

1. PRF#: 56822-DN19

2. **Project Title:** Polyelectrolyte-Clay Dynamics and Assembly in Taylor-Couette Flows for Applications in Improved Oil Production

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Annual Report Summary. Our group studies the effect of fluid flows on the mixing of complex systems. Particularly, this project focuses on the particle behavior and flocculation of tertiary systems containing bentonite, an inorganic clay commonly found in water treatment and drilling fluids, humic acid, an organic acid from decaying plant matter, and cationic polyacrylamide, a polymer used to cause flocculation. Two different types of tests were performed on the flocculation process. The first was jar tests, which allowed for a wide range of chemical systems to be studied. The second was the Taylor Couette (TC) cell, which has tightly controlled hydrodynamic flows. In addition to the different mixing systems, a voltammetric sensor was refined, with the goal of tracking the amount of free cationic polyacrylamide in the system over time.

Narrative of Work. Our group has previously studied two-species flocculation of polymer and clay, and found that generally, increasing pH increased the optimal polymer dose and the final turbidity. However, when flocculating bentonite, there are often other contaminants present, which further complicates the flocculation process. Humic acids are one such common contaminate, and therefore were incorporated into the jar test studies to find the optimal polymer dose for the new tertiary system. The system studied here included: 2 g/L humic acid, bentonite, and a commercially available cationic polyacrylamide, FLOPAM 4190 SH. The whole system was studied under an ionic strength of 1.3 mM, and pH was adjusted using hydrochloric acid (HCl) and sodium hydroxide (NaOH). Three different target pH's were studied, pH 3, pH 6, and pH 11, to see how the flocculation process was affected by acidic, neutral, and basic pH's. The type of humic acid used was varied and included: coal humic acid, from Sigma Aldrich, leonardite humic acid, from International Humic Substances Society (IHSS), and peat humic acid, from IHSS.

The range of polymer doses was varied to lower the final turbidity. The turbidity plots for three different pH values for the three different humic acid types are shown in **Figure 1**. Overall, similar behavior across the different humic acid types is observed. Trends with varied pH are as follows: pH 3, one minimum present, most likely due to the stable charge of the humic acid and bentonite at low pH; pH 6.6, more than one minimum in turbidity, most likely due to the change in functional group charge of the humic acids that occurs around neutral pH; pH 11, two different minimums, most likely due to the competition between the absorption of humic acid onto the bentonite and complexation with the polymer. Future investigations include studying particle (floc) growth over time to track size and shape changes, and varying the humic acid concentration to determine how it effects the adsorption of humic acids onto the flocs.

Additionally, a voltammetric sensor was refined to track the concentration of polyacrylamide during flocculation and, thereby, to improve our understanding of the kinetics and mechanisms of flocculation. Previous work showed that the electrode was sensitive to the polyacrylamide, so further experimentation was used to boost the current response of the sensor, which is related to the concentration of the polyacrylamide in solution. The sensor, shown in **Figure 2A**, was composed of a carbon electrode, with a conductive polymer coating, and an ion sensing membrane, and then used in a three-electrode voltammetric set-up along with a platinum wire counter electrode, and a Ag/AgCl in KCl reference electrode.

Past work focused on cyclic voltammetry, where voltage was varied across a range and the resulting current was measured. New work used stripping voltammetry, where a constant voltage was applied to force the polyacrylamide

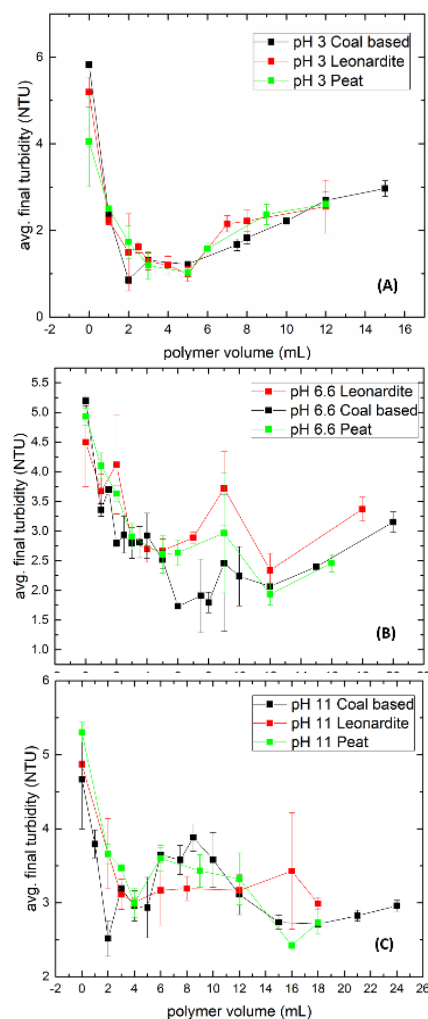


Figure 1. Final average turbidity of polyacrylamide-humic acid-bentonite aqueous systems, for (A) pH 3, (B) pH 6.6, and (C) pH 11.

into the membrane and then the voltage was swept from negative to positive to force the polymer out while measuring the resulting current. The limit of detection of the polymer using this stripping voltammetry was lower than with traditional cyclic voltammetry, as shown in **Figure 2B**.

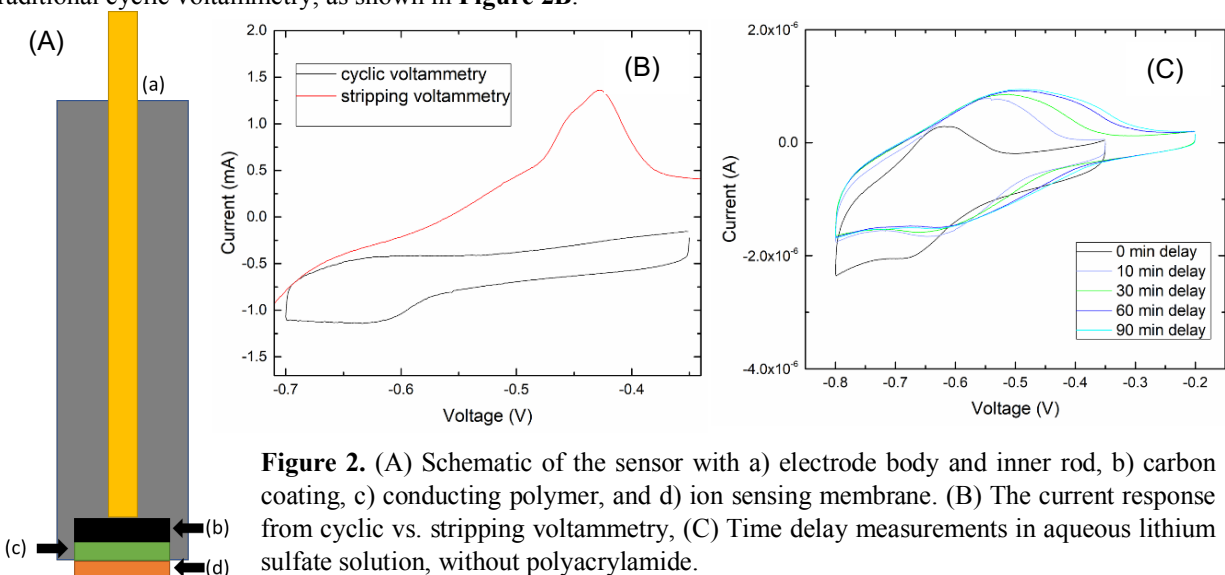


Figure 2. (A) Schematic of the sensor with a) electrode body and inner rod, b) carbon coating, c) conducting polymer, and d) ion sensing membrane. (B) The current response from cyclic vs. stripping voltammetry, (C) Time delay measurements in aqueous lithium sulfate solution, without polyacrylamide.

Additionally, time delay measurements were used to probe the question the polymer also transfers in an electroless mode along with counter anions into the sensing membrane. These experiments were performed by cyclic voltammetry, with the sensor immersed in an aqueous salt solution with or without polyacrylamide present; an example “without polyacrylamide” is shown in **Figure 2C**. The sensor responses did not exhibit sufficient reproducibility; further study will be performed to determine and control the thickness of the ion sensing membrane.

In addition to understanding how varied chemical conditions and polyacrylamide concentrations affect the flocculation process, a TC cell was also used to understand how different hydrodynamic mixing conditions changed the system. Our TC cell is a complex hydrodynamic cell with robust and well understood hydrodynamic flows, and injection ports, allowing flocculation to be studied in-situ. Studies have been done to determine optimal mixing speeds for the different stages of flocculation. Currently, two-species flocculation with bentonite and polyacrylamide is being studied in the cell, but in the future humic acid could be added to study the effect of varied hydrodynamic conditions on the tertiary system. Our group also has the capability to track particle growth over time using a laser-light sheet and high-speed camera to capture images of the flocs throughout the flocculation process. After flocculation, data analysis is done to track floc size and shape changes over time, as shown in **Figure 3**. Flocs grow orders of magnitude in size through the flocculation process, with a rate dependent on the mixing and chemical conditions.

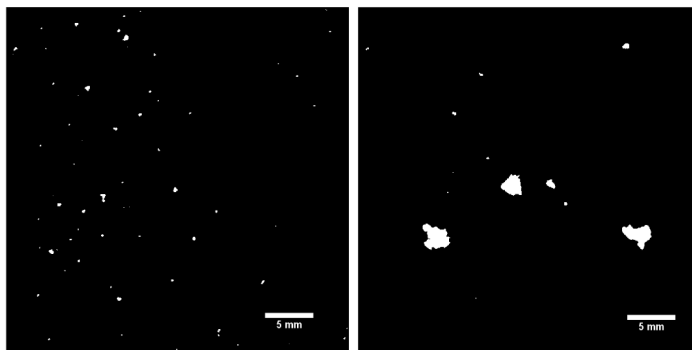


Figure 3. Floc growth, shown with binary images from flow visualization at 210s (left) and 600s (right) into flocculation.

Impact on Career and Students. The ACS PRF grant has supported a Materials Science and Engineering graduate student. While conducting this research, the student has enriched her knowledge of flocculation, electrochemistry, and fluid mechanics. She also continues to learn how to independently plan, perform, and analyze scientific studies. These skills will equip her for success in her post-graduate career. Additionally, the grant has allowed the PI to grow her research program, and to continue an ongoing fruitful collaboration with Professor Phil Buhmann, an expert in electrochemistry and sensor development in the Department of Chemistry. The results of the work and collaboration, e.g., the sensor developed, will enhance the measurements capabilities of the PIs laboratory for years to come.