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ELECTROCHEMICAL COAGULATION OF CLAY SUSPENSIONS

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Abstract—In the electrocoagulation process a suspension of kaolinite and bentonite is coagulated by electrochemical treatment where aluminum anodes are dissolved and aluminum ions react with clay particles, forming flocs which precipitate. Several factors affecting the efficiency of electrocoagulation are investigated. They include NaCl concentration, voltage, and flow conditions within the cell. Increased NaCl concentration led to lower electric resistance and cleaner running electrodes. Enhanced shear associated with recirculation resulted in clear supernatant and more compact flocs. While increasing the feed rate, which was equivalent to decreasing aluminum concentration through the system, reduced cake height but increased turbidity.

Key Words—Bentonite, Coagulation, Electrochemical treatment, Kaolinite.

INTRODUCTION

Electrochemical treatment of turbid water is an effective method for increasing the clarity and purity of water. Sacrificial anodes made of iron or aluminum are known to be used (e.g., Donini *et al* 1993; Kolarik *et al* 1991; Biswas and Lazarescu 1991; Renk 1988; Groterund and Smoczynski 1986, 1992). The anode dissolves introducing coagulating ions of Fe^{2+} (oxidized to Fe^{3+} by any oxygen in solution) or Al^{3+} into the turbid water suspension. These ions interact with clays and other suspended particles leading to the formation of flocs. Aluminum is usually the preferred material since it does not colour the supernatant. The electrocoagulation unit is environmentally friendly. It does not create corrosion or any pollutants. The considerable advantage of this method is the possibility of simultaneous removal of suspended matter, petroleum products, polychlorinated biphenyls (PCB's), metal ions and bacterial contamination (Zolotukhin 1989).

Kaolinite and bentonite have a heterogeneous surface charge. The charge on edges is due to protonation/deprotonation of surface hydroxy groups, and therefore, depends on pH. The point of zero charge (pzc) of kaolinite has been found to be between pH 5.5 and 6.7 (Young and Ohtsubo 1987), depending on conditions. Faces of kaolinite plates are always charged negatively while the edges are positively charged below the pzc, and negatively charged above the pzc, therefore increasing stability of suspension. Aluminum ions added to the clay suspension are known (van Olphen 1963) to play a triple role: (1) as a counter ion; (2) as a cation which adsorbs to the surface of clay, allowing hydrolysis to occur on the clay surface; (3) as a bonding agent between clay particles by the Al-hydroxides. Al-hydroxides are readily formed above pH 4 (Despic and Parkhutik 1989) and they have positively charged double layer (Bertsch *et al* 1989). They are able to form mono- and polymeric hydroxy ions. It has been reported (Gu and Doner 1990; Hsu 1989) that each Al-centre could carry a multi charge from +7 up to +18 at $[OH^-]/[Al^{3+}]$ ratios of 2–2.7. The addition of aluminum ions into clay suspension resulted in the reduction of the kaolinite electrical double layer thickness due to: increase of ionic strength and aluminum adsorption on the clay surface neutralizing the surface negative charge, and therefore, an increase of zeta potential was predicted and actually reported (Young and Ohtsubo 1987). The electrical double layer becomes more compressed and dense when aggregation occurs. This produces flocs that become more open as aluminum concentration increases. This resulted in less compact flocs with a lower settling rate.

The standard potential of aluminum dissolution is lower, −1.662 V, than the standard potential of hydrogen evolution, −0.828 V. However, it is known (Pourbaix 1966) that in solutions containing noncomplexing ions of pH between 4 and 9, aluminum forms a passivating layer of oxides that inhibits reaction with water. In the presence of chloride ions, $[AlCl_4]^{3-}$ ions are formed which accelerate dissolution of metallic aluminum, especially at elevated temperature and in acidic or strongly basic solutions. Two different mechanisms can be expected during anodic aluminum dissolution; one is electrochemical, a strictly faradaic process, and the other is the purely chemical dissolution of aluminum. Therefore the following electrochemical reactions are expected:

Anode

$$Al^0 = Al^{3+} + 3e^- \qquad E^\circ_1 = -1.662\ V \quad (1)$$

$$2\,OH^- = \tfrac{1}{2}O_2 + H_2O + 2e^- \qquad E^\circ_2 = 1.229\ V \quad (2)$$

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Cathode

$$2\,H_2O + 2e^- = H_2 + 2\,OH^- \qquad E^\circ_3 = -0.828\ V \quad (3)$$

additionally, both anode and cathode will be dissolving chemically;

$$Al^0 + 3\,H_2O = Al(OH)_3 + 3/2\,H_2 \quad (4)$$

Note that the dissolution of aluminum is thermodynamically favoured ($E^\circ_3 \gg E^\circ_1$) and that it should proceed spontaneously. It is impossible to deposit metallic aluminum from an aqueous solution of its ions except under special conditions (Despic and Parkhutik 1989; Przhegorlinskii *et al* 1987) determined the contribution of individual reactions [Eqs.(1–4)]. Each of these reactions was evaluated from the weight loss of the corresponding electrode and from the volume and composition of the collected gases. The electrolysis was performed for 30 min at 0.45 A in a suspension containing 1 g/dm^3 NaCl. No oxygen was found; the gas consisted of pure hydrogen. Therefore, reaction 2 did not occur under these conditions. Thus, the main reactions during electrocoagulation with aluminum electrodes were electrochemical [Eq. (1)] and chemical [Eq. (4)] dissolution of the anode; hydrogen evolution [Eq. (3)], and the chemical dissolution of the cathode [Eq. (4)] Since both electrodes were chemically dissolving with time, the current efficiency of aluminum dissolution was above 100% and was in the range of 165%–215%. Higher than 100% aluminum current efficiency was also reported by others (Bozin and Mikhailov 1990; Przhegorlinskii *et al* 1987). There are still not enough data explaining electrocoagulation process, therefore, this article presents more fundamental study performed in our pilot plant in order to examine the influence of feed rate, turbulence, and NaCl concentration on the settling rate and the resulting turbidity of the supernatant.

EXPERIMENTAL METHODS

Sample preparation

Suspensions containing 0.04% bentonite and 0.16% kaolinite were prepared the day before the experiment and allowed to stand overnight. In most cases, NaCl concentration was fixed at 0.03% to yield the desired conductivity of the suspensions. NaCl concentrations were varied from 0% to 0.1% for the investigation of the effect of NaCl concentration on the qualities of electrocoagulation product.

Electrochemical cell

Figure 1 shows the schematic arrangement of the electrocoagulation pilot plant. The essential part is an electrochemical cell containing four aluminum plates that provide three flow-through channels. The flow rate in these channels is controlled by the feed and recycle pumps that partly recycle the effluent. The main pump feeds the suspensions through the cell at flow rates, referred to as feed rates, from 0 to 30 liters/min. The recirculation pump is used to increase turbulence within the cell by recycling effluent at a flow rate of 70 liters/min. Alternate electrodes have opposite polarities to provide a voltage or current gradient across each pair of electrodes. The gap between electrodes is 6 mm and accommodates spacers that promote turbulence within the cell. Each of the four rectangular electrode plates was 16.5 cm high and 58 cm wide.

A DC signal was applied and polarity was switched every 300 s. The power supply was interfaced directly to a computer allowing its control through the commercially available Specifix software. The software recorded voltage, current, and time, as well as the conductivity and temperature of the suspension. These data were imported to Quattro Pro and processed.

Analysis

Settling test was carried out in 1-liter cylinders. The Hach Ratio/XR turbidimeter was used to measure the turbidity of the feed and product. Turbidity of the supernatant sampled from a settling cylinder was tested based on 10, 45 and 90 minutes of settling and indicated on the corresponding graphs. Otherwise, the turbidity values corresponded to 45 minute settling period. Aluminum concentration was measured as described by Wilson and Sergeant (1963). The critical coagulation concentration of aluminum ions in a batch experiment was found to be 20 ppm. The cake height was measured as the height of the sludge/supernatant interface after 20 hours settling.

RESULTS

Effect of flow rate

The clay suspensions were passed through the electrochemical cell described above and, treatment samples were collected. The turbidity and cake height of the total coagulated material were measured. Figure 2a shows that turbidity of the supernatant increased slowly with feed rate. This is related to residence time of the clay suspension in the cell. The longer the residence time the higher the concentration of aluminum ions observed (see Figure 5 where total aluminum content is higher at longer residence times, i.e., lower feed rates); these ions have also more time to react, forming flocs of clay bonded with aluminum. One can see that the turbidity was lower in a suspension where the recirculating pump was used, especially below 17 liters/min. Above 17 liters/min the highest values of turbidity were observed and there was no clear difference in turbidity between circulated and recirculated suspension. There are two main components that influenced the turbidity in an experiment. One is the aluminum

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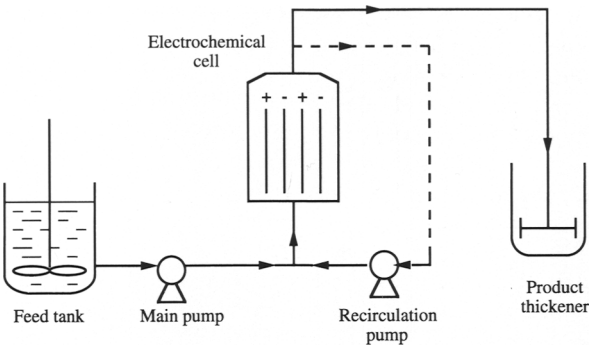


Figure 1. Schematic representation of the electrocoagulation pilot plant unit.

concentration, which is related to the residence time, and the other is the shearing effect. High flow rate through the cell and smaller gap distance between the two neighbouring electrodes result in higher shearing rate on the suspension. Since the aluminum concentration in clay suspension does not change much with higher feed rates (see Figure 5, above 17 liters/min) it is concluded that the increase in turbidity with higher feed rate (>17 liters/min) was mainly due to the flocs shearing.

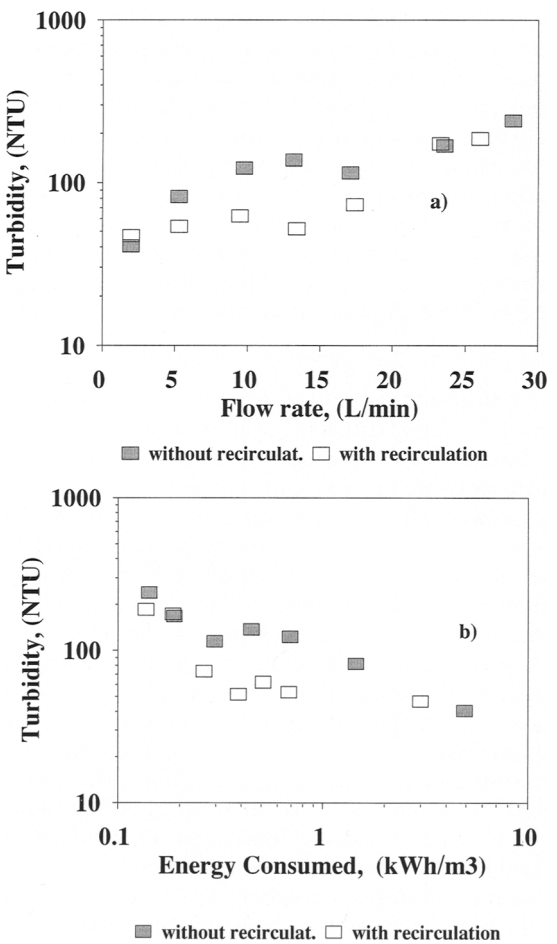


Figure 2. Turbidity, measured after 10 min, as a function feed rate (a) and energy consumption (b) for circulated and recirculated suspension.

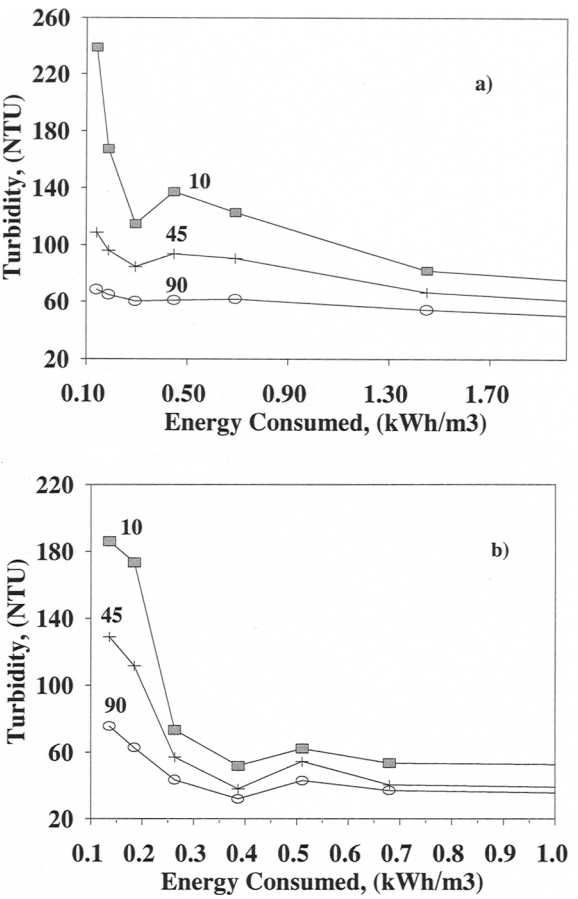
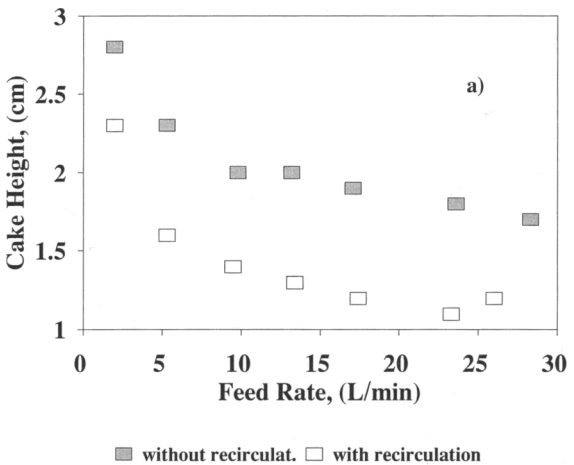


Figure 3. Turbidity of circulated (a) and recirculated (b) suspension as a function of energy and time. Turbidity measured after 10, 45 and 90 minutes.

As shown in Figure 2b, the clarity of supernatant increased with higher input energy which was a consequence of dissolving more aluminum ions. The clarity of supernatant also increased with time (Figures 3a and 3b), and the recirculated suspension had generally lower turbidity than the once-through suspension (Figures 3a and 3b).

The relationships between cake height, feed rate, flow rate, and consumed energy are shown in Figures 4a and 4b. High feed rate reduces the energy consumed per volume of feed and aluminum ion concentration in the suspension (see Figure 5). However, higher flow rate promotes turbulent mass transport and shearing effect. Aluminum ions generated at the anodes are delivered to the clay surfaces more efficiently. Larger and more open flocs are broken into smaller but more compact ones. The cake height was lower for higher feed

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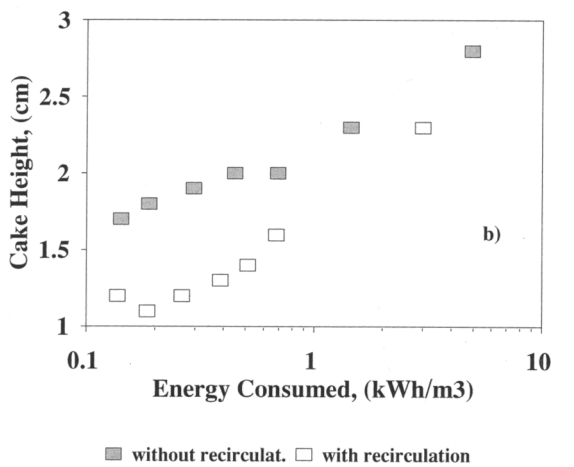


Figure 4. Cake height as a function of feed rate (a) and energy consumption (b) for circulated and recirculated suspension.

rate (Figure 4a) and the flocs were looser (more open in structure and containing more water) with higher consumed energy (Figure 4b). Too high feed rate increased sharply turbidity of supernatant (Figure 2a). Recirculated solution's flocs decreased cake height in comparison to once-through suspension (Figure 4a with and without recirculation). Cake height tended to increase with input energy, which is contrary to turbidity behaviour (Figures 2b and 4b). This means, that as the aluminum concentration increased, supernatant seemed to be clearer but the flocs were looser. In both cases, observed turbidity and cake height were lower in a recirculated suspension.

The aluminum concentrations in the supernatant and cake represent the amount of aluminum dissolved during the electrocoagulation process and are presented in Figure 5. Aluminum content depends mainly on applied voltage [Eq. (1)] and associated chemical reaction [Eq. (4)]. The transport of dissolved ions from anode into the bulk is strongly influenced by flow conditions.

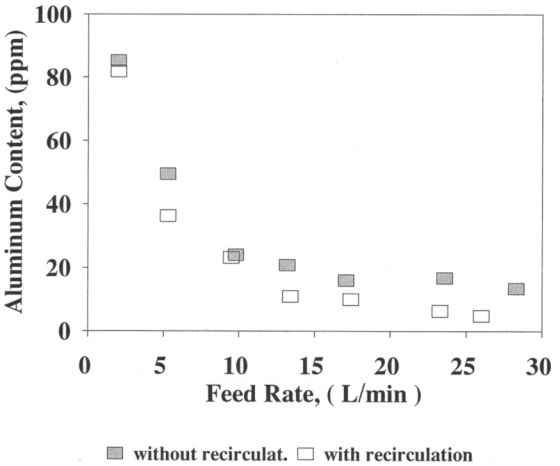


Figure 5. Aluminum concentration as a function of feed rate.

Obviously, the higher the flow rate, the faster aluminum ions migrate towards the clay suspension. As seen in Figure 5, the resulting aluminum ion concentration, and therefore the rate of consumption of the aluminum electrodes, was lower in the recirculated suspension. Accordingly, it would seem that aluminum ions are more efficiently used when they are passed through a recirculation pump due to better mixing with the clay suspension. This leads to the conclusion that better mixing reduces the demand for aluminum ions to coagulate the suspension. Thus, a lower aluminum ion concentration in recirculated suspension, gives better values of supernatant turbidities (Figure 2a) and cake heights (Figure 4a) than non-recirculated suspension.

Effect of NaCl concentration

As expected the conductivity of clay suspensions increased linearly with NaCl concentration. An increase in conductivity decreased the ohmic drop between electrodes and, therefore, more aluminum ions could be produced at the same power input. Also, the formation of $[AlCl]^{3-}$ ions is expected to promote the chemical dissolution [Eq. (4)] of electrodes. A slight pH increase was observed due to the water decomposition reaction on the cathode during electrolysis [Eq. (3)], with an increase in NaCl concentration. The NaCl concentration influence on turbidity is shown in Figure 6. The turbidity decreased with NaCl concentration (Figure 6a), energy (Figure 6b) and time. Since the system was under voltage control, a decrease in ohmic resistance led to an increase in current and a parallel increase in anode dissolution. Therefore, lower turbidity was expected, and actually recorded, in suspensions containing higher NaCl concentration (>0.03%) as compared with suspensions without NaCl (Figures 6a and 2a at 6 liters/min, without recirculation). But still higher NaCl concentration (>0.06%) was needed to obtain the range of turbidity for recir-

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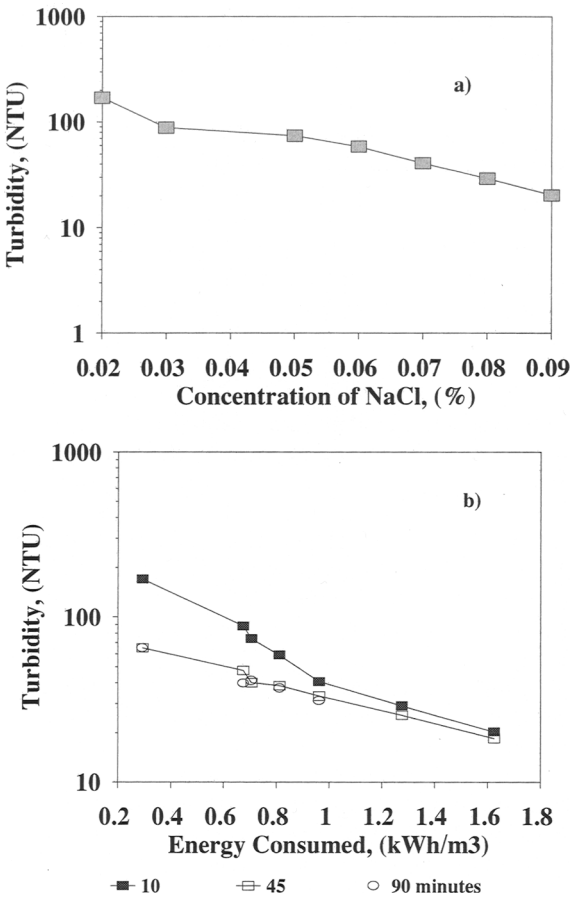


Figure 6. Turbidity, measured after 10 min, as a function of NaCl concentration (a) and consumed energy (b). Feed rate 6 liters/min. In Figure 6b turbidity was measured after 10, 45 and 90 minutes.

culated solution (Figures 6a and 2a, at 6 liters/min with recirculation). Turbidity decreased as a function of energy (Figure 6b). But, if compared with solution without NaCl (Figure 2b, without recirculation), one could

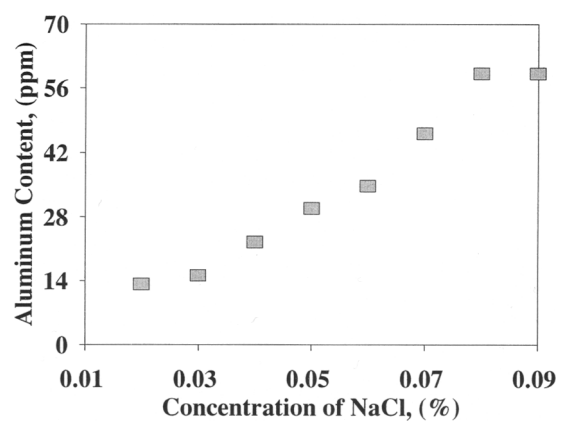


Figure 7. Aluminum concentration as a function of NaCl concentration in a clay suspension. Feed rate 6 liters/min.

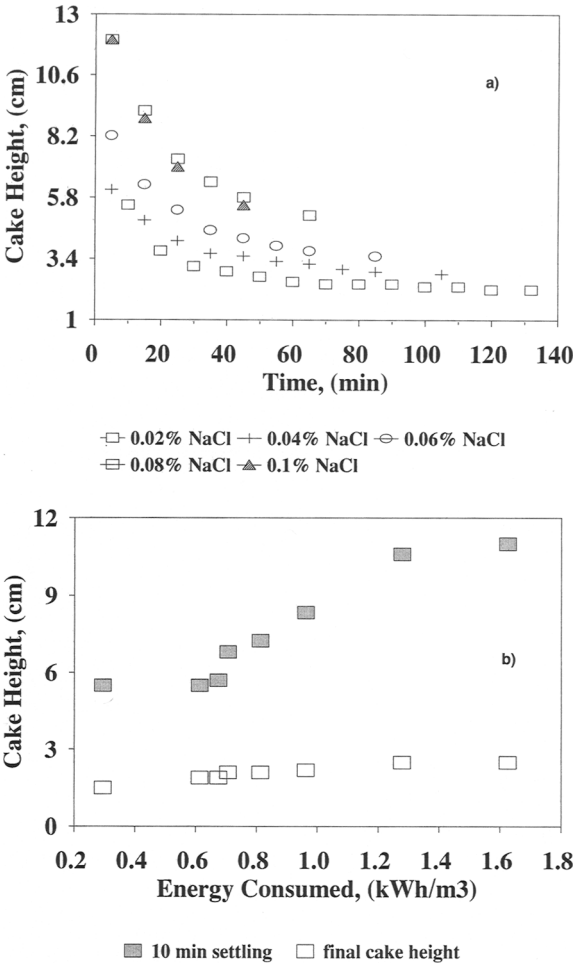


Figure 8. Cake height as a function of NaCl concentration, time (a) and energy (b). Feed rate 6 liters/min.

notice that up to 0.5 kWh/m³ the turbidity in those two solutions was not much different while just after 0.5 kWh/m³ the turbidity significantly decreased in solution containing NaCl. The increase in aluminum ion concentration in the clay suspension as a function of NaCl content is shown in Figure 7. Generally, the presence of NaCl in concentrations higher than 0.03% produced an overdosage of aluminum in the system (>20 ppm). Consequently, aluminum ion concentration influenced the clarity of supernatant as well as the structure of flocs. The supernatant was clearer with higher aluminum ion concentration and, in a suspension initially containing more NaCl, the cake height actually was higher, as depicted in Figure 8a. The cake height decreased with time but increased with NaCl concentration since more aluminum ions were dissolved (Figure 7). Cake height also increased with applied energy (Figure 8b) for the same reason i.e., higher production of aluminum ions. It confirms that if more aluminum were dissolved, the flocs were looser and

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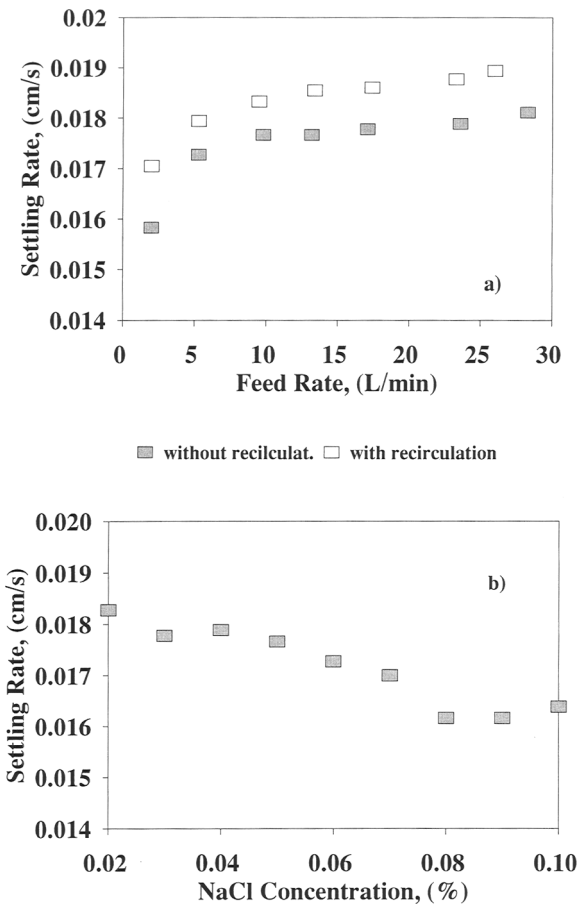


Figure 9. Settling rate as a function of feed rate for circulated and recirculated suspensions not containing NaCl (a) and circulated suspensions containing different amounts of NaCl (b) at 6 liters/min.

more open, which obviously sedimented more slowly. Exactly the same conclusion was found in previous section where increasing the amount of dissolved aluminum (either by decreasing the feed rate of the suspension or by increasing the NaCl concentration), resulted in a clearer supernatant and looser flocs that sedimented more slowly. This is especially evident for flocs produced in the presence of NaCl (Figures 8b and 4b, without recirculation, where the cake height values at 1 kWh/m^3 were *ca.* 8 and 2 cm respectively) due to the large increase in aluminum concentration caused by the increased conductivity of a suspension containing NaCl.

DISCUSSION

The efficiency of the electrocoagulation process is determined by many parameters such as the feed rate, the flow rate of the suspension within the cell, the presence of NaCl and the applied current or voltage. The two most important economic factors are the consumption of aluminum and the electrical energy consumption. It is therefore extremely important to understand the factors that influence aluminum dissolution. The structure of the flocs influences the sedimentation rate. In this study the sedimentation rate was sensitive to feed rate, but was even more sensitive to the flow rate within the cell (i.e., the feed rate plus the recirculation rate), as shown in Figure 9a. This might be due to the more compact flocs obtained when the suspension is recirculated. The settling rate decreased with increasing NaCl concentration (Figure 9b) due to looser flocs structure.

CONCLUSIONS

The clarity of the supernatant as well as the structure and settling rate of the precipitate depended on applied current, voltage, flow conditions and the presence of NaCl. All these factors regulate the dissolution of aluminum electrode and, therefore, aluminum ion concentration in the electrochemical cell. It is this concentration that has a major role in determining the turbidity of the supernatant as well as the resulting cake height.

However, in view of the complexities already presented, it is not yet feasible to fully analyze the factors conducive to the desired result of a clear supernatant and a well-packed cake or sediment containing as little water as possible. It is, however, obvious that some of these factors, especially the clarity and water content of the cake, are conflicting and an optimal trade-off has to be found.

Future work with a cell redesigned to maximize suspension turbulence, will revisit these relationships and attempt to obtain the most economic parameter settings consistent with economy of the total process (i.e., electrocoagulation plus disposal of the cake) and with regulatory standards for supernatant clarity.

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