hardy rule that correlates decreasing concentration of coagulant to increasing valency of metal ion (Lee et al., 2012a, 2012b; Xu and Wang, 2012; Lyklema, 2013).

Highly stable clay dispersions of prevalently used kaolinite, bentonite and montmorillonite are generated in vast amounts of water due to their wide applicability. Treatment of such colloidal dispersions is met with chemical separation methods. Solid-liquid separation of colloidal particles from water is conventionally induced by introduction of chemical substances that modify surface interactions on colloidal particle and destabilize dispersions to induce agglomeration. This combined phenomenon is called coagulation-flocculation. Flocculation techniques are generally simple, feasible, cost and energy efficient, and offer high removal efficiencies (Zhang et al., 2013a, 2013b). Extensive use of inorganic coagulants has dropped dramatically due to numerous associated drawbacks such as formation and handling of toxic sludge, sensitivity of coagulant performance to dispersions characteristics and formation of flocs exhibiting poor shear resistance (Santhosh et al., 2016). There is a constant strive for efficient, economical and environment-friendly alternatives to current coagulants and flocculants (Chatterjee et al., 2009; Barbot et al., 2010; Lee et al., 2012a, 2012b). Therefore, polyelectrolytes are gaining increasing prominence as coagulating-flocculating agents considering the flocculation mechanisms in principle. Major mechanisms underlying flocculation using polyelectrolytes incorporate adsorption, charge neutralization of surface, polymer bridging and sweep flocculation. These mechanisms play an essential role in determining flocculation efficiency of polyelectrolytes (Shaikh et al., 2017a, 2017b).

The influence of various electrolytes has been extensively studied for clay mineral dispersions. Numerous studies have also been conducted to determine the influence of electrolytes on flocculated clay dispersions with synthetic and natural polyelectrolytes. Majority of these coagulation-flocculation studies have been conducted on kaolinite and other clay mineral dispersions, summarized in (Shaikh et al., 2017a, 2017b). Literature pertaining to bentonite dispersions is limited in comparison to kaolinite clays. The structural characteristics of bentonite dispersions under varying conditions of pH, electrolyte types and concentrations have been investigated (Luckham and Rossi, 1999; Penner and Lagaly, 2001; Saka and Güler, 2006; Duman and Tunç, 2009; Abu-Jdayil, 2011; Choo and Bai, 2015). However, flocculation studies on bentonite dispersions are surprisingly few, summarized in (Shaikh et al., 2017a, 2017b). While polymer properties such as charge density and molecular weights were observed to influence electrokinetic, adsorption and flocculation behavior of bentonite dispersions (Shaikh et al., 2017a, 2017b), the combined effect of electrolytes and polyelectrolytes on bentonite flocculation has never been studied. Further, most studies determine optimum coagulant-flocculant doses and report flocculation efficiency in terms of limited parameters such as residual turbidity and zeta potential measurements, adsorption tests, settling behavior and floc sizes.

Therefore, for the first time, the present study analyses bentonite dispersions flocculated with polyacrylamides (varying in charge type, charge density and molecular weights) in the presence of electrolytes. It examines the extent of enhancement or otherwise in the flocculation behavior of polyacrylamides in bentonite dispersions on introducing electrolytes determined by their interaction with different electrolyte ions and the concentration of electrolytes in dispersion. Investigation of the effect of polymer characteristics, such as the charge density and molecular weight, on flocculation in the presence of electrolytes is novel. To study the effect of charge density, cationic, anionic and amphoteric polyacrylamides were used with charge densities varying from low to high. The influence of molecular weight among cationic and anionic polyacrylamides (PAMs) was also assessed, with molecular weights varying from standard to high. Using the optimum flocculant doses formerly established, the jar tests coupled with turbidity and zeta potential analyses were performed to obtain optimum electrolyte doses for flocculated bentonite-PAM dispersions. Dispersion pH was unanimously fixed to 9 since clay minerals are strongly dispersed in water at pH values above 8 (Shaikh et al., 2017a, 2017b). Finally, the effect of electrolytes on floc sizes was established by means of floc size distribution measurements for flocculated bentonite-PAM dispersions.

2. Materials

Lab-grade bentonite procured from Sigma-Aldrich Company Ltd.,