

Electroflocculation as potential pretreatment in colloid ultrafiltration

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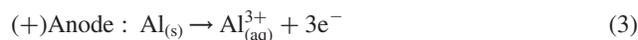
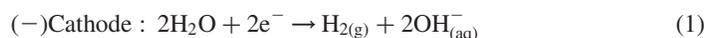
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Abstract Electroflocculation (EF) is a coagulation/flocculation process in which active coagulant species are generated in situ by electrolytic oxidation of an appropriate anode material. The effect of colloidal suspension pretreatment by EF on membrane fouling was measured by flux decline at constant pressure. An EF cell was operated in batch mode and comprised two flat sheet electrodes, an aluminium anode and stainless steel cathode, which were immersed in the treated suspension, and connected to an external DC power supply. The cell was run at constant current between 0.06–0.2A. The results show that pre-EF enhances the permeate flux at pH 5 and 6.5, but only marginal improvement is observed at pH 8. At all pH values cake formation on the membrane surface was observed. The differences in membrane behavior can be explained by conventional coagulation theory and transitions between aluminium mononuclear species which affect particle characteristics and consequently cake properties. At pH 6.5, where sweep floc mechanism dominates due to increased precipitation of aluminium hydroxide, increased flux rates were observed. It is evident that EF can serve as an efficient pretreatment to ultrafiltration of colloid particles.

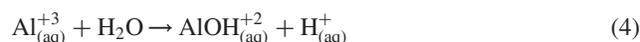
Keywords Coagulation; colloid; electroflocculation; filtration; fouling; ultrafiltration

Introduction

Electroflocculation (EF) is a coagulation/flocculation process in which active coagulant species are generated in situ by electrolytic oxidation of an appropriate anode material. The EF process can substitute for chemical coagulation aimed at destabilizing emulsions and colloidal suspensions. In its simplest form, an EF reactor may be made up of an electrolytic cell containing one anode and one cathode. When connected to an external power source, an oxidation reaction occurs at the anode and a reduction reaction at the cathode. The specific chemical and electrochemical reactions occurring within the EF cell depend upon the type of metal used as the anode. The anode material most commonly used is aluminium or iron because when electrochemically oxidized they produce the most commonly used ionic coagulants, Al^{+3} and Fe^{+3} (or Fe^{+2}) respectively. The basic reactions that occur with aluminium anodes are described in Equations (1)–(3):



The aluminium cation hydrolyses upon addition to solution. Mononuclear complexes are initially formed as described by Equations (4)–(7) (see [Figure 1](#)).



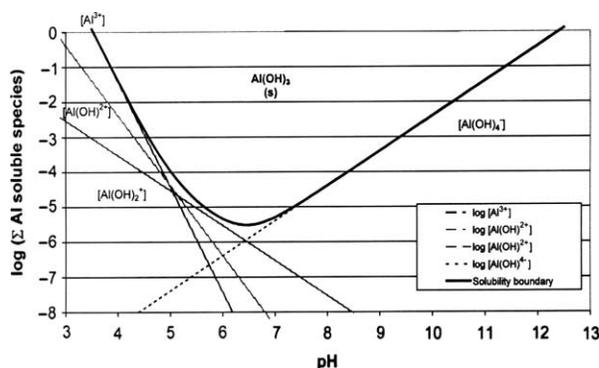
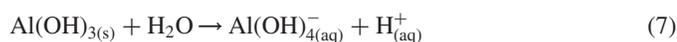
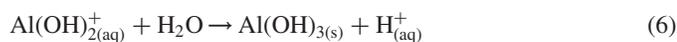
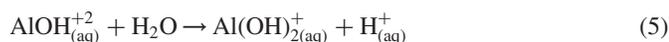


Figure 1 Solubility diagram of aluminium hydroxide $\text{Al(OH)}_{3(s)}$ with mononuclear species



The speciation of aluminium systems has been well documented in the literature (Sposito, 1996; Letterman *et al.*, 1999; Duan and Gregory, 2003). This paper will assume that mononuclear hydrolyzed species adequately predict aluminium hydroxide precipitation.

The type of coagulant required in the system dictates the choice of the anode material in an EF reactor. The theoretical dosage can be calculated using Faraday's law, which describes a linear relationship between current intensity and the amount of metal dissolved. In order to achieve the desired current, and overcome the IR drop (caused by the cell itself and polarization factors), steps can be taken to lower the system resistance (e.g. minimize distance between electrodes, increase conductivity) or a potential greater than the theoretical potential must be applied to the cell. The cathode material is of less importance, although, due to oxygen gas formation at the anode, and hydroxide ion formation at the cathode, the surface of the cathode can become chemically oxidized, producing aluminium oxide, which forms a passivation layer, and also can undergo pitting due to a highly basic local environment. This increases the resistance within the cell, causing a drop in voltage across the cell, which, in turn, decreases the metal dissolution at the anode. Using cathodes made from inert metals, or metals that oxidize slowly, or using an AC generator, can overcome this problem (Ivanishvili *et al.*, 1987).

Only in the past decade has awareness grown as to the advantages of using the technology for electrochemical treatment of water and wastewater. Today, electrochemical processes are being used in a wide range of applications (Mollah *et al.*, 2001; Adin and Vescan, 2002). Treatment of wastewater by EF has been practiced for most of the 20th century, yet limited scientific research has explored the efficiency of the technology as an alternative process for water treatment. Preliminary work has been done on colloid and organic matter removal (Vik *et al.*, 1984; Matteson *et al.*, 1995), although in general, technological developments have focused on commercialization of the process by minimizing electrical power consumption and maximizing effluent throughput rates (Mills, 2000).

Membrane filtration is a widely applied technology in water and wastewater treatment (Bourgeois *et al.*, 2001), although membranes are highly susceptible to fouling. Fouling is caused by a combination of factors: (1) accumulation of materials on the membrane

surface which precipitate or form a layer that resists the flow of permeate (cake formation); (2) internal blocking by materials entering the membrane pores; (3) pore blocking; (4) accumulation of materials near the membrane surface, in the concentration boundary (referred to as the concentration polarization layer); (5) changes in the membrane structure (Carroll *et al.*, 2000). In most cases, when treating water, the concentration polarization layer, if formed, contributes negligible resistance compared to the actual cake resistance (Waite, 1999). The connection between aggregation conditions, either in suspension, or at the membrane surface to cake properties has been acknowledged (Fu and Dempsey, 1998). The porosity of the cake has a major impact on its resistance, and increased porosity results in improved permeate flux. When the pressure across the membrane's surface (trans-membrane pressure—TMP) is constant, the fouling rate can be expressed as J/J_0 (permeate flux/initial flux), which typically declines exponentially. Pre-treatment of the feed, using conventional coagulation/flocculation methods, has proven effective in reducing the fouling behavior of membranes (Lahoussine-Turcaud *et al.*, 1990; Soffer *et al.*, 2000; Judd and Hillis, 2001; Kim *et al.*, 2001).

The introduction of the active coagulant species (metal ions) is an additive process over time, negative counter-ions are not introduced, an electrical field exists which could affect particle transport, the pH rises due to hydroxide formation at the cathode, bubbles are present due to the hydrolysis which occurs and can be a negative steric factor affecting aggregate growth. Moreover, the process forms a dynamic electrochemical environment where many other electrochemical reactions occur, depending on the chemistry of the treated suspension.

This research examines the fouling behavior of an ultrafiltration (UF) membrane in a coupled EF–UF process by measuring flux decline at constant pressure. Cake formation on the membrane surface is examined using electronic microscopy techniques, and correlations between characteristics of an electroflocculated kaolin suspension fed into the system (particle size distribution, ζ potential, pH), cake structure, and membrane performance are investigated.

Materials and methods

Colloidal suspensions. 0.3 g of kaolin was suspended in 20 litres of distilled water (15 mg/l final concentration) and homogenized using an Ultraturax 2000. 1.66 g of NaHCO_3 was added (final concentration 83 mg/l), the pH was corrected to 5, 6.5 and 8, with NaOH or H_2SO_4 , and conductivity was increased to 1 mS/cm with NaNO_3 .

EF. The EF unit was a batch cell comprising of two flat sheet electrodes (an aluminium anode and stainless steel cathode), with an active area of 9 cm^2 , which were immersed in the treated suspension, and connected to an external DC power supply. The cell was run at constant current (range used was 0.06–0.2A), for a fixed 7 minutes dosing period, and the doses were equivalent to aluminium content in 30, 60, 80 and 100 mg/l commercial alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$).

Membranes. The UF membranes used in this study were hydrophilic polyethersulfone flat sheet membranes manufactured by Microdyn-Nadir (Germany), with a nominal molecular weight cut-off of 50 kDa, and pure water flux $> 250\text{ l/m}^2\text{ h}$. Prior to use the membranes were soaked for 12 h in distilled water.

UF unit. The membrane filtration unit comprised a nitrogen gas cylinder, which maintained a constant pressure of 3 bar throughout the unit. A polypropylene feed reservoir, with a volume of 1,250 ml, held the colloidal suspension prior to the membrane

module. The membrane module, made from polypropylene, was operated as a stirred cell. It contained an internal magnetic stirrer bar suspended close to the upper surface of the membrane with motion induced by a magnetic stirrer table placed beneath it. A flat disc membrane with an area of 11.3 cm^2 was held in place with an O-ring. The permeate was collected in a chemical glass mounted onto an electronic balance, which was connected to a computer containing software that calculated the permeate flux from permeate weight accumulation.

Particle size analysis. Particle size distribution measurements were performed over a range of 2–300 μm , using a HIAC Royco liquid particle counting system.

ζ potential. The ζ potential of the post-electroflocculated suspension was measured using a Malvern Zetamaster S.

Cake characterization. Membranes exhibiting cake formation were dried (at room temperature) and photographed using scanning electronic microscopy (SEM).

Aluminium measurements. Residual aluminium in the permeate was measured using ICP (Cole-Parmer).

Experimental procedure. One litre of the kaolin suspension underwent EF for 7 min, in a rapid mix regime (using magnetic stirrer at 120 rpm), and then was transferred to a jar test apparatus (Phipps and Bird, USA) for an additional 20 min slow mixing (30 rpm). Samples were taken from the flocculated suspension for particle characterization (particle size distribution and ζ potential), before filtering through the membrane unit. The flux was measured through the membrane, at room temperature ($\sim 20^\circ\text{C}$) at constant pressure (3 bar) over a 25 min time span.

Results and discussion

Characteristics of an electroflocculated kaolin suspension

The current applied in the EF process has a double effect, both by generating the coagulant species and by causing hydrolysis in which excess hydroxyl ions are formed at the cathode, resulting in an increase in pH (Equation 1). In these dynamic conditions, coagulation mechanisms shift, depending on the current applied. The shift in pH, and consequent shifting speciation of aluminium mononuclear complexes, causes the ζ potential of the electroflocculated suspensions to change, which serves as an indicator for coagulation efficiency. Figure 2 shows the change in pH and ζ potential as a function of applied current for a 15 mg/l kaolin suspension at different initial pH values. The ζ potential of the kaolin suspensions, without applying any current, was: -17.9 mV , -21.7 mV and -23.7 mV for pH 5, 6.5 and 8 respectively.

Membrane filtration

The permeate flux was measured for suspensions that had undergone EF using aluminium as the anode material. The aluminium doses were controlled by the applied current, which was kept constant during each run. The results show that pre-EF enhances the permeate flux, at all initial pH ranges, 5, 6.5 and 8.

pH 5 (initial)

At initial pH 5 filtration of kaolin causes significant flux decline, and by the end of the run it has reached 40% of the initial flux (Figure 3) Pre-EF of the suspension improves

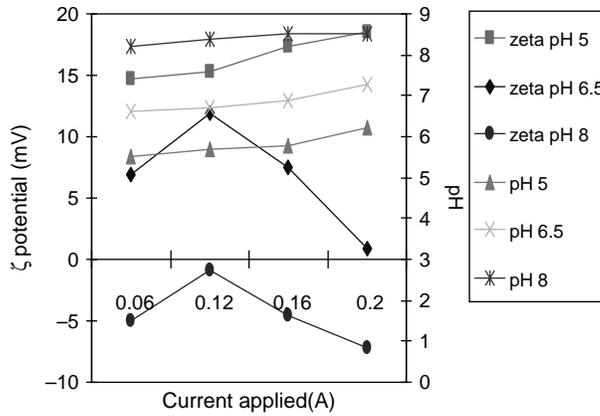


Figure 2 Change in pH and ζ potential vs. applied current for different initial pH values. $C_0 = 15$ mg/l, $t = 7$ min

the filtration, and at all currents we observe flux enhancement. At 0.06A the maximum flux enhancement occurs, by which the flux has improved by 15%, reaching steady state at 55% of the initial flux. At 0.12A, 0.16A and 0.2A similar behavior is observed, by which the permeate flux reaches steady state at 60% of the initial flux. The difference in membrane behavior obtained after EF at 0.06A relatively to the other applied currents can be explained by the transition to a different coagulation mechanism, which occurs at higher doses of aluminium. At pH 5 the governing aluminium species in solution are Al^{+3} and $Al(OH)^{2+}$, and therefore we assume that at this initial pH the dominant coagulation mechanism is adsorption and charge neutralization, although some aluminium hydroxide does precipitate in these conditions. In this case it appears that at the minimum applied current, 0.06A, adsorption and charge neutralization is the dominant coagulation mechanism, thus producing aggregates that form a stable cake on the membrane surface, which has a higher porosity than the dense, compact cake formed by filtration of kaolin (Figure 6). At the higher currents, 0.12A, 0.16A and 0.2A, we observe improved membrane behavior due to increased formation of aluminium hydroxide in solution, which catches the smaller particles (by “sweep floc” mechanism) thereby enhancing the permeate flux. The decline in flux relative to the flux obtained at 0.06A is due to increased cake formation of gelatinous aluminium hydroxide on the membrane surface. From SEM

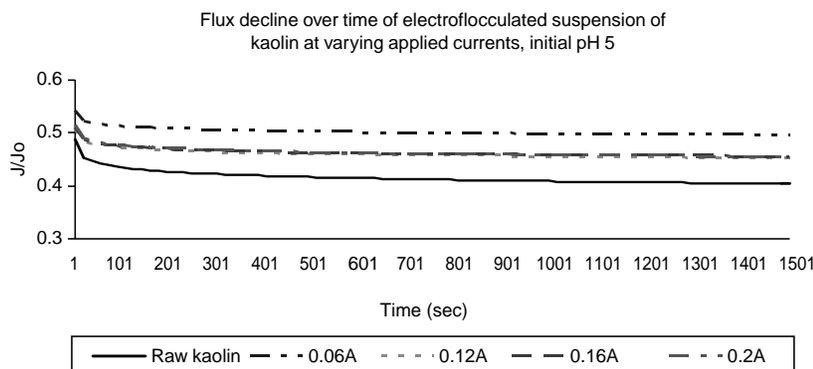


Figure 3 Permeate flux (J) as a fraction of initial flux (J_0) over the course of ultrafiltration of an electroflocculated kaolin suspension, initial pH 5, at various applied currents

analysis, aluminium hydroxide seems to form a “blanket” on the membrane surface, and exhibits different characteristics than the cake formed from filtration of raw kaolin, which appears to be very dense and tightly packed (Figures 6 and 7).

In addition, aluminium hydroxide flocs, unlike kaolin particles (which have an average size of $1\ \mu\text{m}$), are large enough to be sheared from the membrane surface (Weisner *et al.*, 1989). This, however, may not be the sole factor that causes this difference between the two types of suspensions – density and morphology may also play an important role here, which is still a matter of conjecture. Particle size distribution measurements of the electroflocculated suspension show an increase in particle counts for particles in the range $5\text{--}10\ \mu\text{m}$ for the higher applied currents. Since permeability of the filter cake and back transport by hydrodynamic forces both increase with increasing particle size (Fu and Dempsey, 1998), this can also explain the flux enhancement. The residual aluminium measured in the permeate at the higher currents was $0.030\ \text{mg/l}$ and $0.039\ \text{mg/l}$ (for $0.16\ \text{A}$ and $0.2\ \text{A}$ respectively), indicating optimal coagulation–flocculation, in which nearly all the aluminium ($\sim 98\%$) was removed from solution, caught on the membrane surface as an aluminium hydroxide mesh. At $0.06\ \text{A}$ the coagulation mechanisms are in transition due to the formation of a variety of aluminium hydrolysis species. The final pH was 5.5 (Figure 2) and the residual aluminium measured was $0.5\ \text{mg/l}$, which indicates that a large fraction ($\sim 21\%$) of the aluminium was not precipitated as aluminium hydroxide, but was present as soluble species (Al^{+3} and $\text{Al}(\text{OH})^{+2}$). Moreover the positive ζ potential of the suspension indicates a transition through charge neutralization for all the currents, so we can assume that the major factor causing the differences between the lower current and higher currents is the quantity of aluminium hydroxide present.

pH 6.5 (initial)

At initial pH 6.5 filtration of kaolin causes significant flux decline, and by the end of the run it has reached 40% of the initial flux (Figure 4). Pre-EF of the suspension improves the flux, and for applied currents of $0.12\ \text{A}$, $0.16\ \text{A}$ and $0.2\ \text{A}$ identical flux behavior is observed, by which the permeate flux reaches steady state at above 60% of the initial

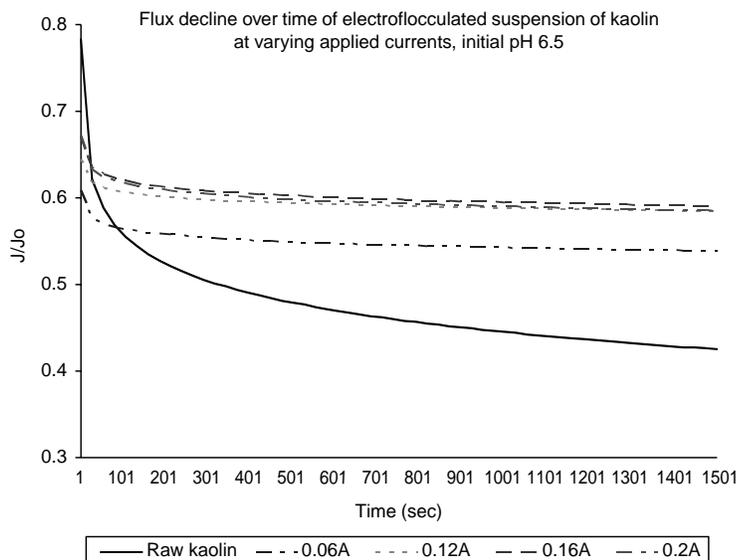


Figure 4 Permeate flux (J) as a fraction of initial flux (J_0) over the course of ultrafiltration of kaolin suspension, initial pH 6.5 , at various applied currents

flux. For an applied current of 0.06A there is a 5% drop in the flux compared to the other currents, and the permeate flux reaches steady state at 55% of the initial flux. At pH 6.5 the dominant coagulation mechanism is sweep floc, due to increased formation of amorphous aluminium hydroxide, although at the higher currents the pH increases significantly (Figure 2) and speciation shifts towards $\text{Al}(\text{OH})_4^-$ which decreases coagulation efficiency – indicated by the less positive ζ potential. This does not seem to affect the membrane behavior within the dosages used at this pH, because a wide range of currents produced the same results. Therefore, the improved membrane behavior observed here was due to the formation of aluminium hydroxide flocs in solution, which catch smaller particles and form a more permeable cake on the membrane surface. Moreover, aluminium hydroxide flocs are large enough to be sheared from the membrane surface and therefore the cake thickness is stable, resulting in a stable flux. Particle size counts performed in the region 5–20 μm indicate that at 0.06A sizes obtained are on average smaller than those formed at other currents; therefore the cake is less porous and a minor difference in membrane behavior is observed. In addition, particle size distribution measurements show that for 0.12A, 0.16A, and 0.2A the counts between 5–20 μm are nearly identical, which can explain the similar flux obtained at these currents.

pH 8 (initial)

At initial pH 8 filtration of kaolin causes significant flux decline, and by the end of the run it has reached 50% of the initial flux (Figure 5). Pre-EF does not improve the flux significantly, and for all currents similar flux behavior is observed, by which the permeate flux reaches steady state at 55% of the initial flux (only a 5% improvement relative to the flux obtained when filtering the raw kaolin). At pH 8 the ζ potential of kaolin is more negative, compared to that at pH 5 and 6.5, therefore the particles are more readily rejected from the membrane (which is hydrophilic and charged negatively), which can explain a slight increase in the flux relative to the flux at pH 5 and 6.5. At pH 8 the dominant species is $\text{Al}(\text{OH})_4^-$, and therefore no real improvement is observed because

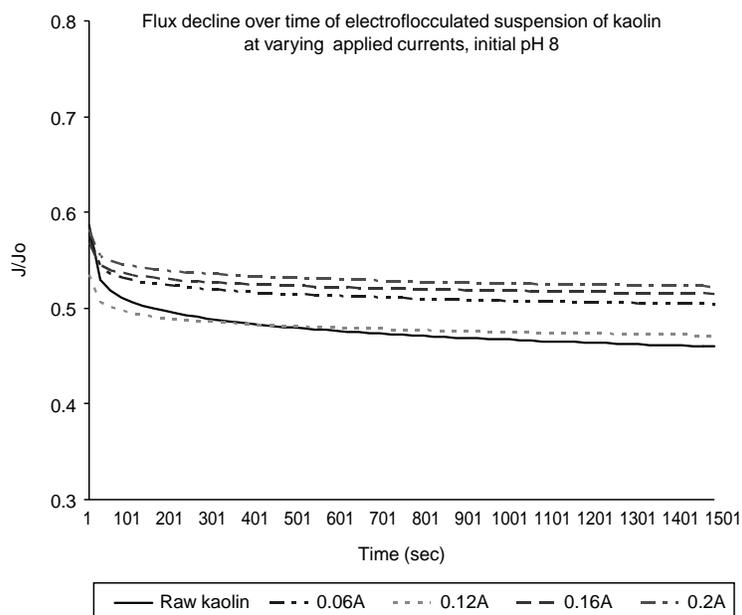


Figure 5 Permeate flux (J) as a fraction of initial flux (J_0) over the course of ultrafiltration of kaolin suspension, initial pH 8, at various applied currents

coagulation conditions are not optimal. Some aluminium hydroxide precipitates, which is visible, and forms a cake on the membrane surface, but still small particles are present in large quantities in solution, because no efficient coagulation occurs.

These particles can enter the cake pores and thus reduce the flux. The minor improvement in membrane behavior observed here was due to some formation of aluminium hydroxide flocs in solution, which catch a fraction of the smaller particles. The permeate aluminium measurements indicate a large quantity of soluble aluminium which increases with applied current (0.68 mg/l (~28%) and 1.76 mg/l (~22%) for 0.06A and 0.2A respectively), thus corroborating the shift in speciation towards soluble aluminium mononuclear species ($\text{Al}(\text{OH})_4^-$ at pH 8).

Particle size distribution measurements show nearly identical counts for all currents, in the range 5–20 μm , which can explain the similar flux obtained at these currents. However, particle distribution measurements show much lower counts than those at pH 5 and 6.5, which indicates that less colloidal particles are present. At pH 5 and 6.5 aluminium hydroxide precipitates as colloidal matter, contributing to the particle counts. At pH 8 the aluminium solubility equilibrium has shifted towards the negative soluble species ($\text{Al}(\text{OH})_4^-$), less aluminium hydroxide precipitates resulting in lower particle counts.

Figures 6 and 7 show the visible differences in cakes formed on the membrane surface from filtration of a kaolin suspension and a pre-electroflocculated kaolin suspension.

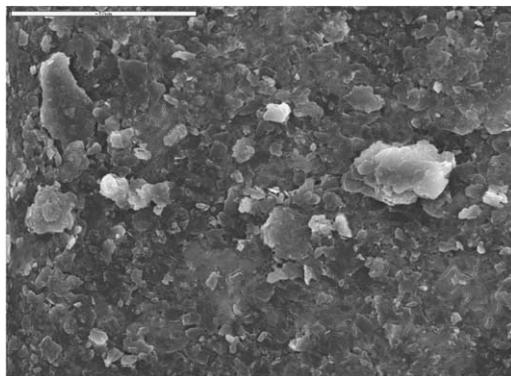


Figure 6 Cake after filtration of raw kaolin (bar denotes ~ 50 μm)

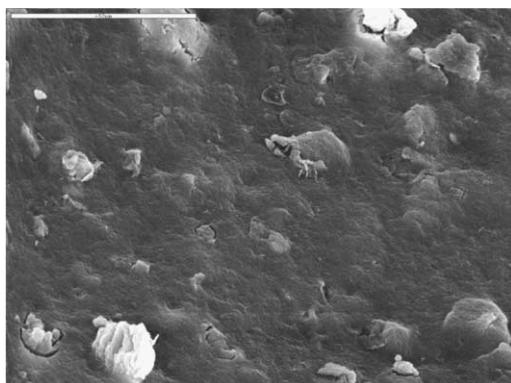


Figure 7 Cake after filtration of pre-electroflocculated kaolin (bar denotes ~ 50 μm)

Conclusions

Electroflocculation can serve as an efficient pretreatment to ultrafiltration of colloid particles. The fouling behavior of the membrane could be explained by applying conventional coagulation theory. Increased flux rates were observed at pH 6.5, and currents of 0.12–0.2A, where sweep floc mechanism dominates due to increased precipitation of $Al(OH)_3(s)$. At all pH values cake formation on the membrane surface was observed indicating that cake resistance is a primary fouling factor. The differences in flux can be attributed to cake properties (i.e., thickness, porosity) which are determined by particle characteristics.

At pH 5 and 8, the flux obtained from pre-electroflocculated suspensions was less than that obtained at pH 6.5. At pH 5 and 8, the solubility equilibrium is in transition and less aluminium hydroxide precipitates; therefore smaller particles are still present in suspension (not removed by sweep floc mechanism). These can enter the cake pores and cause “self contamination”, resulting in increased flux decline. Moreover, particle counts indicate that at pH 6.5 larger flocs are present which can be readily sheared from the membrane surface resulting in a “thinner” cake, which can also explain flux enhancement. These results demonstrate the potential of electroflocculation as pretreatment to ultrafiltration, and stress the importance of research with different types of contaminants.

Acknowledgements

The work was partially supported by BMBF Germany and the Israeli Ministry of Science. The samples of membranes were kindly provided by MICRODYN-NADIR.

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