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A comparative study on the treatment of gelatin production plant wastewater using electrocoagulation and chemical coagulation

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ABSTRACT

Effluents from gelatin production plants are highly complex and difficult to treat by conventional methods. The Electrocoagulation (EC) technique was evaluated to treat effluents that contain a heavy load of Chemical Oxygen Demand (COD) and a large quantity of suspended solids. This paper presents results of laboratory scale studies that compare the performance of Chemical Coagulation (CC) with aluminum salts and EC with aluminum electrodes. The heavy organic load and suspended solids in this kind of wastewater lead to low performance in the secondary treatment. SEM-EDS were used to analyze the sludge formed in the EC process and the removal mechanism of pollutants from the wastewater. The structure and composition of the precipitates at different operation conditions, such as pH, show that EC has increased efficiency of COD removal, compared to CC with the same dose of aluminum (Al^{+3}) as coagulant. The efficiency of COD removal was 73.6% with EC and 55.6% with CC. The in-situ formation of zeolites in the EC process explains the high efficiency of this treatment compared to the CC process. The zeolite formation during the EC process in the wastewater of the gelatin production plant has not been reported until now.

1. Introduction

Gelatin is a heterogeneous mixture of proteins derived from collagen of animal hide and bone. It is commonly used in food, pharmaceuticals, photography, cosmetics and wine fining (Maree et al., 1990; Hoyos et al., 2002). The production process of gelatin from bones includes a variety of unit operations such as acidulation, whitewashing, washing, extraction, filtration, deionization, evaporation, sterilization, drying and mixing.

The process of gelatin production generates a large amount of effluent, approximately 300 m^3 of waste water for every ton of bones processed with a concentration of chemical oxygen demand (COD) of an average 8000 mg/L, and it is rich in nitrogen, calcium, and phosphorus (Hoyos et al., 2002; Lakshmi Kruthika et al., 2013); therefore, the effluent elimination is an important cost factor (Maree et al., 1990). Effluent treatment in this type of industry includes a pretreatment that consists of the elimination of coarse solids, a primary treatment that includes unit operations of neutralization, flocculation and coagulation followed by clarification, sedimentation or floating, and finally a secondary aerobic biological treatment (Badrinath et al., 1991).

Aerobic biological treatment systems are suitable for treating wastewater of low load where COD concentrations should be less than 2500 mg/L (Romero Rojas, 2010). Therefore, an adequate primary treatment is required to reduce the COD concentration before the effluent enters the secondary treatment. Conventional primary treatment consists of adding a chemical coagulant to promote the sedimentation of suspended solids and to reduce the organic load of the effluent before entering the secondary treatment. However, it has been reported that alternative treatments such as electrocoagulation (EC) obtained a greater removal of COD and suspended solids from effluents compared with conventional treatment by chemical coagulation (CC) (Jiang et al., 2002; Gilpavas et al., 2008; Garcia Segura et al., 2017).

The electrocoagulation (EC) process has been successfully employed in removing suspended solids, colloidal material and metals, as well as other dissolved solids (Garcia Segura et al., 2017; Elazzouzi et al., 2017).

The electrochemical reactions are the oxidation of the anode:

$$M \rightarrow M^{n+} + ne^- \tag{1}$$

and the water reduction on the cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}$$

In the case of a high anode potential, secondary reactions may occur

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(Mouedhen et al., 2013). Water can oxidize and lead to the hydronium cation and gaseous oxygen and, in the presence of chloride anions, the Cl^- can be oxidized in Cl_2. The latter is a strong oxidizer that can contribute to the oxidation of dissolved organic compounds or may lead to the formation of ClOH, which also plays a role as oxidant. While in the cathode, water is reduced to hydrogen gas and hydroxyl anions.

Mass-released metallic cations undergo different equilibrium reactions corresponding to acid/base reactions, complexation, precipitation and redox reactions. The role of this elimination mechanisms depends on the polluting species. For aluminum, the oxidation reaction between Al^{3+}/Al follows Eq. (1). In addition, other monomeric species are formed from the spontaneous hydrolysis of the cations according to the acid/base reactions and the concentration of Al^{3+} (Hakizimana et al., 2017).

$$Al^{3+} + 2H_2O \rightarrow Al(OH)^{2+} + H^+$$

$$Al(OH)^{2+} + H_2O \rightarrow Al(OH)_2^+ + H^+$$

$$Al(OH)_2^+ + H_2O \rightarrow Al(OH)_3 + H^+$$

$$Al(OH)_3 + H_2O \rightarrow Al(OH)_4^- + H^+$$

The work done by Kruthika et al., 2013 of wastewater generated from gelatin production plants proposes that the anodic dissolution of aluminum can be represented as:

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2 \text{ (basic condition)}$$

$$2Al + 6H_2O \rightarrow 2Al(OH)_3 + 6H^+ \text{ (acid condition)}$$

mentioning that depending on the pH of the aqueous solution, Al^{3+} could result in the formation of species such as poly $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$, $Al(OH)_4^-$, $Al(OH)_n^{(3-n)}$, $Al_2(OH)_2^{4+}$, $Al_7(OH)_{17}^{4+}$, $Al_{13}(OH)_{34}^{5+}$, $Al_3(OH)_4^{5+}$, $Al(OH)_6^{3-}$ with different load. It is reported that dissolved metal ions and metal oxyhydroxides help the coagulation of suspended solids.

According to Vázquez et al. (2010), when aluminum is used as an anode, the main reactions are:

$$Al^{3+} + H_2O \rightarrow AlOH^{2+} + H^+$$

$$Al^{3+} + 2H_2O \rightarrow Al(OH)_2^+ + 2H^+$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3(ac) + 3H^+$$

$$Al^{3+} + 4H_2O \rightarrow Al(OH)_4^- + 4H^+$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3(s) + 3H^+$$

$$8Al^{3+} + 20H_2O \rightarrow [Al_8(OH)_{20}]^{4+} + 20H^+$$

Such different monomeric species in equilibrium with aluminum ions depend on pH conditions (Cotillas et al., 2013; Duan et al., 2003; Hakizimana et al., 2017; Kruthika et al., 2013; Terrazas Eduardo et al., 2010). For low concentrations of aluminum (Garcia Segura et al., 2017) and pH regions between 6 to 8, the predominant species are the complexes $Al(OH)^{2+}$ and $Al(OH)_4^-$. As aluminum concentration increases, a precipitated form of $Al(OH)_3$ is predominate.

Mansouri et al. (2011a, b) reports that for initial acid pH conditions, pH increase can be explained by the formation of OH^- ions from the reduction of H^+ or H_2O on the surface of the cathode. In these circumstances, it appears that the hydroxide ions formed in the cathode were not fully involved in the formation of hydroxyl-aluminum species. Rather, the excess of OH^- ions increases the pH of the environment. On the contrary, for solutions with an initial pH greater than 9, the decrease in pH could be attributed to the consumption of higher quantities of OH− ions to form anionic species of aluminum hydroxide as $Al(OH)_4^-$ y $Al(OH)_5^{2-}$. pH stabilization at a value close to 9 for initial pH values slightly acidic, neutral and alkaline can be explained by a buffering effect of the hydroxyl-aluminum species which balances the almost static variation of the concentration of hydroxide ions through the formation of monomeric and polymeric aluminum hydroxide complexes (Mansouri et al., 2011a,b; Garcia Segura et al., 2017).

Several authors have discussed the EC mechanism with aluminum electrode. Most agree that the metal cations released by the anode lead to the formation of metallic hydroxides that show low solubility and easily precipitate; as a result, contaminants can physically or chemically adsorb on the precipitates. In general, it is accepted that the EC process involves three successive stages: (a) formation of coagulants by electrolytic oxidation of the "sacrificial electrode"; (b) destabilization of contaminants, particle suspension and emulsions breakage; (c) aggregation of destabilized phases to form flocs. Floc formation, as a result of coagulation, creates a layer of mud that traps and unites colloidal particles that have not been complexed (Can and Bayramoglu, 2014). The details of these steps are missing and require more study.

The purpose of this study is to evaluate the operation of electrocoagulation for treating effluent generated by a gelatin producer, which contains high load of COD and a large quantity of TSS. Because the effluent from the industrial plant was treated with aluminum salts, we use the aluminum electrodes. This allow as to compare electrocoagulation process with chemical coagulation operations using the same ion flocculant (Al^{+3}), and the determination of the influence on electrocoagulation with pH in the COD, turbidity and TSS removal efficiency. In addition, surface analysis techniques were used to study the precipitate in order to confirm a mechanism to remove pollutants from the wastewater.

2. Materials and methods

2.1. *Materials*

To evaluate the electrocoagulation operation a sample of the liquid effluent generated by a gelatin production company was used. The characterization of the sample is shown in Table 1:

2.2. *Methods*

2.2.1. *Analytical determinations*

The conductivity and solution pH were monitored using LaMotte 802 conductive and Thermo Scientific Orion Dual Star pH Meter. The COD of the wastewater was measured by a Hach spectrophotometer (DR2500) and a Hach COD reactor. The COD of the homogenized sample was appointed Total COD (COD_T) and to find the Soluble COD (CODs) the sample was previously filtered with 0.45 μ m (Millipore HA) membranes. An Imhoff cone was used to determine the SS in 10 minutes and 2 hours.

Table 1
Characterization of effluent sample.

Parameter	Value
Appearance	Turbid
PH (25 °C)	7.510
Turbidity	>1000 NTU
Electric Conductivity (μS/cm)	5310
Total Suspended Solids (TSS)	5520 mg/L
Total Dissolved Solids (TDS)	3186
Soluble Chemical Oxygen Demand (CODs)	1900 mg/L
Total Chemical Oxygen Demand (COD_T)	6600 mg/L
Total Phosphorus (P_T)	64.8 mg/L
Total Hardness as $CaCO_3$	295 mg/L
Total Alkalinity as $CaCO_3$	997.5 mg/L
Silicates (SiO_4)	85.4 mg/L

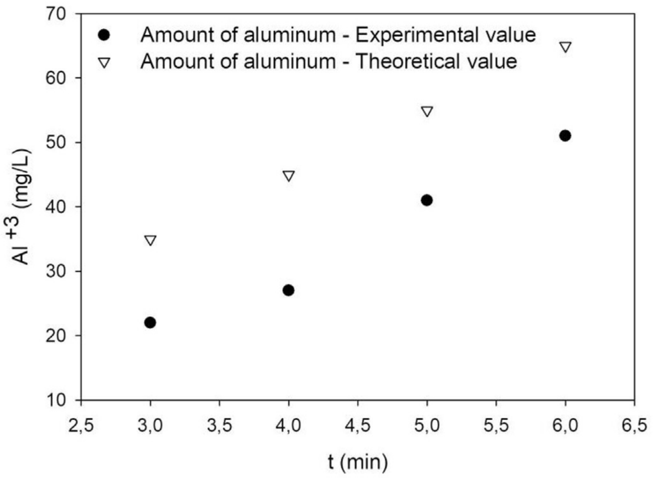

Fig. 1. Amount of aluminum theoretically measured and experimentally measured as a function of time.

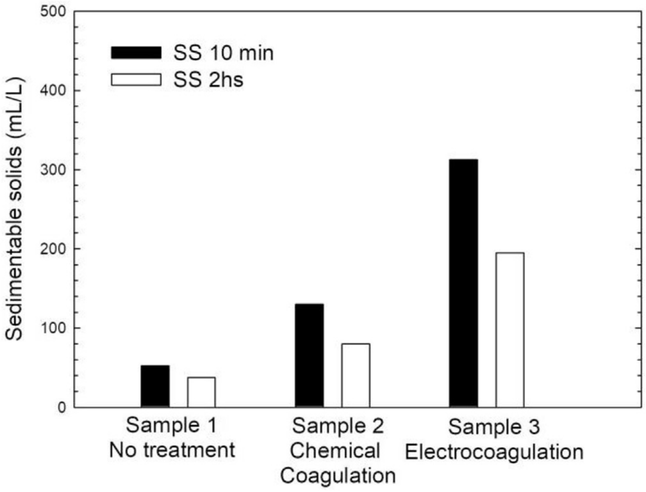

Fig. 2. SS in 10 minutes and 2 hours of untreated effluent (sample 1), treated by chemical coagulation (sample 2) and electrocoagulation (sample 3).

The Total Suspended Solids (TSS) were determined by the difference in weight of samples filtered with 0.45 μ m (Millipore HA) membranes and dried at 105 °C to constant weight. The Aluminum determinations were made by Hach kit, method 8012.

A FEI SEM Quanta 200 device and an EDAX SDD Apollo 40 EDS-EDAX analyzer carried out surface characterization.

2.2.2. *Chemical coagulation*

Coagulation tests were carried out in a jar testing equipment with a commercial coagulant solution ARQUIMIA (Aluminum Polychloride) used by the company in a plant with a concentration of 250 Al^{+3}/L.

2.2.3. *Electrocoagulation*

Aluminum electrodes with an effective area of 21.3 cm^2 were used. The separation between the plates was 15 mm. A 500 ml capacity electrocoagulation reactor, a continuous current source and a current and voltage meter were used. It was continuously stirred with a magnetic stirrer.

The experimental amount of aluminum created at the cathode was compared with the theoretical amount calculated using Faraday's second law. However, Faraday's law ($\varphi = 1$) is only valid when all electrons in the system only participate in the dissolution reaction of the metal at the anode. When parallel reactions occur, the *faradic performance* (φ) is used to account for the gap between theoretical and experimental dissolution. This value is usually less than 1, but φ can be greater than 1 when the chemical and electrochemical mechanisms of metal oxidation proceed simultaneously (Mansouri et al., 2011a,b).

The experiments were performed at constant current intensity (1 A) and the cell voltage was recorded during the electrolysis period, 3–6 min. Electrolyte samples were taken, and the concentrations of dissolved aluminum were determined by spectrophotometry, as indicated in section 2.2.1. Experimental and theoretical data were obtained and are shown in Fig. 1.

The current efficiency was calculated to be approximately 28.2% ± 6% from the experimental results. The amount of Al^{3+} used in the chemical coagulation experiments was equal to the amount of total Al^{3+} dissolved in the electrocoagulation experiments at 5 minutes of electrolysis.

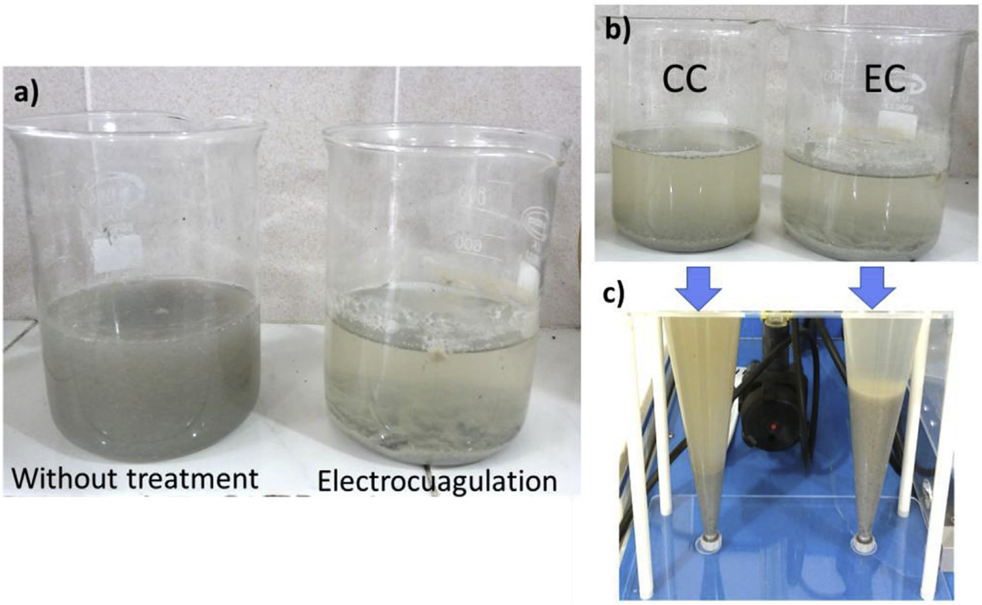

Fig. 3. Comparison photographs a) untreated sample and treated by electrocoagulation b) between chemical coagulation (CC) and electrocoagulation (EC) and c) SS determination in Imhoff cone.

Table 2

Supernatant analysis of the untreated effluent (sample 1), with treatment by chemical coagulation (sample 2) and by electrocoagulation (sample 3).

Parameter	Sample 1	Sample 2	Sample 3
Turbidity (NTU)	460.0	112.8	27.2
TSS (mg/L)	600	340	84
CODs (mg/L)	1845	1830	1649
COD_T (mg/L)	3160	2928	1742
P_T (mg/L)	50.6	29.6	25.4
SiO_4 (mg/L)	85.0	64.4	20.2

3. Results

3.1. Comparison of chemical coagulation and electrocoagulation

Tests were performed using chemical technology and electrocoagulation and were compared with the sedimentation of suspended solids in the gravity sample. Three samples of the effluent were placed in an Imhoff cone; sample 1 did not receive any primary treatment, sample 2 was coagulated and flocculated in the laboratory with the chemical agents used by the company, and sample 3 was subjected to 5 minutes of electrocoagulation. Fig. 2 shows the obtained results of SS.

In Fig. 2 it is clearly seen that the SS at 10 minutes of treatment significantly increase when the sample is treated by chemical coagulant and electrocoagulation with respect to a sample not subjected to any treatment and only settled by action of gravity. When solids present in the raw sample settled without any treatment, the value of sedimentable solids at 10 minutes (SS 10′) was 52.5 mg/L. In the case of the sample treated with coagulant and flocculant used by the company, the value of the SS 10′ was increased to 130 mg/L, whereas when the sample was subjected to the process of electrocoagulation for 5 minutes, the value of SS 10′ was 312.5 mg/L. I.e., the amount of solids that settle in 10 minutes at the bottom of a container in static conditions was increased 2.50 times using chemical coagulation process and 5.95 times using electrocoagulation.

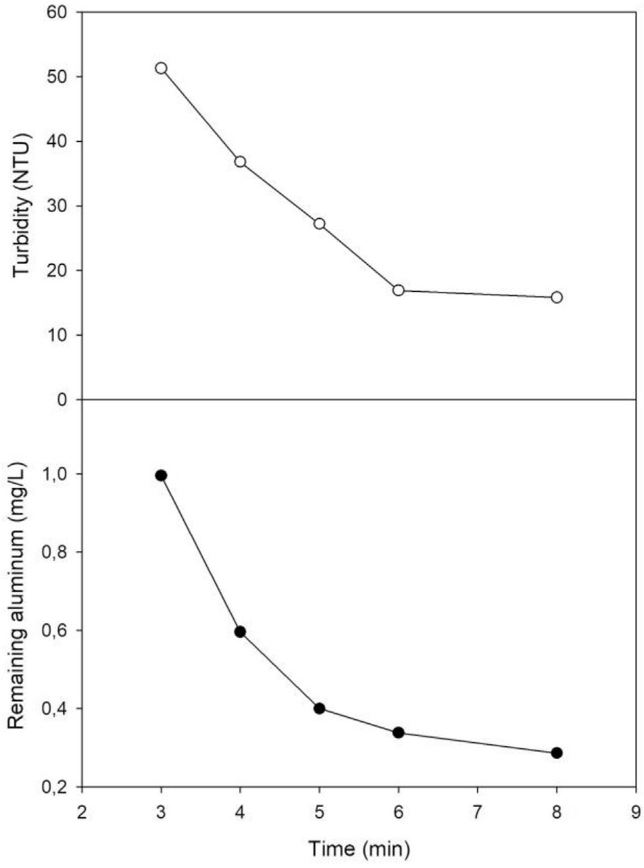

Fig. 4. Turbidity and concentration of aluminum remnant as a function of electrolysis time.

Fig. 3 shows a photograph of samples minutes after the treatment and sedimentation testing with Imhoff cone.

The supernatant of the three samples was separated, and the turbidity, TSS concentration, COD and P_T, were analyzed. The results are shown in Table 2.

It can be observed that turbidity and TSS values obtained with electrochemical treatment were below than those obtained by the chemical coagulation treatment that the company uses. COD_T obtained for treatment by electrocoagulation is acceptable for the effluent to enter the secondary stage of treatment and decreases to values close to the CODs; this means that almost all of the COD remnants from the primary treatment correspond to the CODs and must be removed in the biological treatment to meet the legislation values. The values of phosphorus remnants of the chemical treatment were similar, with a removal percentage among 54,3–60,8%, while the electrochemical treatment capacity to remove silicates was three times higher compared with chemical treatment.

3.2. Evaluation of electrocoagulation parameters

Electrolysis time influences the effectiveness of the treatment in the electrochemical process (Konstantinos et al., 2019). Electrocoagulation tests were performed at different times while maintaining current intensity and constant electrode separation.

Fig. 4 shows that there is a direct relationship between the effluent turbidity decrease and the residual aluminum concentration, and that a higher aluminum concentration produced during electrolysis causes a lower turbidity.

On the other hand, the precise determination on the concentration of residual aluminum is required since a high aluminum value in the effluent may affect the subsequent biological treatment (Mamais et al., 2011).

Fig. 5 shows the decrease of the supernatant COD for increasing electrolysis times. The minimum COD_T value, 1635 mg/L, was recorded at 8 minutes of treatment, and corresponds to a total removal percentage of 75.2% of the initial value of the tributary; in addition, there was a decrease of 16.5% of the measure of soluble COD (COD_S). In the previous section, it was observed that the COD_S was not modified with the chemical coagulation treatment.

The COD values slightly decrease at increasing electrolysis times; for

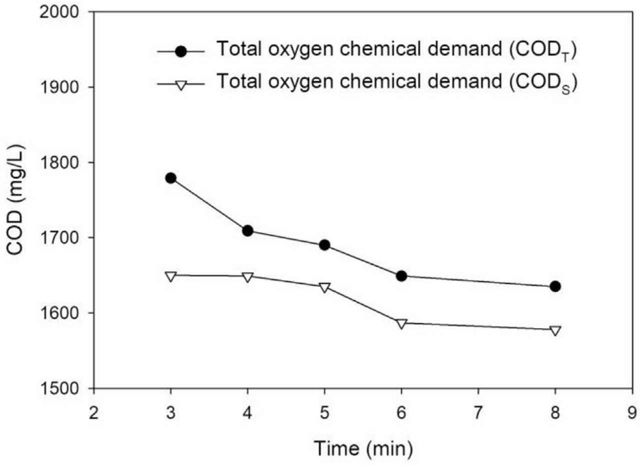

Fig. 5. Total and soluble COD concentration as a function of electrolysis time.

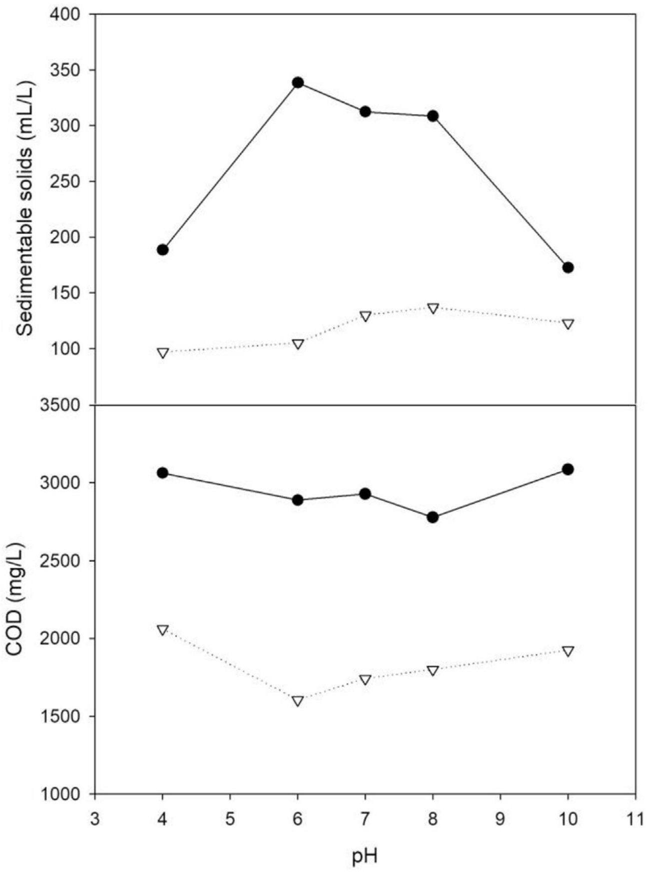

Fig. 6. Influence of the initial pH of the effluent; turbidity, COD in the CC and EC.

the COD_T from 1779.0 mg/L at 3 minutes to 1635.0 mg/L at 8 minutes, and for the COD_S from 1650 mg/L to 1587 mg/L. It can be noted that COD_T and COD_S values of the supernatant are similar; this promptly indicates that all the suspended organic matter was removed by electrocoagulation treatment.

3.3. Influence of pH in the process of chemical coagulation and electrocoagulation

The effluent pH is an important operating parameter, since metal ions, at suitable pH values, can form wide ranges of coagulated species and metal hydroxides that precipitate and adsorb dissolved contaminants or destabilize and aggregate suspended particles (Chellam and Sari, 2016).

To check whether a change in pH can improve results, the desired pH of the raw effluent samples was adjusted by adding sodium hydroxide or hydrochloric acid solution. The variations on turbidity and COD for the effluent samples with various initial pH values are shown in Fig. 6.

The results revealed that, for both EC and CC, when the pH of the solutions was between 6 and 8, there was a maximum efficiency in the elimination of turbidity and COD. Aluminum has the minimum solubility within a pH range of 6.5–7.8 (Hakizimana et al., 2017) and, due to the availability of enough coagulant at the medium and minimum solubility the highest elimination rates at that pH range can be achieved.

3.4. Precipitate formation

The combinations of the SEM-EDS microscopic techniques were used to examine surface morphology and the elemental composition of the precipitate. Fig. 7a and b shows a photograph of the sludge sample obtained from the EC process at pH 7 and dried at 105 °C for 2 hours. The SEM analysis reveals the presence of a discontinuous layer composed of randomly oriented diamond-shaped crystals.

Fig. 8 shows the EDAX analysis performed in precipitates where a predominant peak corresponding to silica is observed. This is consistent with the decrease in the concentration of silicates found in the supernatant after treatment (Table 2).

From the semi-quantitative analysis of the sludge samples obtained in the EC process at pH 6 to 8, it was found that the Si/Al ratio was approximately 4.5, a range in which microporous aluminosilicate minerals called zeolites are usually found (Moshoeshoe et al., 2017). There are different types of zeolite in function to Si/Al ratio and their main cations (Table 3).

4. Discussion

The comparison of the EC and CC processes used for treatment proved electrochemical treatment to have practical advantages in terms of effectiveness. It could be observed that EC values of turbidity, TSS and COD were below those obtained by chemical coagulation using the same dose of Al^{+3}.

Both in CC and EC, the Al^{+3} cations contribute to reducing the stability of suspended organic compounds by reducing their zeta potential. The electro-chemical coagulation processes, where mechanisms such as absorption–ionic interaction are important, may exhibit different removal performances at the same pH, depending on the type of the charged groups carried by the pollutant and the pollutant polarity (Can and Bayramoglu, 2014).

Aluminum can also precipitate in the form of polymerized amorphous hydroxides that promote contamination removal through a non-specific mechanism generally denoted as scavenging flocculation. In this

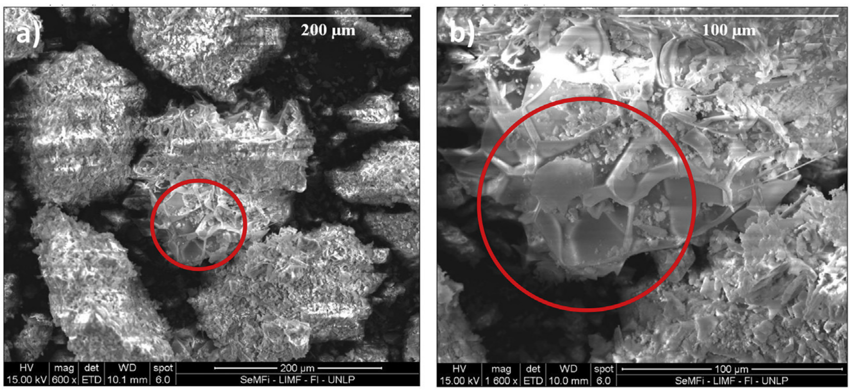

Fig. 7. Precipitate formed in the EC process a) 600X b) 1600X.

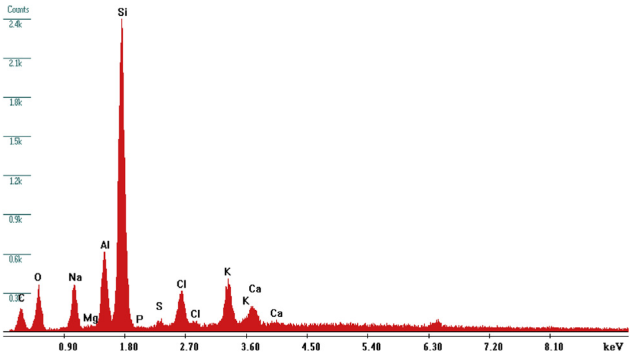

Fig. 8. EDAX study performed on the dried precipitate.

Table 3

Type of zeolite in function to Si/Al ratio and their main cations [12].

Zelotite Name	FCT	Formula	Si/AL ratio	Main Cation
Analcime	ANA	$Na_{16}(Al_{16}Si_{32}O_{96})\cdot 16H_2O$	1.5–2.8	Na
Chabazite	CHA	$Ca_2(Al_4Si_8O_{24})\cdot 12H_2O$	1.4–4.0	Na,Ca,K
Clinoptiolite	HEU	$(Na,K)_6(Si_{30}Al_6O_{72})\cdot 20H_2O$	4.0–5.7	Na,Ca,K
Heulandite	HEU	$Ca_4(Si_{28}\ Al_8O_{72})\cdot 24H_2O$	4.0–6.2	Na,Ca,K,Sr
Mordenite	MOR	$Na_2KCa_2(Al_8Si_{40}O_{96})\cdot 28H_2O$	4.0–5.7	Na,Ca,K
Philipsite	PHI	$K_2(Ca_{0.5}Na)_4(Al_6Si_{10}O_{32})\cdot 12H_2O$	1.1–3.3	Na,Ca,K
Laumontite	LAU	$Ca_4(Al_8Si_{16}O_{48})\cdot 16H_2O$	1.9–2.4	Na,Ca,K
Natrolite	NAT	$Na_{16}(Al_{16}Si_{24}O_{80})\cdot 16H_2O$	1.2–1.7	Na
Erionite	ERI	$(Na_2K_2Ca)_2(Al_4Si_{14}O_{36})\cdot 15H_2O$	2.6–3.8	Na,Ca,K
Faujasite	FAU	$(Na,Ca,Mg)_{3.5}(Al_7Si_{17}O_{48})\cdot 32H_2O$	2.1–2.8	Na,Ca,Mg
Ferrierite	FER	$(Na,K)_2Mg(Al,Si)_{19}O_{36}(OH)\cdot 9H_2O$	4.9–5.7	Ca

mechanism, the impure particles are entangled in the growing precipitate and, therefore, effectively eliminated (Garcia-Segura et al., 2017; Matilainen et al., 2010). The predominance of each mechanism depends on the nature of the pollutant, the type of coagulant and its dosage. However, other effects such as residual water matrix and pH can also significantly influence the performance of the EC (Hakizimana et al., 2017).

The analysis on the composition of wastewater from the gelatin production indicated the presence of phosphate, calcium and silicates, product of the demineralization of bone and cartilage (Kruthika et al., 2013). Maximum removal efficiencies occur at an initial wastewater pH of 6–8 (Fig. 6). The possible explanation for this phenomenon by several authors (Garcia-Segura et al., 2017; Hakizimana et al., 2017; Cañizares et al., 2009) is due to the hydrolysis degree of Al^{3+} depends on pH.

In the acidic pH range, the main aluminum species are hydroxy aluminum cations, which can interact with pollutants to neutralize their charge. Near neutrality, the predominant species are aluminum hydroxide precipitates ($Al(OH)_3$, $Al(OH)^{2+}$, $Al_2(OH)^{4+}$ and $Al_{17}(OH)^{7}_{32}$) which can remove pollutants by their growing precipitate enmeshment. Finally, alkaline pH leads to hydroxy aluminum anions ($Al(OH)^{4-}$) which are not able to interact with pollutants due to their negative charge. However, if this were true, as the EC process goes on, this phenomenon should be reversed since the species $Al(OH)^{4-}$ at pH 6 to 8 prevails when the concentration of Al^{3+} is low, and as seen in Fig. 1, the amount of Al^{3+} increases with electrolysis time. Likewise, in Fig. 6 it can be observed that the effectiveness of the electrochemical process with respect to the chemical treatment is superior in the whole pH range studied, except for the case of pH 10 where the efficiencies of COD removal and turbidity of both treatments appear to be similar.

According to Mohau Moshoeshoe et al., 2017 there is a growing demand in the use of zeolites for the elimination of pollutants in wastewater. It is known that all zeolites are composed of an elementary structure of an aluminosilicate framework comprising a tetrahedral arrangement of silicon cations (Si^{4+}) and aluminum cations (Al^{3+}) that are surrounded by four oxygen anions (O^{2-}). Some Si^{4+} ions are replaced by Al^{3+} ions, which results in a negative net charge in the framework of the tectosilicate. This charge arises from the difference in the formal valence between the tetrahedra $(AlO_4)^{5-}$ and $(SiO4)^{4-}$, derived from $Si(OH)_4$ and $Al(OH)_4^-$. In our case, $Si(OH)_4$ is present in the gelatin wastewater produced by the company, while $Al(OH)_4^-$ is generated in the electrocoagulation process when the aluminum concentration is low (Garcia-Segura et al., 2017).

Initially, the flocculation mechanism will be the generation of zeolite according to the reaction shown in Fig. 9, where the $Si(OH)_4$ concentration controls the reaction. When the amount of $Si(OH)_4$ present in the wastewater is depleted, flocculation due to the formation of $Al(OH)_3$ will be dominant. On the other hand, the presence of rhombic crystals observed in the SEM together with the Si/Al ranges determined by EDS, indicate in-situ formation of hydrated zeolite, the main factor responsible for floc formation.

Mixing sludge with natural zeolites for treatment purposes has been reported (Moshoeshoe et al., 2017) to lead to production of clear water with improved quality parameters such as color (by 92%), suspended particles (by 94%), chemical oxygen demand (by 95%), dissolved oxygen (by 95%), P_2O_5 (by 96%), NH_4 (by 99%), SO_4 (by 97%), NO_3 (by 92%), NO_2 (by 82%), total Cr (by 90%), Mn (by 94%) and Ni contents (by 93%).

The formation of hydrated zeolite in the electrocoagulation process of wastewater is responsible for the increase in the efficiency of the organic matter removal, compared with that of chemical coagulation, where the

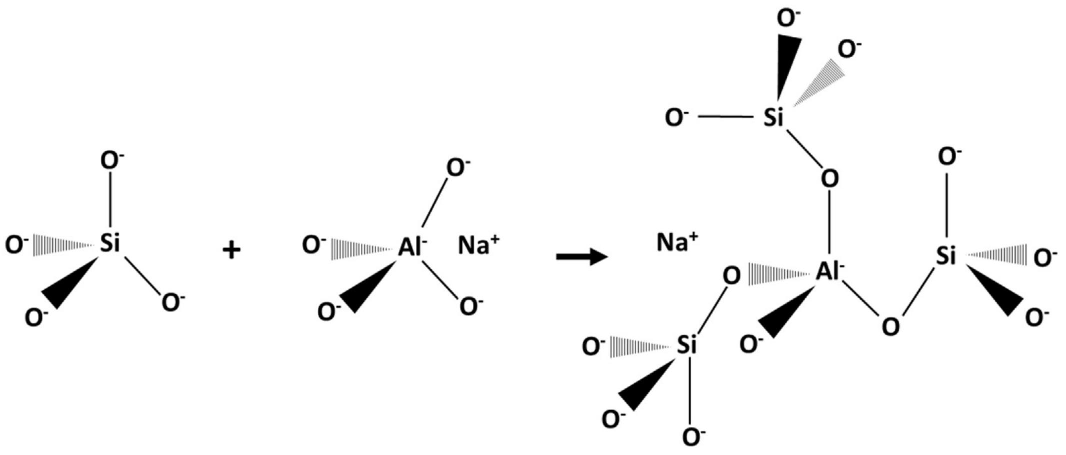

Fig. 9. Hydrated zeolite formed by tetrahedra of $Si(OH)_4$ atoms and by tetrahedra of $Al(OH)_4^-$ atoms.

formation of zeolites has not been observed. The zeolite is able to remove inorganic, organic, and organometallic compounds, as well as gas species, metals and radionuclides from their aqueous solutions. This can be attributed to absorption (mainly ion exchange), absorption and surface precipitation processes (Filippidis, 2010).

The analysis of the effluent supernatant obtained from the different treatment methods (Table 3) showed that silicates concentration is reduced by 76.1% in the EC treatment and only 24.6% using CC.

It is also important to note that the formation of zeolites is favored in acidic or neutral conditions (Moshoeshoe et al., 2017). The fact that removal efficiencies of treatments by EC and CC are similar at high pH (Fig. 6) would coincide with the fact that in this condition (pH 10) zeolites did not form. Therefore, the formation of zeolites is responsible for the increase in the removal efficiencies of the electrochemical treatment compared with the chemical treatment.

5. Conclusions

The results show that EC has greater COD removal efficiency compared to CC at the same aluminum (Al^{+3}) dose. The COD removal efficiency was 73.6% for EC and 55.6% for CC.

The EC flocculation mechanism takes place in two stages. In the first stage, the process is governed by zeolite generation, where the concentration of $Si(OH)_4$ present in the wastewater controls the reaction. When the amount of $Si(OH)_4$ is depleted, flocculation process is dominated by the formation of $Al(OH)_3$; whereas in CC the flocculation is generated by $Al(OH)_3$.

The analysis of the precipitate formed during the EC process indicated the presence of rhombic crystals with a Si/Al concentration ratio that confirms in situ formation of hydrated zeolites. The EC showed a TSS removal efficiency of 86%. The pH solutions for both, EC and CC, was between 6 and 8, where the maximum efficiency in the reduction of SS, turbidity and COD was observed.

The formation of zeolites in the EC process has not yet been reported in this type of wastewater and this is the main factor responsible for the higher efficiency of the electrochemical treatment compared to chemical coagulation.

Declarations

Author contribution statement

Gustavo L. Bianchi: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Carlos Seijas, Tatiana Arturi: Performed the experiments; Contributed reagents, materials, analysis tools or data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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