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Improving the Efficiencies of Batch Coagulation Processes with Small Modifications in the pH

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The aim of this work has been to study the influence of small changes in the pH of kaolin suspensions on the efficiency of batch coagulation with aluminum reagents. To do that, the efficiencies obtained in the removal of kaolin from suspensions have been interpreted taking into account the values of the concentration of aluminum dosed, pH and z-potential. From the results obtained, it seems clear that the raw pH conditions of the wastewater are important to explain the results of batch coagulation processes because they influence on the speciation and coagulation mechanisms, and thus on the efficiency of the coagulation process. In the particular case studied, the small differences in the initial pH are enough to explain a change in the primary mechanisms from a very cost-effective precipitation-charge-neutralization to a less efficient floc-enmeshment mechanism. Thus, a change of 1 unit of pH in the raw wastewater is enough to decrease the dose of aluminum necessary to obtain similar removal efficiencies (around 85%) from 12 to 2 mg Al dm^{-3}. Hence a good knowledge of the system could allow optimizing the performance of operation processes, accepting small doses of reagents in a more robust neutralization charge based process.

Keywords aluminum; coagulation; kaolin suspensions; pH effect

INTRODUCTION

Coagulation is an important process in the treatment of many types of waters and wastewaters. It is particularly efficient in the removal of colloids, where the high specific surface area of the particles and the existence of a surface charge on these colloids explain the prevalence of electric repulsion forces over mass attraction forces. This stabilizes the colloid suspension and eliminates any possibility of removal of the colloid-pollutants by spontaneous settling (1). In such waters or wastewaters, the destabilization of the particles to decrease the repulsion forces is required. In this context, hydrolyzing metal salts, such as aluminum and ferric salts are widely used as coagulants (2–8), because they promote the destabilization and the subsequent aggregation of the particulate pollutants.

Interactions between coagulants and pollutants are one of the more interesting points in the understanding of this technology. Thus, once the coagulant metals salts are dosed to the wastewater, they hydrolyze to form different hydroxo-metallic monomeric and polymeric species, as well as metal hydroxide precipitates (9,10). The speciation (types and amounts of species produced) depends mainly on the metal concentration and on the pH (11). Likewise, the coagulant hydrolysis species define the coagulation/destabilization mechanisms and the corresponding efficiencies of the removal (10).

Thus, the adsorption of the ionic monomeric hydroxo-metallic species (12) or the precipitation of charged metal hydroxide precipitates (metal hydroxide with monomeric or polymeric metallic species adsorbed) onto the surface of the particulate pollutants contributes to the desestabilization of particles by charge neutralization (8,13,14). Likewise, the different functional groups of polymeric hydroxo-metal species can be adsorbed onto several particles (or molecules) of pollutant, neutralizing their superficial charge or joining several pollutant particles at a time (15). Also, the pollutants can be enmeshed into growing metal hydroxide precipitates (12,16) and removed with them (sweep flocculation).

Hence, for every case, the prevalence of a particular mechanism will depend on the particular pollutant and on the speciation of the coagulant (which depends on the pH and concentration). It is important to note that the operating cost of the process are directly related to the required dosage of coagulant, and that the required dose of the coagulant can vary for the same treatment in more than one fold between a charge neutralization and a sweep flocculation.

With this background, it is clear that it is important to optimize the operation conditions in the coagulation processes, in order to attain high removal efficiencies with the smallest required coagulant dosage. Due to the strong dependence of the speciation with the pH (10,11), a change

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in the pH is the simplest way to change speciation. This allows to suggest that small changes in the pH of the raw wastewater can be used to increase the efficiency (in terms of the coagulant dose required) and so, to optimize the results of the coagulation process. In this context, the goal of this work has been to study the influence of small changes in the pH of kaolin (model of colloid pollutant) suspensions on the efficiency of coagulation with aluminum reagents. To do that, the efficiencies obtained in the removal of kaolin from suspensions have been interpreted taking into account the speciation of aluminum for the different operating conditions and the suggested primary coagulation mechanisms involved.

MATERIALS AND METHODS

Experimental Devices

The coagulation experiments were carried out in a bench-scale plant (described elsewhere (17,18)), in a discontinuous operation mode. This plant had a single flow reactor where an aluminum solution was added to the synthetic wastewater by a dosage system, which consisted of a tank to store the aluminum solution, and a peristaltic pump that dosed the solution to the inlet of the reactor.

The kaolin suspension was stored in a glass tank ($5000\,cm^3$), stirred by an overhead stainless steel rod stirrer (HEIDOLPH RZR 2041) and circulated through the flow reactor by a peristaltic pump. A thermostated-bath allowed maintaining the temperature at the desired set point.

The synthetic suspension was composed by kaolin ($1000\,mg\,dm^{-3}$, supplied by Sigma-Aldrich) and NaCl ($3000\,mg\,dm^{-3}$). In addition, to adjust the initial pH of the suspension, HCl, or NaOH were added (only when necessary).

Experimental Procedures

The kaolin suspension was pumped from the feed tank to the reactor and then it was recycled to the feed tank, so the pumping system supplied the mixing between the suspension and the coagulant. 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 inoLabWTWpH meter), and the zeta potential (using a Zetasizer Nano ZS (Malvern, UK)) were measured to the clarified liquid.

Measurement of the Aluminum Concentration

The concentration of aluminum was measured off-line using an Inductively Coupled Plasma LIBERTY SEQUENTIAL VARIAN according to a standard method (19) (Plasma Emission Spectroscopy). To determine the total aluminum concentration, samples were diluted 50:50 v/v with 4 N HNO_3.

Characterization of the Hydrolysis Aluminum Species Generated in the Aluminum Dosing

To characterize the hydrolysis species resulting from the addition of aluminum in the coagulation process, several experiments were carried out, maintaining the same operation conditions and replacing the kaolin suspension by an aqueous solution with the same concentration of NaCl contained in the suspension, but without kaolin. Next, samples were taken and the pH, the zeta potential, and the total and soluble aluminum concentrations (by filtering the samples using membranes of $0.45\,\mu m$) were measured. In addition, the characterization of the hydrolyzed aluminum species generated has been carried out by the ferron method (11,20,21). This method consists of the timed spectroscopy monitoring of aluminum-ferron (8-hydroxy-7-iodo-5-quinolinesulfonic acid) reaction, to form a complex which has a maximum absorbance of 364 nm. Monomeric species react almost instantaneously with ferron, whereas polymeric species have a much slower reaction rate with this compound. The particles of precipitate practically do not react with ferron. Therefore, this method allows distinguishing among monomeric, polymeric, or precipitate species.

The analytical measurement was carried out by filtering the samples using membranes of $0.45\,\mu m$ in order to remove the particles of precipitate. Once the sample is filtered, an aliquot is added to a volume of saturated ferron solution freshly prepared so that ferron is in excess, at pH 5 in an acetate buffered solution. Immediately, the absorbance of the sample is monitored with time, until a constant value is obtained, which is indicative of the end of the reaction. By plotting the logarithm of the unreacted aluminum versus time, the ratio of aluminum species that react quickly and slowly with ferron (that is, monomeric and polymeric species) can be estimated (11,21).

RESULTS AND DISCUSSION

Figure 1 shows the effect of the coagulant dose on the removal of turbidity during the discontinuous coagulation of an alkaline kaolin suspension with sodium chloride as electrolyte. It can be observed that there is a maximum in the removal efficiency for aluminum doses close to $15\,mg\,dm^{-3}$. Outside the range 7–20 $mg\,dm^{-3}$ of aluminum dosed, the efficiencies are low and they do not seem to be affected by the reagent. This suggests that charge neutralization is the primary mechanism in the removal of kaolin in this case, and it also indicates that removal by sweep flocculation is not promoted within the pH conditions used, even for very high coagulant doses.

Figure 2 shows the changes in the pH and in the zeta potential obtained during the coagulation experiment, compared to the values of these parameters measured when aluminum is dosed to an aqueous solution with the same

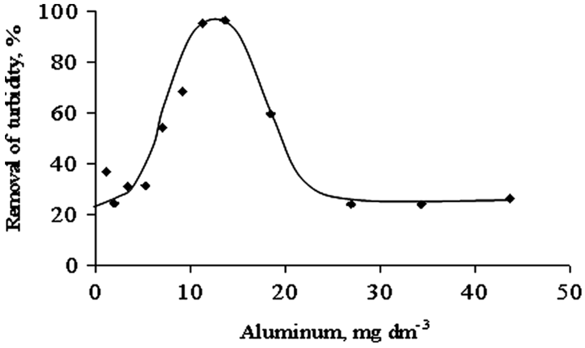
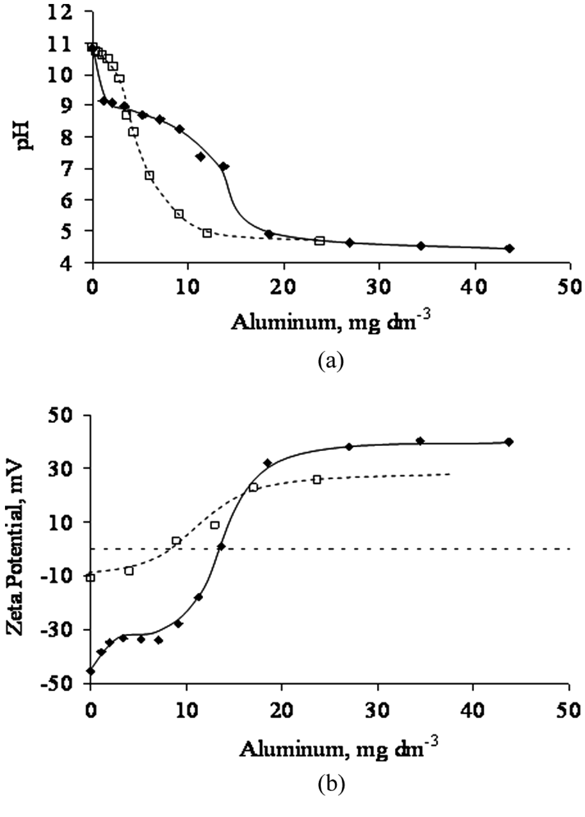


FIG. 1. Changes in the removal of turbidity obtained in the coagulation of a kaolin suspension as a function of the aluminum concentration dosed. Temperature: 25°C; Supporting medium: NaCl 3000 mg dm^{-3}; Kaolin concentration: 1000 mg dm^{-3}; Initial pH: 10.8; Flow rate: 54 dm^{3} h^{-1}; Volume: 1.5 dm^{3}.

pH and sodium chloride concentration but without kaolin particles. Regarding the changes of the pH, it can be seen that the pH obtained with the dosing of large concentrations of aluminum to the kaolin suspension and to the sodium chloride solution is the same, but the changes observed during the process (for smaller aluminum doses) are very different. In the kaolin suspension the changes are more immediate during the first dosages but after this initial stage, the pH changes in a softer way, suggesting some sort of buffering effect of the kaolin particles. In this point, it is worth mentioning that a change of 2 units in the pH requires 17 mg dm^{-3} of aluminum in the kaolin suspension, while a change of about 6 pH units only requires less than 10 mg dm^{-3} in the case of the solution without kaolin particles. The marked differences observed in the changes of the pH suggest a different aluminum speciation. Thus, it seems clear that the presence of kaolin influences on the aluminum speciation in the coagulation process.



(a)

(b)

FIG. 2. Changes in the pH and the zeta potential obtained with the addition of aluminum to a kaolin suspension, compared to those obtained in the dosing to an aqueous solution. Temperature: 25°C; Supporting medium: NaCl 3000 mg dm^{-3}; Flow rate: 54 dm^{3} h^{-1}; Initial pH: 10.8; Volume: 1.5 dm^{3}. ◆ Coagulation of kaolin suspension; Kaolin concentration: 1000 mg dm^{-3}, □ Dosing of aluminium to an aqueous solution.

Also, the changes in the zeta potential are also influenced by the presence of the kaolin suspension (Fig. 2b). As it is known, z-potential is related to the superficial charge of the solid particles contained in the suspension. In the case of the solution without kaolin particles, it gives information about the superficial charge of the aluminum hydroxide precipitates formed during the dosing process. Conversely, during the electrocoagulation of the kaolin suspension, it does not only give information about the superficial charge of the aluminum hydroxide precipitates formed, but most likely about the superficial charge of the kaolin particles.

In the Fig. 2b, it can be clearly observed that in case of the alkaline sodium chloride solution, the initial zeta potential is slightly negative, and the addition of aluminum causes the increase of this parameter to values close to 30 mV. This change can be explained taking into account the adsorption onto the aluminum hydroxide particles of charged aluminum species: hydroxoaluminium anions (negative potential) in the range of alkaline pHs and hydroxoaluminum cations (positive potentials) in the range of acidic pHs.

In this point, it is important to take into consideration that the speciation of aluminum depends strongly on the concentration and on the pH[11]. Figure 3 summarizes this dependence characterized using the ferron-test (11,20,21). The main species in the alkaline range of pH are monomeric hydroxoaluminum ions ($Al(OH)_4^-$), that coexist with polymeric species and very small concentrations of aluminum hydroxide particles. Decreases in the pH (values around neutrality) lead to the extensive formation of aluminum hydroxide precipitates, which can be superficially charged due to the adsorption of ions from the solution. The precipitates coexist with monomeric and polymeric aluminum species (Fig. 3a), and lower aluminum concentrations cause the formation of higher proportion of polymeric hydroxoaluminum ions against precipitates. Further decreases in the pH to the acidic zone, lead to the dissolution of the precipitates to form monomeric hydroxoaluminum ions (Al^{3+}, $Al\ (OH)^{2+}$, and $Al(OH)_2^+$),

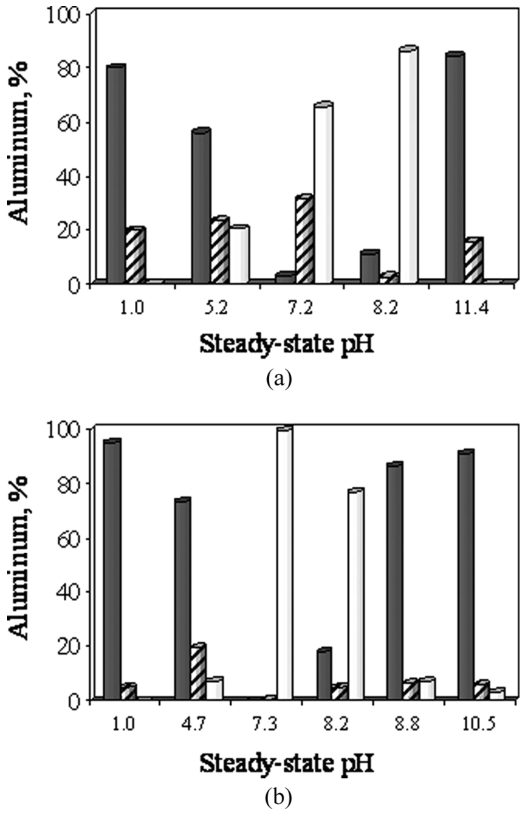


FIG. 3. Aluminum speciation obtained in the dosing of aluminum to aqueous solutions. Temperature: 25°C; Supporting medium: NaCl 3000 mg dm^{-3}. ■ Monomeric hydroxo-aluminum ions, ▨ Polymeric hydroxo-aluminum ions, □ Aluminum hydroxide precipitates. (a) Total aluminium concentration added around 5 mg dm^{-3}. (b) Total aluminium concentration added around 17 mg dm^{-3}.

that coexist with polymeric species for low aluminum concentrations and even with very small concentrations of solid particles of aluminum hydroxide precipitates.

Coming back to Fig. 2, it can be observed that the kaolin suspension has a negative value of zeta potential (close to −40 mV) before aluminum dosage, indicating a negative superficial charge of the kaolin particles in the sodium chloride solution. It can also be observed that the addition of aluminum produces first the charge neutralization of the kaolin particles and later the charge reversal, as the zeta potential of the suspension increases up to achieve positive values (near 40 mV). It can also be seen that the range of aluminum doses in which pH change softly also corresponds to a zone in which the z potential remains almost constant. A last observation that can be drawn from Figs. 1 and 2, is that the maximum in the removal of turbidity in the coagulation process corresponds to values of the pH close to neutrality, and to values of zeta potential close to 0 mV. Hence, the primary coagulation mechanism should be related to charge neutralization although in this point of the discussion it is difficult to propose a single mechanism with only one charged aluminum species as the primary reagent, because there are too many possible aluminum species that can influence on the results.

In this point it is important to observe that the charge reversal is obtained first for aluminum hydroxide particles in the sodium hydroxide alkaline solution (no kaolin particles) and it requires a higher dose of aluminum for the kaolin suspension. This observation confirms that in the charge reversal of the kaolin particles there is an important influence of both charged precipitates and soluble ionic species.

Hence, it is important to know in detail as to what happens during the charge neutralization of kaolin suspensions in order to try to know how to improve the efficiency of this process, and how to minimize the adverse effect of the overdosing of coagulant reagents. In this context, the pH of the raw kaolin suspension should be an important parameter because it can be easily modified, and also because it affects very significantly to the aluminum speciation. To check the significance of this parameter, coagulation tests were applied to kaolin suspensions with initial pHs within the range 9.5–11.0. Results are shown in Figs. 4–6.

Figure 4 shows the changes in the removal of turbidity. In all cases, there is a maximum in the removal of turbidity, but it shifts toward higher aluminum doses with the pH (the more alkaline the higher the dose required to reach the maximum). In addition, there is also a significant difference in the outstanding turbidity obtained for very high doses of aluminum (>20 mg dm^{-3}): the process efficiency worsens with the initial pH of the kaolin suspension (the higher the pH the lower the final efficiency for higher doses).

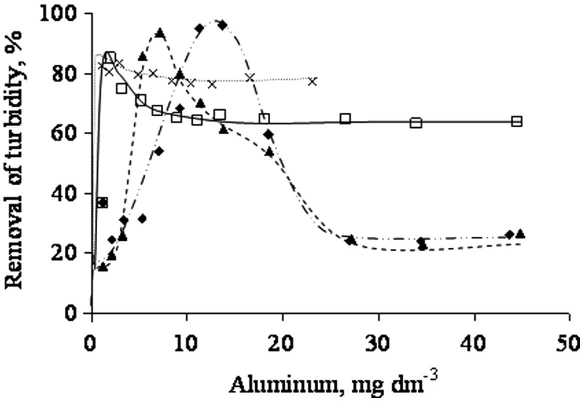


FIG. 4. Removal of turbidity obtained in the coagulation of kaolin suspensions for different initial pHs. Temperature: 25°C; Supporting medium: NaCl 3000 mg dm^{-3}; Kaolin concentration: 1000 mg dm^{-3}; Flow rate: 54 dm^3 h^{-1}; Volume: 1.5 dm^3. ◆ Initial pH: 10.8, ▲ Initial pH: 10.5, □ Initial pH: 10.2, × Initial pH: 9.5.

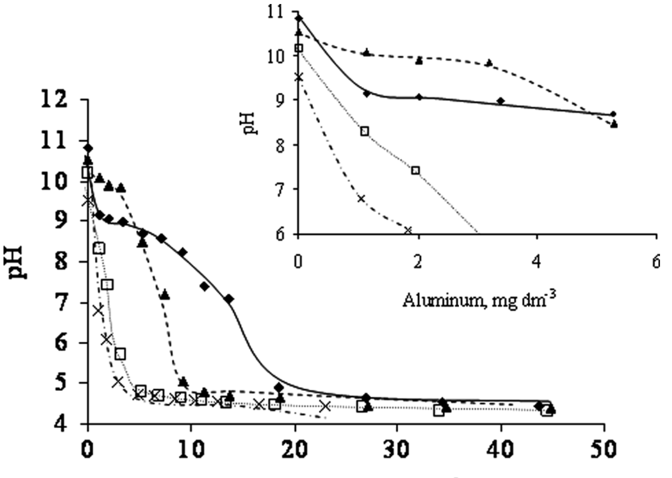


FIG. 5. Changes in the pH obtained in the coagulation of kaolin suspensions for different initial pHs. Temperature: 25°C; Supporting medium: NaCl 3000 mg dm^{-3}; Kaolin concentration: 1000 mg dm^{-3}; Flow rate: 54 dm^3 h^{-1}; Volume: 1.5 dm^3. ◆ Initial pH: 10.8, ▲ Initial pH: 10.5, □ Initial pH: 10.2, × Initial pH: 9.5. Onset: smaller scale for the aluminum concentration.

Figure 5 shows the changes in the pH. In every case the acidic properties of the aluminum reagent make it to decrease and, for very high doses (>20 mg dm^{-3}) it stabilizes in a value around 4.5. The main differences are observed for lower aluminum doses (onset of Fig. 5). There is a range of aluminum dosing in which the variation of the pH depends strongly on the initial pH of the suspension. The higher the initial pH the softer the change observed (it seems like a buffering effect). After this zone, the situation reverses and finally, in all the experiments, it is met the same final pH.

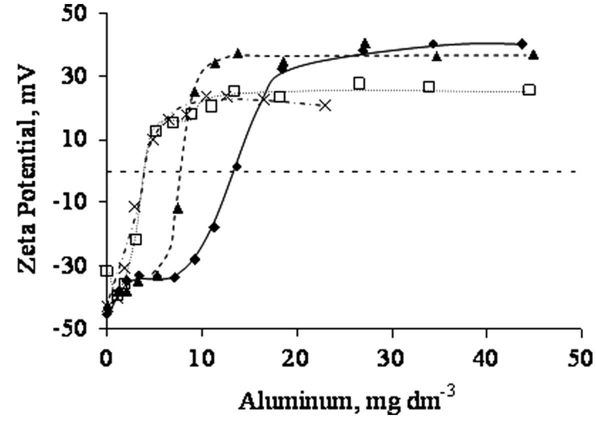


FIG. 6. Zeta potential obtained in the coagulation of kaolin suspensions for different initial pHs. Temperature: 25°C; Supporting medium: NaCl 3000 mg dm^{-3}; Kaolin concentration: 1000 mg dm^{-3}; Flow rate: 54 dm^3 h^{-1}; Volume: 1.5 dm^3. ◆ Initial pH: 10.8, ▲ Initial pH: 10.5, □ Initial pH: 10.2, × Initial pH: 9.5.

Figure 6 shows the changes in the zeta potential. In every case, the initial z-potential values are around −40 mV. These negative values are due to the negative superficial charge of the kaolin particles in the suspension. The addition of aluminum produces first the neutralization of the charge and later the charge reversal. The more significant point to be discussed in this figure is the existence of a range of aluminum dosages that do not produce a significant change in the z-potential and that match with the zone in which the pH changes in a softer way (2–10 mg dm^{-3}). Its width increases with the initial alkalinity of the suspension. Thus, this range is more clearly observed in the coagulation of the more alkaline suspensions and it seems to be negligible in the treatment of the suspensions with initial pHs below 10.2. It is also remarkable that the initial pH of the kaolin suspension also influences on the value in which the z-potential stabilizes for large aluminum dosages. The higher the pH, the higher the z-potential in which the treatment stabilizes.

Taking into account the results, it can be affirmed that the removal of turbidity attained in the coagulation process is strongly related to the pH and the zeta potential. Thus, in all cases, the maximum efficiencies are obtained for pH close to neutrality, and zeta potential values close to 0 mV. These results indicate that the aluminum hydroxide precipitates, which are the main species at neutral pH, and are very effective in the removal of kaolin particles. Also, these species achieve the charge neutralization of the kaolin particles, according to the zeta potential changes. However, due to the different initial pHs of the kaolin suspensions, the aluminum doses necessary to attain high removal of turbidity are very different, and the efficiency observed after the maximum varies significantly.

Thus, in case of initial pH below 10.2, aluminum precipitates are formed for low doses, due to the values of pH around neutrality. These aluminum precipitates can neutralize the superficial charge of the kaolin particles by precipitating onto their surfaces (8,13,14), (Precipitation Charge Neutralization, PCN), as it can be seen in the graphic model of Fig. 7. The strong interaction between the superficial aluminum precipitates and the kaolin particles avoid the dissolution of the precipitates with further decreases of the pH. For this reason, the efficiency of the process does not worsen markedly with the decrease of the pH.

For initial pHs above 10.5, small aluminum doses lead to alkaline pHs, and so the formation of anionic monomeric and polymeric aluminum species. According to the results, these species are not effective in the kaolin removal as they do not neutralize their charges (22). Increases in the aluminum dose cause pHs around neutrality, and the subsequent precipitation of aluminum. In this case,

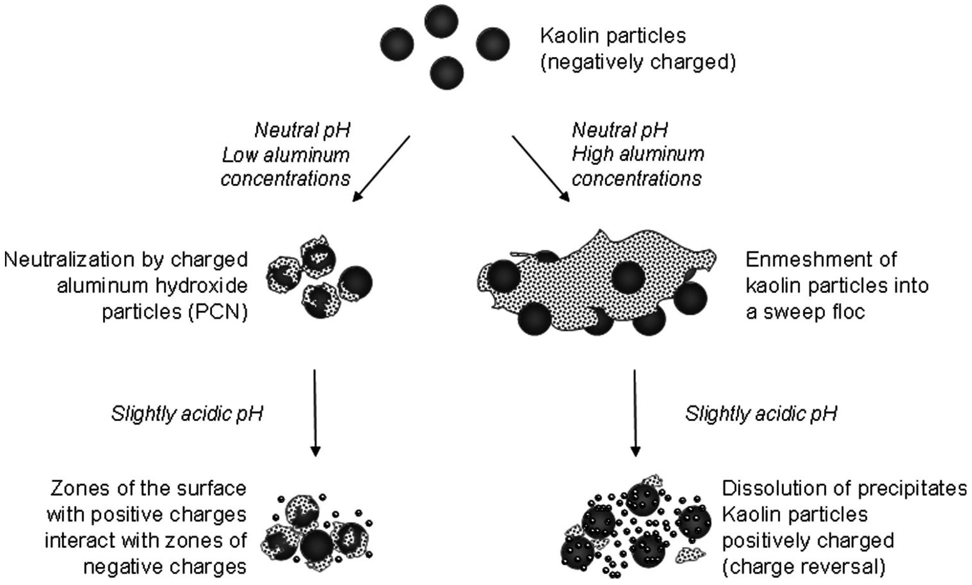


FIG. 7. Graphic model showing the coagulation mechanisms.

the aluminum concentrations are higher, and the formation of a growing precipitate that enmesh kaolin particles inside is possible (10,12) (sweep floc, Fig. 7). The aluminum precipitates can be positively charged, due to the adsorption of cations from the solution (10,11) (Fig. 2). For this reason, the net charge of the overall system (kaolin particles enmeshed into growing precipitates) is near neutral. However, further decreases in the pH produce the partial dissolution of the precipitates to form monomeric and polymeric aluminum cations. Therefore, the efficiency of the process is worsened due to the release of the kaolin particles from the precipitates. Also, the aluminum cations formed produce the charge reversal of the kaolin particles, and avoid their removal (see the zeta potential values in Fig. 6).

The results obtained in this work show that the efficiency of the coagulation processes depend importantly on the pH of the wastewater, as this parameter affects the coagulant speciation and therefore, the main coagulation mechanisms. Thus, a good knowledge of the system, in terms of the interaction of the pollutant and the coagulant species, can allow the optimization of the process. Of course, these observations can also be extended to actual wastewaters—in case of complex aqueous matrixes, the different pollutants present in the system, like soluble organic matter, interact with the coagulant species by means of different coagulation mechanisms (like bridging coagulation or adsorption onto precipitates) depending on the pH (15). Therefore, it seems clear that the behavior observed in the model system can be extrapolated to actual or complex wastewaters—small changes in the pH can lead to important savings of coagulant reagent, obtaining high efficiencies of the coagulation process.

CONCLUSIONS

According to the results obtained, it is important to bear in mind that the dosing of aluminum in the coagulation process causes the decrease in the pH of the system, it seems clear that the raw pH conditions of the wastewater are important to explain the results of batch coagulation processes because they influence on the speciation and coagulation mechanisms, and thus on the efficiency of the coagulation process. A change of less than 1 unit of pH is enough to explain a change in the primary kaolin coagulation mechanisms from a very cost-effective precipitation charge neutralization to a less efficient floc enmeshment mechanism. Hence a good knowledge of the system could allow optimizing the performance of operation processes, allowing using small doses of reagents in a more robust neutralization charge based process.

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