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Rapid Communication

Internal structure visualization of polymer — clay flocculants using fluorescence

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ABSTRACT

Polymer flocculation is commonly used to remove colloidal material from solution, improving separation performance. The structure of the mesoscale formation (floc) affects process performance, as well as the amount of polymer required. By visualizing polymer in flocs using fluorescently-tagged polymers and laser confocal microscopy, we directly observe effects of ionic strength on polymer–clay floc internal structure. At low ionic strength, I < 10 mM NaCl, the polymer forms a continuous, interconnected internal network, whereas at high ionic strength, the polymer no longer forms this network and simply coats the larger bentonite aggregates. This method offers the ability to visualize the polymer structure without drying or freezing the solution, making it ideal for observation of delicate aggregates. While especially applicable to water purification, the structure observations shown here yield important fundamental insights for polymer adsorption dynamics onto inorganic heterogeneous particulate or surface structures.

Ionic polymers, or polyelectrolytes, are widely used in water treatment to aid in the removal of nano- and micro-scale colloidal contaminants. They form mesoscale structures (flocs) that can be removed with gravitational settling, reducing downstream filter loading and improving treatment efficiency and performance. However, unlike their mineral coagulant counterparts, there are many different assembly mechanisms that can occur during polymeric flocculation, including charge neutralization, polymer depletion, polymer bridging, polymer adsorption, and patch flocculation [1,2]. The flocculation process is governed by highly interdependent properties, including suspension composition [3], coagulant type [4,5], surface properties of the particle [6], and dosing and mixing conditions [4,7]. These complexities make developing optimal dosing difficult, leading to poorly optimized, empirical dosing levels used at many water treatment plants.

The structure of the flocs is important for determining removal performance in a treatment process since the flocs are subject to varied hydrodynamic stresses, which may affect flocs with unique structures differently. Therefore, knowledge of the three dimensional internal structure is vital in process design, as the floc structure informs floc strength and density, and, in turn, the polymer's suitability as a flocculant in the treatment process. Weakly interconnected floc structures easily break, and low-density flocs settle more slowly, which are both detrimental to efficient process operation. There are a few studies that have probed floc structural information from transmission electron microscopy [8–12] and atomic force microscopy (AFM) [13], but these experiments involve drying or freezing the flocs before imaging for preparation, which can alter the structure. Despite these challenges, Audsley and Fursey [9] were able to directly observe polysaccharide extension from the surface of a kaolinite particle. Calabi-Floody et al. [13] were able to differentiate organic surface coverage patterns on nanoclays from different treatments using AFM. There are also studies of floc structure using low-angle laser light scattering [e.g. 14], but this mainly yielded floc size and fractal dimension information. Additionally, optical microscopy methods can be used for structure determination. For example, Pham Hoai Nam et al. [15] used polarized optical microscopy to characterize the crystallite morphology of maleic anhydride modified polypropylene–organoclay nanocomposites.

Fluorescently labeling chemicals of interest is a frequently used technique in the biological sciences for both determining biochemical mechanism and macromolecule fate in cells, as well as for determination of intracellular structure [16–18]. However, there has been only limited application of fluorescence to study flocculation in water treatment. Fan et al. [19] used fluorescence spectra of a two-part fluorescence labeling to determine extent of polymer coiling when using a dual polymer system. Fluorescence can also be used to study micelle–polyelectrolyte interactions to determine interaction parameters, such as binding and association rate constants [20]. Fluorescence has been used to determine the residual free polymer after flocculation down to

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10–40 μg/L [21]. All of these studies give valuable information about the flocculating system, but they do not yield information about the greater floc structure or polymer distribution inside the floc. Confocal microscopy has also been used to obtain the spatial distribution of aerogel metal oxide nanoparticles and bacteria in solution for bactericidal applications. Fluorescent and transmission confocal microscopy experiments have confirmed heteroaggregation of metal oxide nanoparticles and bacteria suspended in water [22].

It is well known that increasing the ionic strength of a solution containing colloidal particles reduces the repulsive force between colloidal particles, decreasing their stability and increasing natural aggregation. Specifically for bentonite, individual bentonite platelets can aggregate together into much larger particles where the morphology of bentonite particles is dependent on the ionic strength due to the anisotropic shape and charge distribution of individual bentonite platelets. Individual bentonite platelets have an aspect ratio of ~1/10, with lateral diameters of ~60 nm and thicknesses of ~6 nm [23]. At low ionic strength, the bentonite is in a porous, edge–face structure. As ionic strength increases, the structure changes to an edge–edge structure, and upon further ionic strength increase, the bentonite greatly densifies to a face–face structure [e.g. 24]. Therefore, the polymer flocculates material that is structurally very different in terms of both size and surface morphology, due to solution properties, which can greatly alter interactions between the polymer and bentonite clay. Because the particle size increases dramatically and optimal polymer dose decreases with increasing ionic strength, a corresponding change in flocculated structure is expected. This change in structure could diminish the role of the polymer in flocculation as ionic strength increases.

This communication aims to directly observe the polymer in its native fluid environment using fluorescence in order to determine the mechanism of flocculation and to observe how changes in solution ionic strength affect polymer organization in flocs during the flocculation process. The distilled water that was used for these experiments was supplied by Premium Waters, Inc. Powdered Na-bentonite and NaCl of ACS grade from Fisher Scientific was used as received. The polymers used in this study are cationic polyacrylamide (FLOPAM FO 4190 SH, SNF Polydyne) with 10% quaternary amine monomer charge groups and a molecular weight of 6×10^6 g/mol, and cationic polyacrylamide (FLOPAM FO 4990 SH, SNF Polydyne) with a 100% quaternary amine monomer charge groups and a molecular weight of 6×10^6 g/mol. A fluorescent analogue of the commercial 10% charged polymer was synthesized for these experiments. Cy5-labeled PAEMAm-s-PMAAPTA used in the study was designed to mimic the commercial cationic polyacrylamides by keeping the percentage of quartenary ammonium hard charge groups at 10%, i.e. equivalent to the commercial polymer. Furthermore, the fluorescent labeling was carried out such that only a few primary amine groups per polymer were labeled to maintain the chemical and physical properties of the polymer backbone intact.

Synthesis of PAEMAm-s-PMAAPTA was completed by adding N-(2-aminoethyl)methacrylamide·HCl (AEMAm, 165 mg, 1 mmol, 10 wt.%), [3-(methacryloylamino)propyl]trimethylammonium chloride (MAAPTA, 1987 mg, 9 mmol, 90 wt.%) and 4,4′-Azobis(4-cyanovaleric acid) (ACVA, 14 mg, 0.05 mmol) to a round-bottomed flask containing a 0.1 M acetate buffer (pH 5.2, total volume = 4 mL) and stirred until a homogeneous solution was obtained. The solution was purged with nitrogen for 30 min, and stirred at 70 °C for 18 h. The sample was dialyzed (50 kD MWCO, Spectrum Laboratories Inc.) against water (pH adjusted to 5.5 with conc. HCl) for 3 days and freeze-dried to obtain PAEMAm-s-PMAAPTA as a white solid (Mn = 3.3 MDa, dn/dc (experimental) = 0.1081, Mw/Mn = 1.247). Cyanine5 (Cy5)-labeled PAEMAm-s-PMAAPTA was synthesized by dissolving PAEMAm-s-PMAAPTA (825 mg, 0.25 μmol) in 0.2 M $NaHCO_3$ in a round-bottomed flask and adding Cy5 NHS ester (3.85 mg, 6.25 μmol Lumiprobe Corp.) dissolved in DMSO. More $NaHCO_3$ and DMSO were added to adjust the polymer concentration to 20 mg/mL and 10% DMSO. The reaction was stirred in a dark room overnight at room temperature. The sample was dialyzed (50 kD MWCO, Spectrum Laboratories Inc.) against water (pH adjusted to 5.5 with conc. HCl) for 3 days and freeze-dried to obtain Cy5-labeled PAEMAm-s-PMAAPTA as a dark blue solid. Fig. 1 summarizes the reaction scheme.

In bentonite flocculation experiments, a bentonite concentration of 30 mg/L was achieved by first dissolving the required amount of NaCl to reach the desired ionic condition in 250 mL of distilled water within a 600 mL beaker, then adding 7.5 mg of bentonite. This solution was then stirred for 30 min at 300 RPM in a VELP Sceintifica JTL4 Flocculator. The polymer dose was then added and mixed at 150 RPM for 30 s, at which point the RPM was lowered to 20 RPM for 20 min, following standard flocculation methods. After settling, the flocs were pipetted out of the beaker onto a microscope slide with (~3.2 mm deep) PDMS wells, then covered with a glass cover slip. A Nikon C2plus laser confocal instrument was used with a Nikon Eclipse Ti Microscope with a 20× objective to image the structure of the polymer within the flocs. A Cy5 filter cube was used to image the flocs with excitation wavelengths of 488 and 637 nm and emission wavelength of 447 nm. The images were recorded with a resolution of 2048 × 2048 (0.31 μm/pixel) and the depth between each scan was 2.4 μm for the predissolved 1000 mM and 0 mM flocs, 5 μm for the 1 and 10 mM flocs, and 10 μm for the delay dissolved 1000 mM flocs. The density of the bentonite and composition of the flocs formed vary greatly, which limits index-matching and resultant depth resolution. The pinhole radius was 30 μm. Flocs imaged were chosen based on being representative of the entire population observed. In order to determine the robustness of the technique, particle size distributions of bentonite were measured with a Microtrac BLUEWAVE laser diffraction system. This system is capable of measuring particle sizes from 0.01 to 2000 μm using a modified MIE scattering calculation and ISO TC24. Bentonite particle size distributions were measured prior to polymer injection and were measured immediately after sampling from the flocculator jar.

The polymer–bentonite floc structure as a function of NaCl ionic strength is shown in the representative fluorescent microscopy images in Fig. 2, for 0 mM (2A), 1 mM (2B), 10 mM (2C), and 1 M (2D). In Fig. 2A and B, which correspond to low ionic strength, I ≤ 1 mM, the polymer forms a continuous, interconnected network throughout the floc volume. However, in Fig. 2C and D, where I ≥ 10 mM, the polymer behaves differently. The polymer coats large aggregates of bentonite that have self-aggregated, where the self-aggregation is due to the reduction in electrostatic repulsion. This behavior is most readily apparent in Fig. 2D. The polymer still plays a role in connecting larger aggregates, but does not form the internal structures seen at lower ionic strengths, resulting in very low, yet non-zero, polymer dosing levels. For the representative flocs shown here, the images depict a single floc in Fig. 2A and B, one large floc surrounded by several smaller distinct flocs around it in Fig. 2C, and a collection of several distinct flocs in Fig. 2D.

The effect of salt addition timing on the polymeric behavior inside the floc was also explored, shown in Fig. 3, to test the possibility of kinetically trapping the bentonite particles in a smaller size distribution with a delayed addition of salt. Here, the fluorescence visualization technique was applied to two different 1 M NaCl systems, one where the salt was dissolved before the bentonite, as in Fig. 2, and one where the salt was dissolved 27 min after the bentonite was dissolved. The result is a clear difference in internal structure between 1 M NaCl predissolved (Fig. 3A and C) and 1 M NaCl 27 min delay (Fig. 3B and D). Fig. 3C and D visually shows the stark difference in bentonite particle size between the two different salt timing approaches. In Fig. 3B, corresponding to dissolving the salt 27 min after the bentonite is dissolved, the small bentonite particles are held together by a large, highly interconnected polymer network. However, in Fig. 3A, where the salt is fully dissolved before the addition of bentonite, this network does not form and the polymer simply coats the larger bentonite particles. This suggests that the initial particle size distribution affects how the polymer interacts with the bentonite, and that it is just as important to know as the final solution conditions for determining flocculation behavior.