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Pablo Cañizares[a]; Fabiola Martínez[a]; Carlos Jiménez[a]; Justo Lobato[a]; Manuel A. Rodrigo[a]
[a] Facultad de Ciencias Químicas, Department of Chemical Engineering, Universidad de Castilla La Mancha. Campus Universitario, Ciudad Real, Spain

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Coagulation and Electrocoagulation of Wastes Polluted with Colloids

**Pablo Cañizares, Fabiola Martínez, Carlos Jiménez,
Justo Lobato, and Manuel A. Rodrigo**
Facultad de Ciencias Químicas, Department of Chemical Engineering,
Universidad de Castilla La Mancha. Campus Universitario, Spain

Abstract: The goal of this work has been to compare for both, continuous and batch processes, the efficiencies of the chemical and the electrochemical coagulation processes with hydrolyzing aluminum salts, and to determine the similarities or differences that exist between both coagulation processes. To meet the objective, experiments of both coagulation technologies have been carried out in the same operation conditions and the results have been interpreted in terms of the mechanisms previously proposed in literature for kaolin coagulation. The charge neutralization by the adsorption of monomeric hydroxocations onto the kaolin surface can be the primary coagulation-mechanism for low concentration of aluminum and acidic pHs (below 4). In the range of pH 4–7, two primary mechanisms can explain the experimental behavior of the system: sweep flocculation for high concentration of aluminum, and a combination of precipitation-charge-neutralization and charge neutralization by adsorption of monomeric or polymeric aluminum, for low concentration of aluminum. In the continuously-operated processes, the efficiency in the turbidity-removal seems to be much related to the aluminum species present in the treated waste, and not to the way of adding aluminum to the reaction system. For the same steady-state pH and aluminum concentration, the same turbidity removal is obtained in both, the chemical and the electrochemical coagulation processes. For high aluminum/kaolin ratios, kaolin suspensions which contain sulfate as electrolyte, achieve better removals of turbidity than those containing chloride ions. The operation mode (continuous or discontinuous) influences greatly on the efficiency of the electrocoagulation processes. Similar efficiencies are obtained for low (below

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Address correspondence to Manuel A. Rodrigo, Facultad de Ciencias Químicas, Department of Chemical Engineering, Universidad de Castilla La Mancha. Campus Universitario, 13005, Ciudad Real, Spain. Tel.: +34 902204100; Fax: +34 926 29 53 18; E-mail: manuel.rodrigo@uclm.es

5 mg dm^{-3}) and high doses of aluminum (above 20 mg dm^{-3}). However, at intermediate doses a strong difference is observed, with a more marked decrease in the efficiency in the discontinuous process. This observation has been explained considering that the addition of aluminum in the continuous process is instantaneous (and not progressive as in the discontinuous one), and thus, the sweep coagulation mechanism is more favored in this operation mode.

Keywords: Coagulation, electrocoagulation, electrochemistry, aluminum electrodes

INTRODUCTION

Particulate pollutants are present in domestic and industrial wastewaters. Natural waters also contain a wide variety of particulate impurities. To remove these particles sedimentation, flotation, and/or filtration are commonly used. The efficiency of these technologies depends on the size of the particles, and for colloids it is normally very low. In this case, the separation efficiency can be greatly enhanced if the small particles are aggregated into larger flocs (coagulation/flocculation). Because of their surface charge, many impurities in natural waters and many pollutants in wastewaters are often colloidally stable and resistant to aggregation.

The aggregation of colloids can be accomplished either by destabilization or by the enmeshment of the colloidal particles in a growing hydroxide precipitate formed in the waste (sweep coagulation). Two are considered to be the main processes involved in the destabilization of colloidal suspensions (1, 2):

- Decrease in the thickness of the diffuse part of the electrical double layer, caused by an increase in ionic strength.
- Neutralization of the particle charge by the specific adsorption of counterions.

It is unlikely that a sufficient increase in ionic strength would be a practical coagulation method (1). Hence, counter-ion adsorption is considered to be the primary mechanism in most coagulation processes. This process can be promoted by the addition of monomeric or polymeric ionic reagents. In the latter case, the aggregation of particles can also be caused by polymer bridging (1) (adsorption of different functional groups of a polymer onto different colloids).

Hydrolyzing metal (aluminum or iron) salts are widely used as coagulants. The speciation of Al or Fe solutions is complex and it is strongly related to the pH. According to literature (1–4), for strongly acidic pHs the primary species are monomeric hydroxometalic cations. At higher pHs (acidic and close to neutrality), both hydroxometalic cations (monomeric and polymeric) and metal hydroxide precipitates coexist, and these latter species can be positively charged (due to the adsorption of cations from the solution). For higher pHs the net charge on the surface of the amorphous metal hydroxide precipitates changes from positive to negative, and monomeric and polymeric hydroxometalic cations can still be present in the solution. Finally, in strongly alkaline media monomeric hydroxometalic anions are the primary species.

Conventional coagulation processes use aqueous solutions of aluminum or iron salts as reagents (5–8). These salts promote the different processes involved in the charge destabilization, as they increase the ionic strength, the ions can be adsorbed onto the colloidal surface compensating its former electrical charge (9), and they also can promote the formation of precipitates (hydroxides) (10). It is also reported that the appearance of large hydroxymetallic ions (e.g. $Al_7\ (OH)_{17}^{+4}$), which can be adsorbed simultaneously onto the surfaces of several particles, can increase the effective particle size (1).

An alternative to the direct use of a solution containing the coagulant salts, is the in situ generation of coagulants by electrolytic oxidation of an appropriate anode material (e.g. iron or aluminum) (11–17). This process is called electrocoagulation or electrochemically assisted coagulation, and in literature (18–20) the following advantages are reported for this technology:

- A promotion in the flocculation process, since the charged colloids can move easily within the electric field generated in the electrochemical cell (electroflocculation process) (21, 22)
- A promotion in the separation process, due to the hydrogen bubbles produced in the cathode during the electrolysis, which can carry the solids to the top of the solution, where they can be easily collected and removed (electroflotation process) (23–25)
- A more compact residue, as it is reported that the electrocoagulation process produces a smaller amount of sludge than the chemical coagulation, and that the solids produced are more hydrophobic
- An easier operation mode, since no mixing of chemicals is required, the dosing of coagulants can be easily controlled by manipulating the cell voltage (or the current density), and thus the operating costs are much lower compared with most of the conventional technologies.

Kaolin suspensions have been widely used as model colloid-polluted wastewaters. In such suspensions, kaolin particles are negatively-charged due to the exchange of aluminum and silicium atoms (contained in the structure of these clays) by monovalent or divalent ions (f.i. sodium, potassium) contained in the water (26). This charge is responsible for the electric repulsion between kaolin particles, and thus of the stability of the colloidal suspension. The coagulation of kaolin suspensions has been widely studied in literature. From these works it can be concluded that the primary mechanisms are charge neutralization at low aluminum concentrations and pHs (9, 27), and sweep flocculation at high aluminum concentrations and near neutral pHs (27, 28). Precipitation charge neutralization (PCN) is also reported (29, 30) as a possible primary coagulation mechanism. It consists of the deposition of aluminum hydroxide species onto the colloidal surfaces and results in charge neutralization or charge reversal of colloidal particles. The metal hydroxide is positively charged, whereas the original colloids are typically negatively charged. This promotes the aggregation of particles with a very high efficiency.

The goal of this work is to compare for both, continuous and batch processes, the efficiencies of the chemical and the electrochemical coagulation processes with hydrolyzed aluminum, and to determine the similarities or differences that exist between both coagulation processes. Since the continuous operation mode is more frequently used in full-scale applications, more attention has been paid to it. To meet the objective, experiments of both coagulation technologies have been carried out in the same operation conditions and the results have been interpreted in terms of the mechanisms previously proposed in literature for kaolin coagulation, in order to determine the advantages and disadvantages of both technologies. The work is organized in four different sections. The three first describe the experimental behavior of the coagulation and electrocoagulation systems. The last section (discussion) interprets the results in terms of the aluminum speciation.

EXPERIMENTAL

Experimental Devices

The coagulation experiments were carried out in a bench-scale plant (described elsewhere (15, 31)). In the electrochemical experiments, the coagulant reagent came from the dissolution of aluminum electrodes (type HE 18) placed in a single compartment electrochemical flow cell (Fig. 1). Both electrodes (anode and cathode) were square in shape (100 cm^2) and the electrode gap was 9 mm. The electrical current was applied using a DC Power Supply FA-376 PROMAX. The voltage and the current flowing through the cell were measured with a multimeter (KEITHLEY 2000 Digital Multimeter). The kaolin suspension was stored in a glass tank

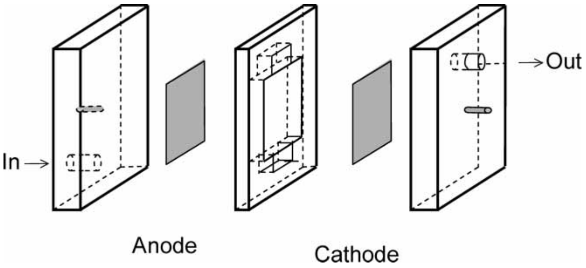

Figure 1. Sketch of the electrocoagulation cell.

(5000 cm^3), stirred by an overhead stainless steel rod stirrer (HEIDOLPH RZR 2041) and circulated through the electrolytic cell by a peristaltic pump. A thermostated-bath allowed maintaining the temperature at the desired set point. To carry out the chemical coagulation experiments, the experimental bench-scale plant was modified by changing the electrochemical flow cell by a single flow reactor (with the same geometry but without aluminum electrodes) and by including an aluminum-solution ($AlCl_3$ or $Al_2(SO_4)_3$) dosage system. The aluminum solution was stored in a tank, and a peristaltic pump dosed the solution to the inlet of the reactor, point in which took place the mix between the wastewater and the coagulant solution.

The synthetic suspension is composed by kaolin (1000 mg dm^{-3}, supplied by Sigma-Aldrich) and a supporting electrolyte to increase its conductivity (2450 mg dm^{-3} NaCl or 3000 mg dm^{-3} Na_2SO_4). In addition, to adjust the initial pH of the suspension, HCl, H_2SO_4, or NaOH were added (only when necessary).

Experimental Procedures

Electrochemical coagulation experiments were carried out under galvanostatic conditions (with current densities between 0.1 and 5.5 mA cm^{-2}). Previous to every experiment the electrodes were treated (by rinsing) with a solution of 1.30 M HCl, in order to diminish any effect due to the different prehistory of the electrodes.

In the continuous operation mode, the kaolin suspension was pumped from the feed tank to the cell (or reactor) and then it was collected in a different tank. Samples were taken at the outlet of the cell and left 20 minutes to allow the settling. This period was fixed after some preliminary tests. After that time the turbidity (using a 115 VELP SCIENTIFICA Turbidimeter), the pH (using an inoLab WTW pH meter), and the zeta potential (using a Zetasizer Nano ZS (Malvern, UK)) were measured to the clarified liquid. Zeta potential was measured to the samples by setting the temperature at 25°C, and the voltage at 20 V. Each sample was measured 3 times (until obtaining a constant value).

The discontinuous-operation experiments were carried out by recirculating the effluent of the treatment to the feed tank. Samples were taken and analyzed in the same manner than those of the continuous processes.

Measurement of the Aluminum Dissolved in the Cell

The accurate measurement of the total aluminum dissolved in the electrochemical cell in every experiment is difficult due to the aluminum-content of the kaolin particles and also to the adsorption capabilities of this colloid towards aluminum species. Consequently, many sources of errors can be present in the analyses. To obtain precise data, every experiment (continuous or batch) was repeated maintaining the same operation conditions and changing the kaolin suspension by an aqueous solution with the same concentration of electrolyte. These experiments were used to quantify the total aluminum supplied by the electrochemical system. The results obtained in the preliminary experiments (with the total dissolution of kaolin with hydrogen fluoride and determination of the total aluminum) demonstrate that the concentration of aluminum is not affected by kaolin and then a simple and more accurate measurement is obtained with the procedure proposed. After the experiments, the concentration of aluminum was measured off-line using an Inductively Coupled Plasma LIBERTY SEQUENTIAL VARIAN according to a standard method (32) (Plasma Emission Spectroscopy). To determine the total aluminum concentration, samples were diluted 50:50 v/v with 4 N HNO_3.

RESULTS

Dynamic Response of Continuous Coagulation Processes

Although most studies of coagulation are carried out in discontinuous-operation lab-scale or bench-scale plants, the full-scale plants normally operate in a continuous-operation mode. Very few works compare the performance of both operation modes (31). For this reason it is important to study processes in continuous operation mode.

In a continuous-operation mode it is important to characterize both the dynamic response (changes in parameters from the start-up to the steady-state) and the steady-state values of all parameters. To compare the dynamic response of the chemical and electrochemical coagulation processes, some experiments were prepared in order to attain the same steady-state concentration of aluminum in the treated waste.

To know the concentration of aluminum dissolved in the electrochemical experiments, a previous study of characterization of the aluminum dissolution process in the electrochemical cell was carried out (33). The most remarkable point in this previous study is the super-faradaic yield obtained in the electrochemical dissolution of aluminum, with values higher than 300% for alkaline pHs. Similar results were obtained by other authors (11, 13, 16). These results can be explained in terms of the simultaneous chemical dissolution of the electrodes.

Figure 2 shows the typical dynamic responses observed during several chemical and electrochemical coagulation experiments. It can be observed that the time required to achieve the steady-state is shorter for the chemical coagulation experiments and that in both cases, it is lower than ten-times the hydraulic residence time of the reactor (20 seconds). Likewise, as it can be observed in Fig. 2b, the pH value increases during the transitory-state of the electrochemical experiment, since the electrochemical system leads

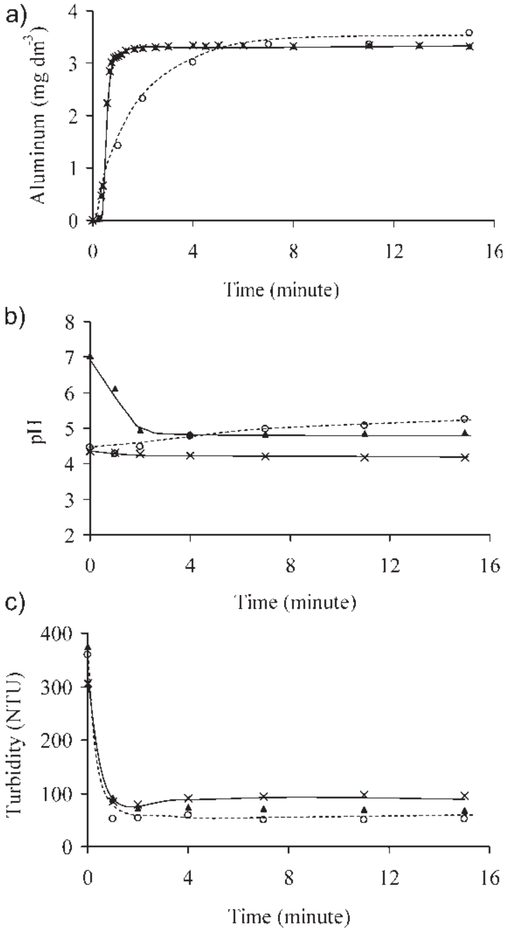

Figure 2. Aluminum concentration, pH and turbidity profiles with time (dynamic responses) observed during several chemical and electrochemical coagulation experiments. Temperature: 25°C; Flow rate: 19 $dm^3\,h^{-1}$; Kaolin concentration: 1000 mg dm^{-3}; Supporting media: 2450 NaCl mg dm^{-3}. ○ Electrocoagulation experiment, Current density: 0.5 mA cm^{-2}, initial pH: 4. Chemical coagulation experiments: ▲ initial pH: 7, × initial pH: 4.

to the formation of aluminum hydroxide as a net final product from the electrochemical (eqs. 1 to 3) and the chemical dissolution processes (eq. (4).

$$\text{Cathode:}\quad H_2O + e^- \longrightarrow 1/2H_2 + OH^- \tag{1}$$

$$\text{Anode:}\quad Al \longrightarrow Al^{3+} + 3e^- \tag{2}$$

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \tag{3}$$

$$\text{And,}\quad 2Al + 6H_2O \longrightarrow 2Al^{3+} + 3H_2 + 6OH^- \tag{4}$$

Conversely, the pH decreases during the chemical experiments, as a consequence of the acid properties of the added $AlCl_3$ (it was not possible to add the aluminum concentration formed by the electrochemical procedure as an aluminum hydroxide solution due to its small solubility). In Fig. 2c it can be observed that both the processes are able to diminish the turbidity of the kaolin suspension. However, and in spite of their similar steady-state aluminum concentration, different turbidity removals are obtained when the steady-state pHs are different.

To obtain the same steady-state pH and aluminum concentration in both, the chemical and the electrochemical processes, several chemical experiments were carried out with different initial-pH suspensions. Figure 2 also shows the results of the experiment in which both steady-state pHs match. As it can be observed if the steady-state pH and aluminum concentration coincide, the same steady-state turbidity is obtained. As it will be discussed in the next section, this behavior was observed in all the experiments carried out in this work. Thus, for continuous-operated coagulation processes the efficiency in the turbidity removal seems to be related only with the aluminum species present in the treated waste, and not with the way of adding aluminum to the reaction system.

Figure 3 shows experiments carried out with very acidic or alkaline wastes. In these cases, the effect on the steady-state pH of the cathodic formation of hydroxyl ions (electrochemical process), or the acidification carried out by the aluminum chloride addition (chemical process), is negligible. Consequently, the same pH and aluminum concentration are measured at steady-state. This justifies the similar turbidity removals obtained for both the chemical and the electrochemical processes. On the other hand, it can be observed that in spite of the higher concentration of aluminum in alkaline conditions (due to the higher chemical dissolution rate under this pH condition) the turbidity removal is lower than that obtained in acidic conditions. This will be explained in the last section in terms of the primary coagulation mechanisms at both pH conditions.

Influence of the Operation Parameters on Continuous Coagulation Processes

To determine the influence of the main parameters on the efficiency of the chemical and electrochemical coagulation processes, several experiments were carried out. Taking into account the results discussed in the former section, the experiments were planned to achieve the same values of pH and aluminum concentration at the steady-state and also to find the same value of the studied parameter. For this reason, the initial pHs of the kaolin suspensions in the chemical and the electrochemical experiments were different.

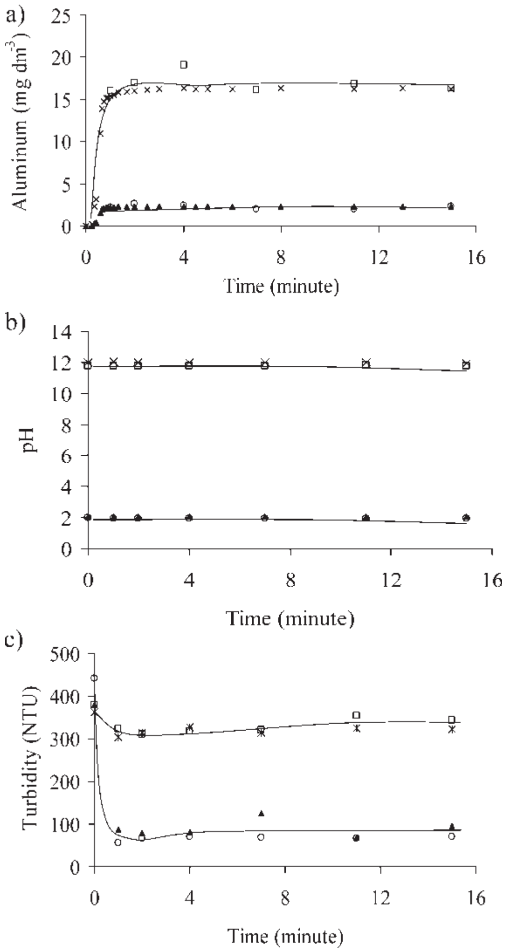

Figure 3. Concentration of aluminum, pH and turbidity profiles with time (dynamic responses) observed during several chemical and electrochemical coagulation experiments at acidic and alkaline conditions. Temperature: 25°C; Flow rate: 19 dm^3 h^{-1}; Kaolin concentration: 1000 mg dm^{-3}; Supporting media: 2450 NaCl mg dm^{-3}. Electrocoagulation experiments: Current density: 0.5 mA cm^{-2}, ○ initial pH: 2. □ initial pH: 12. Chemical coagulation experiments: ▲ initial pH: 2, × initial pH: 12.

Figure 4 shows the influence of the steady-state pH value on the removal of kaolin by both methods. Again, it can be observed that there are no significant differences between the results obtained by the chemical and the electrochemical technologies. Acidic pHs lead to high turbidity-removal efficiencies whereas neutral and specially alkaline pHs lead to lower efficiencies. In the electrochemical process, a slight increase in the pH at initial pH close to 4

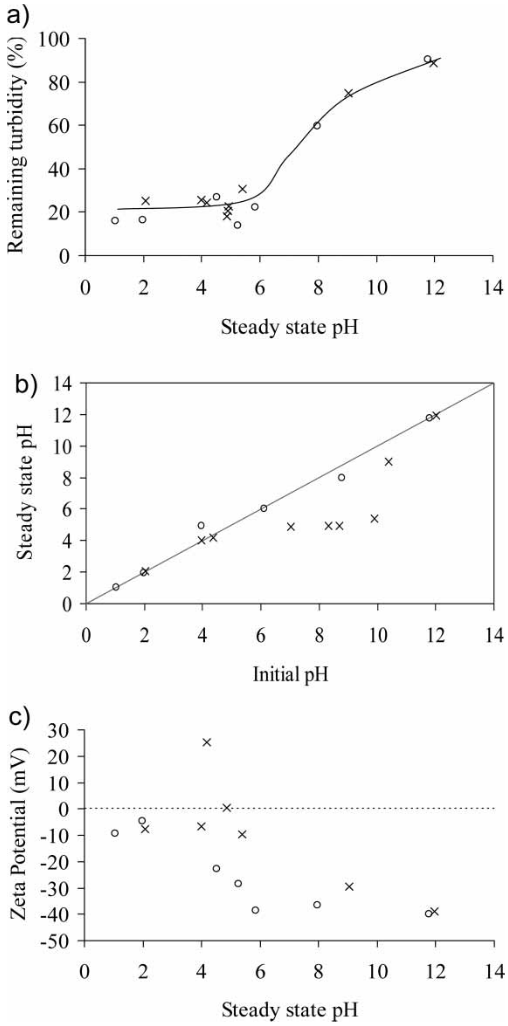

Figure 4. Influence of the steady-state pH on the remaining turbidity, variation of pH and zeta potential in the chemical and electrochemical experiments. Temperature: 25°C; Flow rate: 19 $dm^3\,h^{-1}$; Kaolin concentration: 1000 $mg\,dm^{-3}$; Supporting media: 2450 NaCl $mg\,dm^{-3}$. ○ Electrocoagulation experiments, Current density, 0.5 $mA\,cm^{-2}$, × Chemical coagulation experiments.

can also be observed, and a slight decrease when working at initial pH close to 9. All these changes of pH in the bulk solution are the consequence of the electrochemical (eqs. 1 to 4) and chemical reactions that take place in the cell. According to the concentration-pH aluminum-species diagram (31) the equilibrium reactions between the monomeric aluminum species (from alkaline to acidic pH) are summarized in (eqs. 5 to 9). In addition, it is known that there are many possible oligomeric and polymeric forms (1) of aluminum that should be considered, and that also influence the value of the pH.

$$Al(OH)_4^- + H^+ \rightleftharpoons Al(OH)_3 + H_2O \tag{5}$$

$$Al(OH)_3 + H^+ \rightleftharpoons Al(OH)_2^+ + H_2O \tag{6}$$

$$Al(OH)_2^+ + H^+ \rightleftharpoons Al(OH)^{+2} + H_2O \tag{7}$$

$$Al(OH)^{+2} + H^+ \rightleftharpoons Al^{+3} + H_2O \tag{8}$$

$$Al(OH)_3(s) \rightleftharpoons Al^{3+} + 3OH^- \tag{9}$$

In the chemical process, the steady-state pHs for the treatment of wastes with inflow-pH in the range 6 to 10, seem to be buffered in a value close to 5 (as it is shown in Fig. 4b). All these changes of pH observed in the chemical coagulation experiments can also be explained in terms of the chemical equilibrium reactions that take place in the systems; thus, the aluminum added to the system (as $AlCl_3$) is combined with hydroxyl ions according to the equilibrium reactions, to form monomeric, as well as oligomeric and polymeric hydroxo-aluminum species, leading to decreases in the pH.

Figure 4c shows the values of zeta potential achieved in the steady state as well. The initial values measured to the kaolin suspensions were around −50 mV. It can be observed that the treatment led to an increase in the zeta potential. This increase is more marked at acidic pHs, with steady-state values close to zero.

Figure 5a shows the influence of the steady-state aluminum concentration. As can be observed, both the chemical and the electrochemical processes achieve the same removals. In the range of aluminum concentration studied, a maximum of outstanding turbidity is found for an aluminum dosage of around 9 mg dm^{-3}, whereas higher removals of turbidity are obtained for lower aluminum concentrations (near 3 mg dm^{-3}) and for values of this parameter higher than 20 mg dm^{-3}. As well, the influence of the kaolin concentration on the removal of turbidity for both processes is shown in Fig. 5b. It can be observed that the results attained by the chemical and the electrochemical methods are very similar: the residual turbidity decreases with the kaolin concentration, and reaches a constant value for kaolin concentrations higher than 1 g dm^{-3}. This trend may not be explained in terms of destabilization, but by the flocculation (aggregation) process, due to the higher possibilities of collisions at higher kaolin concentrations. In addition, Fig. 5c shows the influence of the electrolyte concentration (NaCl) on the turbidity removal attained by both, the chemical and the electrochemical coagulation methods. As it can be observed, the results obtained are practically the same. Thus, the salinity does not have a marked influence on the coagulation in the range of concentration studied (only a small increase with increasing concentration is observed for very low concentration of NaCl).

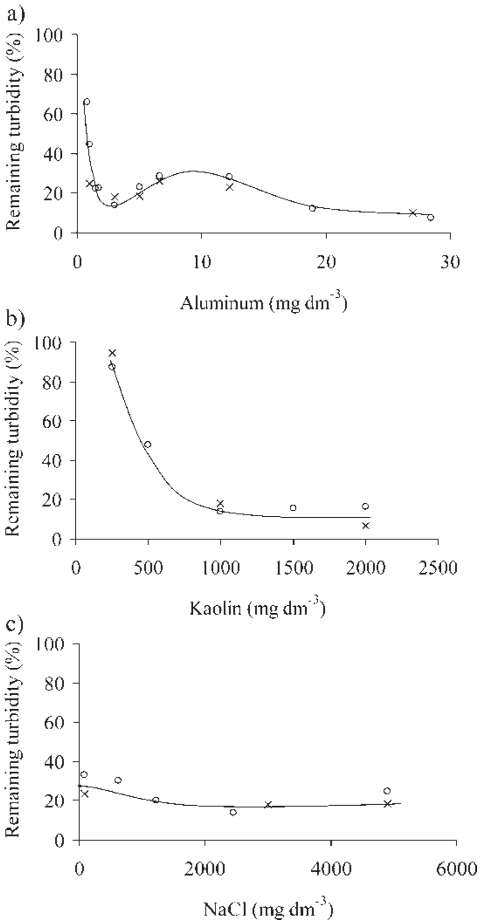

Figure 5. Comparison between the continuous chemical and the electrochemical coagulation processes. a) Influence of the aluminum concentration added by both methods, b) Influence of kaolin concentration, and c) Influence of electrolyte (NaCl) concentration. Temperature: 25°C; Flow rate: 19 $dm^3 h^{-1}$. ○ Electrocoagulation experiments, initial pH: 4. × Chemical coagulation experiments, initial pH: 7. a) Supporting media: 2450 NaCl mg dm^{-3}, Kaolin concentration: 1000 mg dm^{-3}. b) Supporting media: 2450 NaCl mg dm^{-3}. c) Kaolin concentration: 1000 mg dm^{-3}.

The influence of the type of electrolyte is shown in Fig. 6a, for suspensions which contain chlorides and sulfates. Results at low and at high aluminum concentrations (and so electrical charges passed) are similar, but for intermediate concentrations a different behavior is observed: there is no maximum but a plateau in the outstanding turbidity (Fig. 6a) in the treatment of sulfate-containing suspensions.

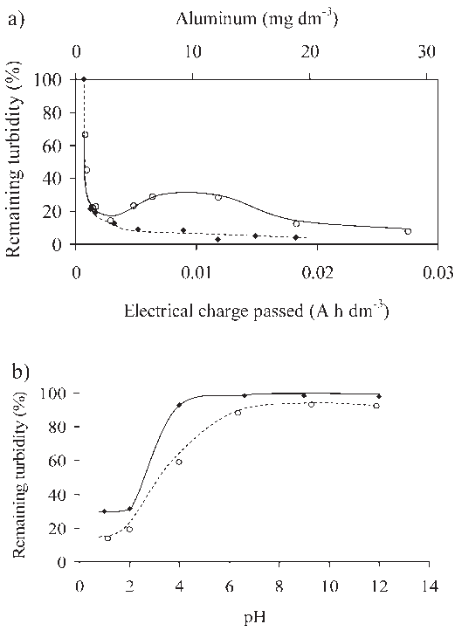

Figure 6. a) Influence of the type of electrolyte on the continuous electrocoagulation process, b) Influence of the type of electrolyte on the coagulation of kaolin suspensions without aluminum addition. Supporting media: ○ 2450 NaCl mg dm^{-3}, ◆ 3000 Na_{2}-SO_4 mg dm^{-3}. Temperature: 25°C; Flow rate: 19 dm^3 h^{-1}. Kaolin concentration: 1000 mg dm^{-3}.

Figure 6b shows the influence of pH on the turbidity removal of kaolin suspensions (without aluminum dosing). These experiments were carried out following the same procedure that in the chemical coagulation experiments but no aluminum solutions were added to the reactor. It can be observed that strongly-acidic kaolin-suspensions coagulate. It can also be observed that the electrolyte influences strongly on the results and that lower removals are obtained in the treatment of sulfate-containing suspensions. This observation can only be explained in terms of the adsorption of protons onto the kaolin surface and, consequently, in the resulting colloid-suspension destabilization by surface charge neutralization. The lower efficiency obtained in the treatment of sulfate-containing suspensions can be explained in terms of the adsorption of this anion onto the surface and the corresponding increase in the negative superficial charge.

Influence of the Operation Mode on the Electrocoagulation Processes

To study the influence of the operation mode, several experiments in batch operation mode were carried out. Figure 7 shows the comparison between

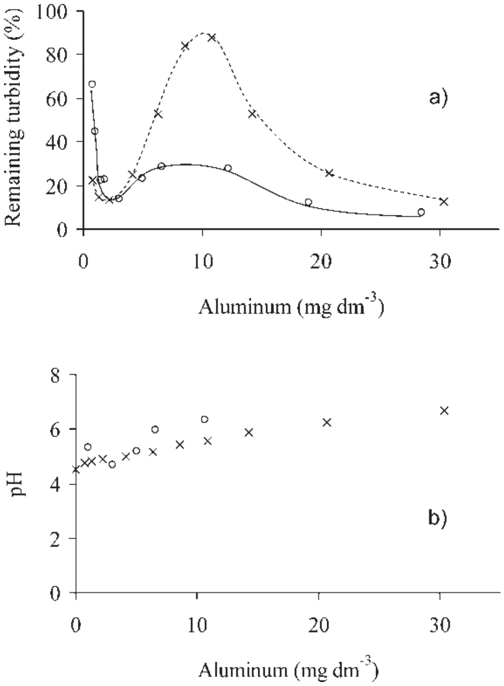

Figure 7. Comparison between the continuous and the discontinuous electrocoagulation processes. Temperature: 25°C; Supporting media: 2450 mg NaCl dm^{-3}; Kaolin concentration: 1000 mg dm^{-3}. ○ Continuous process, Flow rate: 19 $dm^3\,h^{-1}$, × Discontinuous process, Flow rate: 54 $dm^3\,h^{-1}$; Current density: 0.5 mA cm^{-2}; Volume: 1.5 dm^3; Time: 45 minutes.

the continuous and batch electrocoagulation of kaolin suspensions as a function of the aluminum concentration generated in the processes. As it can be seen, similar removals are yielded by both processes at low and at high concentrations of aluminum, whereas at intermediate concentrations a strong difference is observed.

DISCUSSION

According to literature (1–4, 34), at very acidic pHs (below 4) the primary aluminum species are monomeric hydroxoaluminum cations such as Al^{3+}, $AlOH^{2+}$ and $Al(OH)_2^+$. The behavior in the range of pHs between 4 and 7 is more complex. In this range, monomeric and polymeric hydroxoaluminum cations (polynuclear species such as the tridecamer) and aluminum hydroxide precipitates coexist. The surface of this latter species can be positively or negatively charged by the adsorption of ions from the solution. In alkaline media, monomeric hydroxoaluminum anions are the predominant species in the solution.

In this context, it is widely reported that the presence of sulfate can have a large effect on hydroxide precipitation (9, 27, 35), and thus, it can have a great influence on the results when charge neutralization and precipitation play different parts in the coagulation process (it influences on the relative importance of charge neutralization and precipitation mechanisms). Sulfate can reduce the positive charge of the precipitates in the acidic region, so that large flocs are formed over a wider pH range.

In addition, the way of addition of aluminum in the coagulation process can influence the species generated in the system (36). Thus, it must be considered that the addition of aluminum in the continuous process is instantaneous (the wastewater only passes through the cell once) and in the batch process is progressive (the wastewater is continuously recycled into the cell and the concentration of aluminum increases continuously with time during an experiment). This means that for a given dose of aluminum, the formed aluminum species can be different, as in the batch process the aluminum species formed can react with the kaolin previous to further additions of aluminum (in the following pass of the waste through the cell) and in the continuous process a given body of waste receives abruptly all its corresponding aluminum.

Taking into account the qualitative speciation of aluminum, the experimental observations obtained in this work can be easily explained. Therefore, with regard to the influence of the pH, only at acid and near neutral pHs high removals of turbidity are attained. Thus, in the acidic range of pH, the monomeric positively-charged species can be adsorbed onto the kaolin surface particles, and this explains that the addition of aluminum (either chemical or electrochemical) in this pH-range allows achieving a great efficiency in the removal of kaolin. Hence, the charge neutralization should be the primary mechanism of coagulation for low concentration of aluminum and acidic pHs. This mechanism also explains that at alkaline pHs (over 8) only small turbidity-removal efficiencies were obtained, as the primary aluminum species is the negatively-charged $Al(OH)_4^-$. The values of zeta potential obtained in these experiments (influence of the pH) are in agreement with this explanation, as values of this parameter close to zero are reached in the experiments carried out under acidic conditions, this observation being indicative of the charge neutralization of kaolin particles for acidic pHs.

For pHs around neutrality and the high concentration of aluminum, sweep flocculation should be the primary kaolin removal mechanism, whereas for low concentrations of aluminum, the precipitation charge neutralization (formation of a charged precipitate onto the surface of the kaolin particles) or the charge neutralization by adsorption of monomeric or polymeric aluminum cations should explain the results. Except for the study of the aluminum influence, and the cases of chemical and electrochemical coagulation at pH 12, all the continuous experiments of this work were carried out for concentrations of aluminum in the range 2–5 mg dm^{-3}. This means that it is unlikely that sweep-flocculation would be responsible for the results obtained and suggests that PCN or adsorption of monomeric and polymeric aluminum species should explain the results.

Regarding the results obtained at different aluminum concentrations, a maximum of outstanding turbidity for an aluminum dosage of around 9 mg dm^{-3} was observed, whereas higher removals of turbidity were obtained for lower aluminum concentrations (near 3 mg dm^{-3}) and for values of this parameter higher than 20 mg dm^{-3}. This behavior is indicative of two coagulation mechanisms in the system. The high removals of turbidity obtained under low aluminum dosages can be explained in terms of precipitation charge neutralization (formation of a charged precipitate onto the surface of the kaolin particles) or charge neutralization by the adsorption of monomeric or polymeric aluminum cations, whereas sweep flocculation should be the primary mechanism at high aluminum dosages (above 20 mg dm^{-3}). For intermediate dosages, none of these mechanisms are favored, and therefore a small maximum in the outstanding turbidity is observed.

With regard to the effect of the electrolyte concentration (the small influence of this parameter on the coagulation processes (chemical and electrochemical)), it can be assumed that the increase in the ionic strength does not play an important role in the colloids destabilization, at least in the range of sodium chloride concentration studied.

Regarding the differences obtained in the electrocoagulation process in a sulfate and a chloride medium, it was observed that for intermediate aluminum concentrations better efficiencies were obtained in the sulfate medium, and it can be explained in terms of the large effect of sulfate ions on the aluminum hydroxide precipitation: thus, in the sulfate medium, the formation of flocs can be favored in a wider range of aluminum dosage, leading to a plateau zone in the outstanding turbidity against the aluminum concentration (instead of the maximum for intermediate dosages observed in chloride medium). Hence, the maximum in the turbidity removal obtained in the chloride-containing suspensions with the electrical charge passed can be explained by the prevalence of the adsorption of monomeric and polymeric hydroxoaluminum cations (and the higher possibilities of charge reversal) whereas the plateau zone can be explained by the control of the PCN mechanism observed in the sulfate media. Anyhow, both mechanisms take place simultaneously in the treatment of the kaolin suspensions in this range of pHs.

Finally, with regard to the effect of the operation mode, it can be assumed that according to literature, and taking into account the pHs range, the primary mechanisms that explain the removal of kaolin are charge neutralization (by adsorption or by precipitation) at low aluminum concentrations and sweep flocculation at high aluminum concentrations. The transition zone corresponds to a zone in which neither of the two mechanisms is favored. Hence, in the discontinuous process the addition of aluminum is progressive, and in the continuous one the addition is instantaneous. This means that for a given dose of aluminum, in the latter case there is a higher "free aluminum" concentration in the moment of addition, and consequently the aluminum produced can form a bigger quantity of charged aluminum hydroxide precipitates. Consequently, the sweep flocculation can start in the continuously-operated process for smaller aluminum addition than in the batch process, and likewise, the precipitation charge neutralization can also be favored in these conditions.

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