Growth and structure of flocs following electrocoagulation

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ABSTRACT

The growth and structure of iron precipitate flocs produced in salt water from a bench-scale electrocoagulation (EC) system was investigated. During floc growth, changes in the scattering exponent, an indicator of a flocs' degree of compaction, were reflected by changes in the particle size (diameter of a volume equivalent sphere). Flocs initially formed loose, open structures that spanned broad size ranges, suggesting low repulsion between particles. The initial aggregates then broke and reformed into more compact structures. Comparing plots of scattering exponent against time, it was found that operating at higher currents caused this process to occur more quickly; however, the plots were all similar in shape, suggesting that the structural progression of the EC flocs was not affected. The final floc structures had an average scattering exponent of 2.34 (standard deviation 0.02), which is consistent with literature for flocs produced from iron-based chemical coagulants despite differences in electrolyte ionic strength. Analysis via transmission electron microscopy (TEM) suggested that EC flocs also exhibited amorphous, fractal structures. Operating at higher currents (providing larger iron concentrations) resulted in larger flocs. The average steady-state floc sizes when operating at 0.087, 0.174, and 0.261 A were 93, 147, and 191 μm, respectively. Floc size distributions also reached steady-state more quickly due to the higher frequency of particle collisions. Using a stainless steel (SS) cathode rather than an aluminum one resulted in 15% larger flocs (154 μm and 134 μm, respectively). However, given that experimental conditions (mixing and current) were otherwise equivalent, more research is required to determine the cause of this difference. The results of this work were consistent with literature regarding chemical coagulation (CC) and may have implications for the design of downstream clarification processes.

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1. Introduction

1.1. Electrocoagulation

Electrocoagulation (EC) is a water treatment technology that has been investigated in a variety of bench-scale water treatment scenarios. These include the pretreatment of surface water for microfiltration [1], the removal of silica from brackish water as a pretreatment to membrane filtration [2], and the treatment of high conductivity black liquor resulting from the paper industry [3]. Like chemical coagulation (CC) using metal salts, EC works by releasing metal cations into solution in order to destabilize small particles in water, thereby making particle collisions more likely to result in aggregation [4]. However, instead of using metal salts such as ferric chloride or alum, EC uses sacrificial electrodes to provide a direct source of cations.

An EC system is an electrolytically operated electrochemical cell. As such, by controlling the current, an operator can control

the rate of cation generation. In its simplest form, an EC system must consist of a power source, an electrolyte, and at least one anode–cathode pair. At the anode, metal cations are released into solution and react with water molecules to form metal hydroxide species. At the cathode, the evolution of hydrogen gas occurs. These electrochemical reactions are discussed in further detail elsewhere [5,6].

1.2. Floc growth and structure

Floc growth in coagulation processes occurs over several phases. Initially, aggregation is dominant, and flocs rapidly increase in size, forming large, open structures. Using higher coagulant doses tends to result in large, fast growing flocs, due to the higher concentration of particles available for collision [7,8]. Eventually, floc aggregation and breakage balance to create a steady-state particle size distribution, with flocs reaching a limited size. This occurs because the rate of aggregation decreases as a result of increased floc size (as the number of particles in the system is reduced). Larger flocs are also more vulnerable to breakage. In addition, there is evidence that floc breakage is somewhat

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irreversible, as flocs do not completely reform after being broken by high shear [7,9]. Operating at higher shear forces increases particle fragmentation and restructuring, thereby producing smaller, more compact aggregates [8,10–12].

Diffusion limited aggregation (DLA) and reaction limited aggregation (RLA) are particle aggregation models designed with the assumption that particle collisions occur only via Brownian motion (random movement caused by thermal energy). Although most systems apply some form of shear, invalidating this assumption, the models are still useful in illustrating the formation of different floc structures. The DLA model assumes that there is negligible repulsion between particles, such that when they collide, they adhere to each other easily and form loose, open structures. In contrast, the RLA model assumes that there is significant repulsion between particles, such that many collisions are required in order to form an attachment; this allows aggregates to break and reform, resulting in more compact structures [4,12].

1.3. Flocs produced from electrocoagulation

There is limited research available regarding the characteristics of flocs produced from EC. One study by Harif et al. [13] found, when comparing CC against EC, that the latter process created more fragile flocs, albeit more quickly and over a broader pH range. Furthermore, based on settling data, Larue and Vorobiev [14] found that the density of EC flocs ($1050.0 \pm 2.0 \text{ kg/m}^3$) was very similar to the density of flocs from ferrous sulfate ($1053.0 \pm 2.0 \text{ kg/m}^3$), but greater than the density of flocs from ferric chloride ($1026.4 \pm 0.0 \text{ kg/m}^3$). However, ferric chloride produced the largest flocs ($213 \pm 4 \text{ }\mu\text{m}$), followed by EC ($141 \pm 4 \text{ }\mu\text{m}$), and finally ferrous sulfate ($100 \pm 6 \text{ }\mu\text{m}$). In general, more research on this subject is required.

Floc characteristics, such as size and structure, will impact the effectiveness of downstream clarification methods. EC unfortunately does not share the same breadth of research that is available to CC. This work attempts to help close this gap by investigating the effect of cathode material and current intensity on the growth and structure of EC flocs using particle size distribution data, structural analysis over time, and transmission electron microscopy (TEM). Prior work has suggested that the cathode material affects the power consumption of an EC system [15]; however, the effect on the flocs produced was not explored. This research was conducted using salt water, as EC is inherently more efficient when treating a high conductivity solution. Furthermore, for simplicity, no pollutant was added to the solution; in other words, this experiment forms and aggregates only iron hydroxide precipitates.

2. Materials and methods

2.1. Bench-scale EC system

Fig. 1 gives a diagram of the bench-scale EC system used for this experiment. The system was operated in batch mode using an 1170 mL working volume. A magnetic stir bar was used to keep the solution well mixed during operation.

A single anode–cathode pair was used for the electrodes. The anode was a pure iron cylindrical wire with a 2 mm diameter and a submerged height of 5.1 cm, resulting in a submerged surface area of 3.20 cm^2. Two cathodes were made for comparison, one of stainless steel (SS) and one of aluminum. The cathodes were identically shaped half-cylinders with a 0.25 cm wall thickness, a 2.1 cm outer diameter, and a submerged height of 5.1 cm, resulting in a submerged surface area of 32.2 cm^2. The surface area ratio of the cathode to the anode was thus 10.0. The gap between the anode and the inner surface of the cathode was 0.7 cm. The
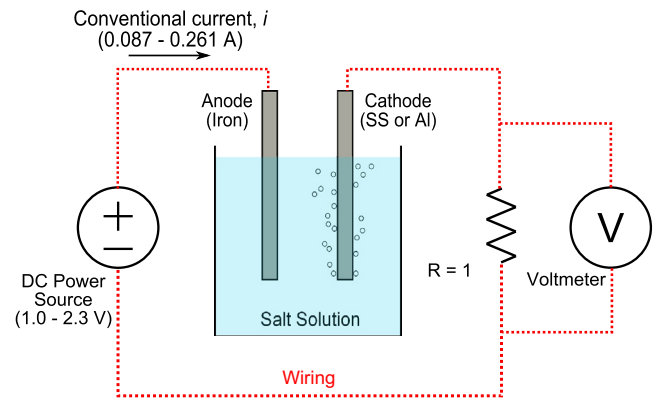

Fig. 1. Schematic diagram of bench-scale electrocoagulation system.

electrodes were physically clamped into place using plastic plates, allowing for easy assembly and disassembly. Between experimental runs, the electrodes were scrubbed with steel wool and rinsed with distilled water.

Current was supplied from a GPS 3030DD DC power source (GW Instek, New Taipei City, Taiwan). As indicated in Fig. 1, a high accuracy 1 Ω resistor (1% tolerance) was connected in series with the EC cell. A Volt101A data-logging voltmeter (MadgeTech, Warner, NH, USA) was placed in parallel with the resistor. The voltmeter was used to measure the current of the system; by Ohm's law and Kirchhoff's laws, the magnitude of the system current was equal to the magnitude of the voltage across the resistor. The logged currents typically reached a plateau within a few seconds and, barring minor fluctuations, remained constant. For each test, the median current was calculated and taken as the steady-state current.

2.2. Electrolyte

The electrolyte was made by dissolving 25 g/L of sodium chloride and 15 g/L of calcium chloride dihydrate (Fisher Scientific, Waltham, MA, USA) into reverse osmosis water. Averaging all tests, the initial conductivity and pH were respectively 60.38 mS/cm (standard deviation 2.05 mS/cm) and 5.46 (0.05). Likewise, the final conductivity and pH were respectively 59.76 mS/cm (2.32 mS/cm) and 5.99 (0.08). The solution's ionic strength was 0.73 M, which was comparable to that of sea water. The approximate ionic strength of sea water was calculated to be 0.7 M, based on a list of major ionic species provided by McLellan [16]. As no target pollutant was added, this experiment studied the formation and characteristics of iron hydroxide precipitates.

2.3. Experimental design and procedure

This experiment studied the effect of cathode material on particle growth and structure at 3 different currents. As listed in Table 1, this resulted in 6 unique cases (with 1 replicate, 12 total runs). The operating voltage, theoretical current, and approximate power for each experimental combination are also given in Table 1. The operating voltages were calculated using Eqs. (1) and (2) for the SS cathode and the aluminum cathode, respectively. These equations, which were determined experimentally and are specific to the bench-scale system and the electrolyte, relate the mass of iron produced in 1 min to the operating voltage:

$$F = 3.38V - 2.32 \quad R^2 = 0.944 \tag{1}$$

$$F = 2.37V - 1.89 \quad R^2 = 0.928 \tag{2}$$

where F is the mass of iron (mg), and V is the operating voltage (V).