

### Treatment of nixtamalization wastewater (nejayote) using electrocoagulation and combined chemical coagulation/electrocoagulation processes

Teresa Zayas<sup>a,b,\*</sup>, Alejandra de Gante<sup>b</sup>, María Guadalupe Tenorio Arvide<sup>c</sup>, Miriam Vega Hernández<sup>d</sup>, Guillermo Soriano-Moro<sup>a</sup>, Leonardo Salgado<sup>e</sup>

<sup>a</sup>Centro de Química, Benemérita Universidad Autónoma de Puebla - ICUAP, C.P. 72570, Puebla, México, email: teresa.zayas@correo.buap.mx (T. Zayas)

<sup>b</sup>Posgrado en Ciencias Ambientales, Benemérita Universidad Autónoma de Puebla, C.P. 72570, Puebla, México <sup>c</sup>Depto de Investigación en Ciencias Agrícolas (DICA) – ICUAP, Benemérita Universidad Autónoma de Puebla, C.P. 72570, Puebla, México

<sup>d</sup>Facultad de Ingeniería Química, Benemérita Universidad Autónoma de Puebla, C.P. 72570, Puebla, México <sup>e</sup>Departamento de Química, Universidad Autónoma Metropolitana Iztapalapa, Av. Ferrocarril San Rafael Atlixco 186, Col. Leyes de Reforma, Alcaldía Iztapalapa, C.P. 09310, CDMX, México

Received 13 June 2022; Accepted 4 November 2022

#### ABSTRACT

Nejayote is a wastewater byproduct of traditional processes used to make corn tortilla flour, and needs to be treated to protect the environment. In this work, nejayote was treated by subjecting it to coagulation/flocculation and electrocoagulation processes. These two processes were evaluated independently and in combination. In the coagulation/flocculation process, the dose of coagulant/ flocculant and the influence of pH were determined. The electrocoagulation process was carried out using an Al/Fe (anode/cathode) system, and the effectiveness of the electrocoagulation as a function of pH and electrolysis time was studied. The control variables were the cell potential difference and NaCl concentration. The nejayote treatments was analyzed by measuring the resulting color, turbidity, and chemical oxygen demand (COD), and carrying out a UV-Vis analysis. The results showed that exclusive application of the electrocoagulation process to the nejayote was the most effective, having nearly completely eliminated color (99.4%), turbidity (98.08%) and COD (84.0%) after 150 min of electrolysis. The coagulation/flocculation process using the Sudflock P-63/Sumex Biofloc A-01 system was the least effective in reducing color (86.7%), turbidity (82.7%) and COD (34.2%), while the combined process (coagulation/flocculation-electrocoagulation), at a pH of 9.0 and 195 min of electrolysis, managed to remove 98.5% of the color, 97.7% of the turbidity and 78.0% of the COD.

Keywords: Wastewater from nixtamalization (nejayote), Chemical coagulation/flocculation, Electrocoagulation

#### 1. Introduction

Nixtamalization is a traditional process in Mexico and Central America whereby corn is treated with calcium hydroxide, cooked, then dried and ground to produce the flour used to make tortillas; this process is known as nixtamalization and the residual effluent, that is, wastewater, from this operation is called nejayote. The fresh nejayote is light yellow and contains lime, husk residues, endosperm corn, and a large amount of organic matter; it also shows

<sup>\*</sup> Corresponding author.

<sup>1944-3994/1944-3986</sup>  $\odot$  2022 Desalination Publications. All rights reserved.

an alkaline pH (10-12) and high chemical oxygen demand (COD > 24,000 mg/L) and biological oxygen demand (BOD ranging from 7,000 to 10,000 mg/L) [1,2]. Large amounts of nejayote are produced in Mexico as a consequence of the large production of corn tortilla, which is the basis of the population's diet; specifically, 14.4 million m<sup>3</sup>/y of nejayote is produced by the corn processing industry in Mexico [3–5]. Nejayote is considered a pollutant because of its high pH and high organic matter load. It is commonly dumped into the sewer system, bodies of water, or into the soils, without performing legally required treatments. Studies related to the treatment of nejayote have emphasized the importance of such treatment; they have explored the possible uses of derivatives of nejayote as well as the decreases in nejayote contamination afforded by different treatment methods, including biological, physical, chemical and/or physicochemical methods [6-11]. Treating nejayote using aerobic or anaerobic bioreactors is able to reduce its chemical oxygen demand (COD) [4,12–14]. In general, these systems remove between 40% and 90% of the COD of an effluent [11-13]. A physical-mechanical method to filter nejayote and hence reduce its COD was reported by Valderrama-Bravo et al. [2–15]. The authors evaluated a constant-pressure filtration cell under optimal filtration conditions using different filtration media. Filtration, as a physical mechanical method, allows for separating insoluble solids from nejayote and is considered to be an alternative to wastewater reuse or the use of value-added material. Castro-Muñoz et al. [10] used a coupled membrane system to analyze nejayote fractionation under three separation stages, with which it was possible to reduce total soluble solids (by 100%), turbidity (by 99.5%), total organic carbon (by 87.2%) and concentrate the polyphenols (by 79.94%) and keep 92.5% of the carbohydrates. Applying the coagulation-flocculation process to nejayote using chitosan as a non-hazardous substance was reported by Suárez et al. [16]. Their results showed that chitosan can be used as an adsorbent at pH 5.5 to obtain 80% efficiency in turbidity reduction. An enzymatic oxidative treatment of nejayote with laccase and in the presence of chitosan under optimal conditions (pH 6, 35°C, 24 h, and 0.3025 nmol laccase) resulted in a 70% reduction of phenolics and 78% reduction of COD [17]. The authors suggested that the process involving a single enzymatic step could be adequate to decrease the effluent COD and to generate polymers with potential applications in the food and pharmaceutical industries. The electrocoagulation process for removal of color in biodigester effluent of maize (corn) based starch industry wastewater (BDE-MSIWW) was investigated in an electrolytic batch reactor using aluminum as a sacrificial electrode [18]. A significant electrocoagulation-mediated reduction in the color of the effluent occurred at pH values < 7 and the extent of color reduction also increased with current density. A patent for treating nejayote by using electrocoagulation was presented by González Martínez et al. [19], with the patent claiming a 98.7% reduction in the COD resulting from the electrocoagulation treatment. The authors considered that electrocoagulation is an efficient process to treat nejayote water and avoid its direct deposition in the drain. In our current work, coagulation/flocculation and electrocoagulation treatments of nejayote were evaluated independently and in combination in order to test their abilities to reduce color, turbidity and COD of residual water of the nixtamalization process.

#### 2. Experimental

## 2.1. Characterization of nixtamalization process wastewater (nejayote)

The nejayote used in the current work was collected from a nixtamal mill in Puebla City, Mexico. The wastewater sampling protocol was followed as recommended by the Official Mexican Standard (NMX-AA-003-1980). The nejayote was characterized, before and after each treatment, for pH, turbidity, color, and chemical oxygen demand (COD) as well as by performing UV-Vis absorption spectroscopy. The raw nejayote was filtered using filter paper, Brand Ahlstrom No. 5 and refrigerated at 4°C. All coagulation/flocculation and/or electrocoagulation experiments were carried out with filtered nejayote. To facilitate the notation referring to nejayote, we use the following abbreviations: raw nejayote (RN), filtered nejayote (FN), nejayote treated using coagulation/flocculation (CFN), nejayote treated using electrocoagulation (ECN) and nejayote treated using coagulation/ flocculation combined with electrocoagulation (CFN + ECN).

#### 2.2. Materials and methods

#### 2.2.1. Reagents

Sodium hydroxide and hydrochloric acid solutions were both prepared at 1% w/w using deionized water and, respectively, sodium hydroxide (Merck, AR) and concentrated hydrochloric acid (37% w/w, Merck, AR). These solutions were used to adjust the pH of the nejayote samples. Sudflock P-63 (5% w/w suspension; activated alkaline aluminosilicate or alkaline bentonite) and Sumex Biofloc A-01 (0.1% w/w suspension; polyacrylamide, cationic polymer) were used in the treatment of nejayote as coagulant and flocculant, respectively. These reagents were supplied by SUD CHEMIE DE MEXICO S.A. DE C.V. The specifications of the coagulant and flocculant are described in Table 1. Sodium chloride (J.T. Baker, AR) was used as a supporting electrolyte in the electrochemical cell used for electrocoagulation experiments.

#### 2.2.2. Coagulation/flocculation methodology

The coagulation/flocculation experiments were conducted in a jar test device with multiple agitators using 1 L of sample. The coagulation/flocculation process was analyzed based on the relation of coagulant (Sudflock P-63)/flocculant (Sumex Biofloc A-01) and pH of the sample. The effect of pH was tested on samples of nejayote with different coagulant/flocculant ratios. The pH values of the nejayote samples were adjusted by adding hydrochloric acid or sodium hydroxide solution. The nejayote samples were stirred at 120 rpm for 60 s in order to homogenize the medium and then at 40 rpm for 20 min to enhance the formation of flocs. The experiments were performed in triplicate to assess the reproducibility of the experimental results.

	Coagulant	Flocculant
Tradename	Sudflock <sup>®</sup> P-63*	Sumex Biofloc <sup>®</sup> A-01*
Chemical name	Activated alkali aluminosilicate (alkaline bentonite)	Polyacrylamide (cationic polymer)
Composition	Bentonite (95%) crystalline silica (<5%)	Polyelectrolyte (100%)
Density	2.2 g/cm <sup>3</sup>	0.82–0.84 g/cm <sup>3</sup>
рН	7–10	7–10

Table 1 Specifications of the coagulant and flocculant used to treat nejayote

\*Supplier: SUD CHEMIE DE MEXICO S.A. DE C.V.

#### 2.2.3. Electrocoagulation methodology

All of the experiments were carried out in an electrolytic cell with a capacity of 150 mL. The volume of each nejayote sample in the cell was 100 mL. NaCl (5.0 g/L nejayote) was used as supporting electrolyte with constant agitation. The electrocoagulation process was performed using an Al/ Fe anode/cathode system. The dimensions of each electrode were 3 cm  $\times$  15 cm with a contact area of 10.5 cm<sup>2</sup>. The two electrodes were placed vertically and 2.0 cm apart in the electrochemical cell. Both electrodes were connected to an external dc power supply. Electrocoagulation effectiveness was studied as a function of pH (3-9) with a controlled cell potential difference (9 V) and constant electrolysis time. Current and voltage were measured using a conventional multimeter. This methodology was applied to the CFN and FN samples, with electrolysis times of 195 and 150 min, respectively. The cell potential of 9 V and electrolysis times were selected based on experiments using the same electrochemical system with an applied potential of 6, 9 or 12 V; specifically, the combination of cell potential and electrolysis time that gave the maximum percentage reductions of color, turbidity and COD was selected for each nejayote sample (CFN or FN).

#### 2.2.4. Coupled treatment: coagulation/flocculation + electrocoagulation

The combined treatment involved first carrying out the coagulation/flocculation process and then the electrocoagulation process. The nejayote obtained from the coagulation/flocculation process under the most favorable experimental conditions to reduce color, turbidity and COD, was subjected to the electrocoagulation process following the methodology indicated in section 2.2.3.

#### 2.2.5. Analytical measurements

COD, color and turbidity data were obtained using a spectrophotometer (SQ118, Merck). COD was evaluated using COD vials (Merck, Germany) with different sensitivity ranges. The procedure corresponds to DIN ISO 15705 and is analogous to EPA 410.4, APHA 5220 D and ASTM D1252-06 B. The evaluation of COD assumes that chloride is the dominant source of inorganic interference and is masked by mercuric sulfate. Nejayote samples were subjected to a digestion process in a Thermoreactor Merck model TR 300 for 2 h at 148°C. pH was determined using a Conductronic PC 45 instrument. UV-Vis absorption spectra of treated and

untreated nejayote samples were obtained using a Perkin Elmer Lambda 20 spectrometer.

#### 3. Results and discussion

#### 3.1. Characteristic parameters of nejayote

The physicochemical parameters of raw nejayote (RN) and filtered nejayote (FN) are shown in Table 2. The raw nejayote effluent showed a highly alkaline character (pH 12.4) and high organic load (COD 24,580 mg/L). Application of the filtration process to raw nejayote (to produce filtered nejayote: FN) reduced the magnitude of some physicochemical parameters: COD was reduced by 8%, and turbidity by 55%. However the color and pH did not change substantially as a result of the filtration process.

#### 3.2. Coagulation/flocculation of nejayote

The coagulation/flocculation process applied to the filtered nejayote (FN) was carried out with the Sudflock P-63 coagulant (activated alkaline aluminosilicate or alkaline bentonite) and the Sumex Biofloc A-01 flocculant (polyacrylamide: cationic polymer) described above. The coagulation/flocculation process has been shown to be influenced by the pH of the solution, coagulant/flocculant ratio, order of the addition of coagulant and flocculant, and stirring conditions [20]. Preliminary tests of the application of coagulation/flocculation to filtered nejayote (FN) allowed for a determination of the appropriate coagulant/flocculant combination (Sudflock P-63/Sumex Biofloc A-01) and the pH conditions to best reduce COD, color and turbidity. In a first set of tests, it was found that treatment of nejayote at pH 5 with a combination of Sudflock P-63 coagulant at 0.05 mL/L sample and flocculant Sumex Biofloc A-01 at 0.02 mL/L sample led to a 78.5% reduction in color, 71.2% reduction in turbidity and 29.9% reduction in COD, as shown Fig. 1.

The variation of the percent reductions of color, turbidity and COD in nejayote FN samples as a function of pH under a constant coagulant/flocculant ratio (Fig. 1) suggests that varying the pH induces a reconfiguration of surface charges of the coagulant-flocculant system, with pH 5 giving the maximum percent reductions.

Based on this result, the coagulant/flocculant ratio was analyzed at pH 5; in these experiments the flocculant concentration (Sumex Biofloc A-01) was kept constant (0.02 mL/L sample) while various coagulant (Sudflock P-63)

46



Fig. 1. Percent reductions of color, turbidity and COD in FN nejayote samples as a function of pH with a constant coagulant/ flocculant ratio of 2.5.

concentrations in the range of 0.05 to 0.27 mL/L sample were tested. The color, turbidity and COD were observed to be reduced to greater extents when the coagulant concentration (Sudflock P-63) in the nejayote sample was increased, as shown in Fig. 2.

That is, when the concentration of Sudflock P-63 was 0.21 mL/L, the coagulation/flocculation process was most effective, yielding the greatest percent reductions in color, turbidity and COD, namely 86.7%, 82.7% and 34.2%, respectively, in relation to FN. For concentrations greater than 0.21 mL/L of coagulant (Sudflock P-63), slight decreases in the percent reductions of color, turbidity and COD were observed. Therefore, at pH 5, 0.02:0.21 mL/L was determined to be the ratio of coagulant (Sudflock P-63) to flocculant (Sumex Biofloc A-01) that yielded the greatest reduction of color, turbidity and COD from nejayote. The Sudflock P-63/ Sumex Biofloc A-01 system applied to nejayote as a coagulant/flocculant at pH 5 was shown according to the obtained results to have favorable properties for the removal of organic matter, color and turbidity, as can be seen in Table 2 when comparing the values of FN and CFN.

The coagulant used in our experiments, Sudflock P-63 (commonly known as bentonite), with the general formula  $Al_4Si_8O_{20}(OH)_4 \cdot nH_2O_1$  also known as hydrated aluminum silicates, mainly made up of montmorillonite that has a high affinity for organic species, particularly oils, fats, and natural dyes or pigments in certain chemical reactions promoted by its excessive charge [21]. Consequently, Sudflock P-63 (bentonite) has the ability to destabilize the charges of contaminating particles during the chemical coagulation process. The Sumex Biofloc A-01 flocculant consists of cationic polymers and has been used to help promote coagulation for inducing flocculation and sedimentation-with this function due to the action of several functional groups (generally,  $-NH_{2}^{+}=NH_{2}^{+}\equiv N^{+}$ ) that can adsorb pollutant or colloidal particles, specifically with one end of the polymer able to adsorb a colloidal particle and the other end able to adsorb other particles, hence forming large agglomerates [22]. Therefore, combining the coagulant (Sudflock P-63) with the Sumex Biofloc A-01 flocculant (cationic polyacrylamide) has been found to cause the formation of large aggregates with a spongy and



Fig. 2. Percent reductions of color, turbidity and COD in FN nejayote samples. The dose of the coagulant (Sudflock P-63) was varied while the concentration of flocculant (Sumex Biofloc A-01) was maintained at 0.02 mL/L; pH 5.

compact structure held together by van der Waals interactions and electrostatic forces [21]. The pH of the medium has a significant effect on this process: Bouras et al. [23] reported that, at low pH values, the surface of colloidal bentonite particles becomes positively charged as a result of the protonation of hydroxyl groups (Al-OH, Si-OH) and interacts with any permanent negative charge to form a bridge and promote the coagulation process; as the pH is increased, the hydroxyl groups on the surface of the colloidal bentonite particles undergo successive deprotonation and the positive charges on the surface revert to being negative charges-and this new charge configuration of the bentonite particles may also promote the coagulation process depending on the dominant charge in the contaminants. In our experiments, a pH of 5 was the most favorable pH in the coagulation/flocculation process applied to nejayote wastewater. Thus, use of the coagulant/flocculant system (Sudflock P-63/Sumex Biofloc A-01) at a pH of 5 and with a 0.02:0.21 mL/L ratio of coagulant to flocculant was found to promote the purification of nixtamalization-derived residual water (nejayote) as can be seen in Table 2 for CFN.

# 3.3. Nejayote subjected to electrocoagulation after being subjected to chemical coagulation

Some of the nejayote samples subjected to the coagulation/flocculation process (CFN) were then subjected to an electrocoagulation treatment in order to further reduce its color, turbidity and COD.

The electrocoagulation process applied to CFN was performed at various pH conditions in an electrolytic cell with an Al/Fe electrodes array (anode/cathode). The sample had a volume of 100 mL and included NaCl (5.0 g/L) as a support electrolyte. CFN nejayote samples in the cell were stirred continuously during the electrolysis. The cell potential difference was set to 9 V and the electrolysis time to 195 min. Fig. 3 shows the percent reductions in the color, turbidity and COD of the CFN nejayote then subjected to electrocoagulation under the different pH conditions. For all pH values, the CFN nejayote samples then subjected to electrocoagulation became nearly completely colorless and non-turbid, indicating a decrease in the concentration of the species responsible for the color. The COD was also reduced considerably—by 65% in the pH range of 3–7, and by 78% at pH 9.0.

The fundamental reactions in the electrocoagulation process using the Al/Fe anode/cathode system have been shown to include in situ generation of  $Al^{3+}$  ions at the anode [Eq. (1)] and the oxygen evolution reaction [Eq. (2)] when the anode potential is high enough, and the water reduction reaction at the cathode [Eq. (3)] [24–26].

Anode:

$$Al \to Al^{3+} + 3e^{-} \tag{1}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
 (2)

Cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{3}$$

Gao et al. [26] considered that the electrochemical reduction of  $O_2$  could also take place at the cathode [Eq. (4)].

$$O_2 + H_2O \rightarrow 4e^- + 4OH^- \tag{4}$$

The Al<sup>3+</sup> ions generated as a result of electrolytic dissolution of the anode [Eq. (1)] have been indicated to immediately undergo spontaneous hydrolysis reactions to produce monomeric and polymeric Al species such as Al(OH)<sup>2+</sup>, Al(OH)<sup>+</sup><sub>2</sub>, Al<sub>2</sub>(OH)<sup>4+</sup><sub>2</sub>, Al(OH)<sup>-</sup><sub>4</sub>, Al<sub>6</sub>(OH)<sup>3+</sup><sub>15</sub>, Al<sub>7</sub>(OH)<sup>4+</sup><sub>17</sub>, Al<sub>8</sub>(OH)<sup>4+</sup><sub>20</sub>, Al<sub>13</sub>O<sub>4</sub>(OH)<sup>7+</sup><sub>24</sub>, Al<sub>13</sub>(OH)<sup>5+</sup><sub>34</sub>, Al(OH)<sup>3</sup><sub>34</sub>, Al(OH)<sup>3</sup><sub>34</sub>, Al(OH)<sup>3</sup><sub>34</sub>, al(OH)<sup>3+</sup><sub>20</sub>, [27]. The mode of action of the Al species generated in the electrocoagulation process is generally explained in terms of two mechanisms: charge neutralization of negatively charged colloids by hydrolyzed cationic products and incorporation of impurities into the amorphous hydroxide precipitate (sweep flocculation) [24]. These processes were apparently mainly responsible for the reduction of color, turbidity and COD in the pH range of 3–7, as shown in Fig. 3.

On the other hand, the presence of NaCl used as a support electrolyte in aqueous medium also promotes other types of competitive reactions that occur in the electrode and that depend on electrolysis conditions such as electrode potential, electrolyte concentration and pH. The beneficial effect of chloride ions on the performance of the electrocoagulation process has been reported by several investigators [24-26,28]. This beneficial effect of chloride ions has been attributed to three modes of action of these ions: (a) their ability to increase the electrical conductivity of the treated water; (b) their ability to promote the breakdown of the insulating oxide film (Al<sub>2</sub>O<sub>2</sub>) through pitting corrosion [24] and (c) the oxidation of chloride ions that can lead to the formation of active chlorine species according to Eqs. (5)–(7), as occurs in the case of dimensionally stable anodes (DSAs) [29-31].

$$2\mathrm{Cl}^{-} \to \mathrm{Cl}_{2} + 2e^{-} \tag{5}$$



Fig. 3. Percent reductions of color, turbidity and COD in CFN nejayote samples then subjected to electrocoagulation, as a function of pH. Electrolysis conditions: CFN as the nejayote sample, NaCl (5.0 g/L) as the electrolyte, system of Al/Fe electrodes (anode/cathode), potential difference of 9 V, and electrolysis time of 195 min.

$$Cl_2 + H_2O \rightarrow HClO + HCl$$
 (6)

$$HClO \rightarrow H^{+} + ClO^{-} \tag{7}$$

Molecular chlorine (Cl<sub>2</sub>), hypochlorous acid (HClO), and hypochlorite ions (ClO<sup>-</sup>) are all strongly oxidizing chlorine species and are collectively referred to as active chlorine [29–31]. The active chlorine species in a solution depend fundamentally on the pH [32]. At pH < 7, HClO predominates, whereas hypochlorite ions predominate at pH > 7. These species are responsible for the mechanism of indirect oxidation of organic matter that occurs in the bulk solution [31–33]. Consequently, the pollutants are destroyed in the bulk solution by the oxidation reaction with the generated oxidant (active chlorine species). The active chlorine might, by oxidizing the pollutants, improve the efficiency of their removal, thus enhancing the performance of electrocoagulation [26].

Therefore, the electrocoagulation process may be accompanied by possible side reactions such as the formation of chlorine, formation of hypochlorous acid/ hypochlorite ions, oxygen formation and precipitation reactions [34,35]. Based on these considerations, the greater percent reduction of COD observed at pH 9 compared to other pH levels (Fig. 3) could be concluded to be due to the presence of chloride ions having promoted the formation of the hypochlorite ions under such a basic condition, with the hypochlorite ions then oxidizing the organic matter in the solution and hence accelerating the reduction of COD. The mechanism of oxidation of organic matter induced by the hypochlorite intermediate has been extensively studied and is recognized to be an indirect electrooxidation [29,31]. Additionally, the electrocoagulation process was shown in the current work to have the capacity to increase the extent of the reduction of color, turbidity and COD in nejayote (CFN), implying that the electrocoagulation process is capable of eliminating or transforming the species responsible for color and turbidity, as well as further reducing its COD.

#### 3.4. Nejayote treated exclusively by electrocoagulation

The electrocoagulation treatment applied to filtered nejayote (FN) was analyzed as a function of pH in the presence of NaCl (5.0 g/L), under a potential difference of 9 V and electrolysis time of 150 min. Specifically, as shown in Fig. 4, the percent reductions in the color, turbidity and COD were determined at various pH conditions for FN samples subjected to the electrocoagulation treatment. Here, the measurement of color and turbidity showed the same behavior, namely an approximately 95% reduction in each of these parameters throughout the pH range 3–9. On the other hand, the percent reduction of COD depended on pH, with the lowest percent reduction (67%) observed at pH 3, highest value (84.5%) at pH 5, and intermediate values (approximately 70%) at pH  $\geq$  7.

A comparison of the graphs of the results of the electrocoagulation processes applied to the CFN (Fig. 3) and FN (Fig. 4) effluents showed similar behaviors of color and turbidity reductions in both cases, with percent reductions on the order of 95%. This set of results indicated that the electrocoagulation process is capable of removing color and turbidity either from the nejayote effluent previously subjected to chemical coagulation treatment (CFN) or from filtered nejayote (FN). In contrast, the effect of pH on the COD reduction percentage differed for the effluents (Figs. 3 and 4), suggesting that the properties of the CFN effluent could be different from those of the FN effluent, with these differences manifested in the electrocoagulation process. And the electrocoagulation process applied directly to the FN yielded the greatest reduction in COD (84.5%) at pH 5. Under these operating conditions (pH 5; NaCl 5.0 g/L; electrolysis with a potential difference of 9.0 V for 150 min), the removal of organic matter could be favored with the contribution of the HClO that in general predominates in slightly acid conditions and promotes the oxidation of organic matter; therefore, it significantly decreased the reduction in COD from filtered nejayote (FN) in relation to nejayote previously subjected to the coagulation/flocculation process (CFN). The presence of NaCl may have affected chlorine formation, which in turn has been shown to contribute to the removal of organic load from solutions by participating in oxidation reactions [36].

The results obtained suggested that removal of pollutants carried out using electrocoagulation could be accompanied by an indirect electrooxidation process mediated by the presence of chloride ions [36]. Taking into account the above, we can assume that the reductions of COD resulting from the electrocoagulation process applied to CFN and FN proceeded with different mechanisms. For CFN, the better reduction of COD in alkaline conditions apparently proceeded through an indirect electrooxidation mechanism with the participation of hypochlorite ions; in contrast, for FN, the better reduction of COD in acidic conditions apparently proceeded through an electrocoagulation mechanism with the participation of HCIO.

Fig. 5 shows the UV-Vis spectra obtained of the FN, CFN, CFN + ECN, and ECN nejayote samples. The UV-Vis spectrum of the filtered nejayote showed two contributions to the absorption energy, one between 400 and 500 nm (visible region) and other between 200 and 400 nm (UV region)-with the UV absorption peaks in the spectrum so broad that it was difficult to identify the chromophore groups. Similar characteristics in UV-Vis spectra were reported by Wang et al. [37] in a study of organic pollutant characteristics of Lurgi coal gasification wastewater. The UV-Vis spectra of the nejayote samples subjected to the different applied treatments (FN, CFN, CFN + ECN, ECN) each showed three absorption bands: one between 200 and 250 nm and two between 250 and 350 nm, with all three bands associated with  $\pi$ - $\pi$  electronic transitions of the aromatic organic compounds. The intensities of the absorption bands were observed to be dependent on the type of treatment applied-with the most intense



Fig. 4. Percent reductions of color, turbidity and COD as a function of electrolysis time. Electrolysis conditions: filtered nejayote as the sample (FN), NaCl (5 g/L) as the electrolyte, system of Al/Fe electrodes (anode/cathode), potential difference of 9 V, electrolysis time of 150 min.



Fig. 5. UV-Vis spectra of nejayote samples subjected to different treatments: (a) FN, (b) CFN, (c) CFN + ECN, and (d) ECN.

Nejayote	рН	Color (m <sup>-1</sup> )	% Reduction of color	Turbidity (NFU)	% Reduction of turbidity	COD (mg/L)	% Reduction of COD	
RN	12.4	58.0	_	197.0	-	24,580	_	
FN	12.4	47.6	_	87	_	20,160	_	
CFN	5.0	6.3	86.7	15	82.7	13,260	34.2	
CFN + ECN	9.0	0.7	96.6	2	97.7	4,336	78.5	
ECN	5.0	0.3	99.3	1	98.8	3,164	84.3	

Table 2				
Color, turbidi	ty and COD of r	ejayote subject	ted to different t	reatment conditions

\*% Reduction is relative to FN.

bands observed for FN, followed by progressively weaker bands for CFN and then CFN + ECN, and the weakest bands for ECN. This set of results indicated that the electrocoagulation treatment applied exclusively to filtered nejayote at pH 5 was more effective than was the chemical coagulation treatment followed by electrocoagulation at pH 9.

Table 2 summarizes the effects of the different treatments applied to the residual water from the nixtamalization process (nejayote) on the reduction of color, turbidity and COD.

#### 4. Conclusions

The electrocoagulation process applied with a constant difference potential of 9 V and electrolysis time of 150 min directly to nejayote samples (NF) at a pH of 5 and including NaCl (5.0 g/L) showed better results than did the coagulation/flocculation (CFN) treatments or the combination of coagulation/flocculation treatment plus electrocoagulation (CFN + ECN); specifically, it reduced the color by 99.4%, turbidity by 98.8% and COD by 84.5%. That is, the effectiveness of the Sudflock P-63/Sumex Biofloc A-01 coagulant/flocculant system was lower than that of the electrocoagulation process, and the electrocoagulation applied directly to nejayote was more effective than was the electrocoagulation applied after the coagulation/flocculation process. This set of results suggested different electrocoagulation mechanisms for the two conditions and greater effectiveness of electrocoagulation when applied directly to nejayote. The presence of NaCl as an electrolyte support apparently promoted the indirect electrooxidation of organic matter through active chlorine species, thus favoring the synergy of the electrocoagulation process with the action of active chlorine species. This phenomenon occurred more effectively in the nejayote electrocoagulation process than in the electrocoagulation applied to nejayote previously subjected to Sudflock P-63/Sumex Biofloc A-01 coagulation/flocculation treatment, which apparently modified the composition of the medium and made the promotion of oxidation of organic matter with active chlorine species more difficult.

#### Acknowledgments

The authors thank CONACYT and VIEP-BUAP for financial support.

#### References

- K.A. Rosentrater, A review of corn masa processing residues: generation, properties, and potential utilization, Waste Manage., 26 (2006) 284–292.
- [2] C. Valderrama-Bravo, E. Gutiérrez-Cortez, M. Contreras-Padilla, I. Rojas-Molina, J.C. Mosquera, A. Rojas Molina, F. Beristain, M.E. Rodríguez-García, Constant pressure filtration of lime water (nejayote) used to cook kernels in maize processing, J. Food Eng., 110 (2012) 478–486.
- [3] G. Niño-Medina, E. Carvajal-Millán, J. Lizardi, A. Rascon-Chu, J.A. Marquez-Escalante, A. Gardea, A.L. Martínez-Lopez, V. Guerrero, Maize processing wastewater arabinoxylans: gelling capability and cross-linking content, Food Chem., 115 (2009) 1286–1290.
- [4] A. Salmeron-Alcocer, N. Rodriguez-Mendoza, V. Pineda-Santiago, E. Cristiani-Urbina, C. Juarez-Ramirez, N. Ruiz-Ordaz, J. Galindez-Mayer, Aerobic treatment of maize processing wastewater (nejayote) in a single stream multi-stage reactor, J. Environ. Eng. Sci., 2 (2003) 401–406.
  [5] B.A. Acosta-Estrada, S.O. Serna-Saldívar, J.A. Gutiérrez-
- [5] B.A. Acosta-Estrada, S.O. Serna-Saldívar, J.A. Gutiérrez-Uribe, Chemopreventive effects of feruloyl putrescines from wastewater (nejayote) of lime-cooked white maize (*Zea mays*), J. Cereal Sci., 64 (2015) 23–28.
- [6] E. Díaz-Montes, R. Castro-Muñoz, J. Yáñez-Fernández, An overview of nejayote, a nixtamalization byproduct, Ing. Agric. Biosis., 8 (2016) 41–60.
- [7] E.A. López-Maldonado, M.T. Oropeza-Guzman, J.L. Jurado-Baizaval, A. Ochoa-Terán, Coagulation–flocculation mechanisms in wastewater treatment plant through zeta potential measurements, J. Hazard. Mater., 279 (2014) 1–10.
- [8] E. España-Gamboa, J.A. Domínguez-Maldonado, R. Tapia-Tussel, J.S. Chale-Canul, L. Alzate-Gaviria, Corn industrial wastewater (nejayote): a promising substrate in Mexico for methane production in a coupled system (APCR-UASB), Environ. Sci. Pollut. Res., 25 (2018) 712–722.
- [9] M.S. Argun, M.E. Argun, Treatment and alternative usage possibilities of a special wastewater: nejayote, J. Food Process Eng., 41 (2018) e12609 1–7, doi: 10.1111/jfpe.12609.
- [10] R. Castro-Muñoz, C. Orozco-Álvarez, J. Yáñez-Fernández, Recovery of bioactive compounds from food processing wastewaters by ultra and nanofiltration: a review, Adv. Bioresour., 6 (2015) 152–158.
- [11] R. Castro-Muñoz, V. Fíla, E. Durán-Páramo, A review of the primary by-product (nejayote) of the nixtamalization during maize processing: potential reuses, Waste Biomass Valorization, 10 (2019) 13–22.
- [12] E. Civit, C. Duran de Bazúa, G. Engelmann, S. González, L. Hartmann, Anaerobic treatment of maize processing wastewater (nejayote) in a packed bed reactor cascade, Environ. Technol. Lett., 5 (1984) 89–96.
- [13] R. Pedroza-Islas, C. Durán de Bazúa, Aerobic treatment of maize-processing wastewater in a 50-liter rotating biological reactor, Biol. Wastes, 32 (1990) 17–27.
- [14] V.M. Luna-Pabello, M.A. Aladro-Lubel, C. Durán de Bazúa, Biomonitoring of wastewaters in treatment plants using ciliates, J. Ind. Microbiol. Biotechnol., 17 (1996) 62–68.

Table 2

- [15] C. Valderrama-Bravo, E. Gutiérrez-Cortez, M. Contreras-Padilla, A. Oaxaca-Luna, A. del Real, D.G. Espinosa-Arbelaez, M.E. Rodríguez-García, Physico-mechanic treatment of nixtamalization by-product (nejayote), CyTA J. Food, 11 (2013) 75–83.
- [16] K.A. Suárez, S.M. Ponce, J.T. López, J.M. Cornejo, M.T. Oropeza, E.A. López, Eco-friendly innovation for nejayote coagulation– flocculation process using chitosan: evaluation through zeta potential measurements, Chem. Eng. J., 284 (2016) 536–542.
- [17] J.L. García-Zamora, M. Sánchez-González, J.A. Lozano, J. Jáuregui, T. Zayas, V. Santacruz, F. Hernández, E. Torres, Enzymatic treatment of wastewater from the corn tortilla industry using chitosan as an adsorbent reduces the chemical oxygen demand and ferulic acid content, Process Biochem., 50 (2015) 125–133.
- [18] B. Mazumdar, P.K. Chaudhari, Electrochemical treatment of biodigester effluent of maize- based starch industry: COD and color removal, Desal. Water Treat., 54 (2015) 1872–1880.
- [19] I. González Martínez, M.A.G. Ramírez Romero, A. Torres Mendoza, M.R. Cruz Díaz, F.J. Almazán Ruiz, F. Vidal Caballero, D.E.P. Rivero Martínez, J.J. Ambríz García, Pat. MX2013008235A, 2015.
- [20] M.H. Zonoozi, M.R.A. Moghaddam, M. Arami, Removal of acid red 398 dye from aqueous solutions by coagulation/flocculation process, Environ. Eng. Manage. J., 7 (2008) 695–699.
- [21] M. Abdelaal, Using a Natural Coagulant for Treating Wastewater, 8th International Water Technology Conference, IWTC8, Alexandria, Egypt, 2004, pp. 781–791.
- [22] F.S. Zhou, J. Li, L. Zhou, Y. Liu, Preparation and mechanism of a new enhanced flocculant based on bentonite for drinking water, Adv. Mater. Sci. Eng., 2015 (2015) 579513, doi: 10.1155/2015/579513.
- [23] B. Bouras, T. Hocine, K.I. Benabadji, K. Benhabib, A. Mansri, Optimizing the coagulation/flocculation process for bentonite suspension with poly(acrylamide-co-(N-methyl-4-vinylpyridinium tosylate)), Turk. J. Chem., 42 (2018) 748–758.
- [24] G. Mouedhen, M. Feki, M. De Petris Wery, H.F. Ayedi, Behavior of aluminum electrodes in electrocoagulation process, J. Hazard. Mater., 150 (2008) 124–135.
- [25] J.L. Trompette, H. Vergnes, On the crucial influence of some supporting electrolytes during electrocoagulation in the presence of aluminum electrodes, J. Hazard. Mater., 163 (2009) 1282–1288.

- [26] S. Gao, M. Du, J. Tian, J. Yang, J. Yang, F. Ma, J. Nan, Effects of chloride ions on electro-coagulation-flotation process with aluminum electrodes for algae removal, J. Hazard. Mater., 182 (2010) 827–834.
- [27] A. Akyol, Treatment of paint manufacturing wastewater by electrocoagulation, Desalination, 285 (2012) 91–99.
- [28] M.G. Arroyo, V. Pérez-Herranz, M.T. Montañés, J. García-Antón, J.L. Guiñón, Effect of pH and chloride concentration on the removal of hexavalent chromium in a batch electrocoagulation reactor, J. Hazard. Mater., 169 (2009) 1127–1133.
- [29] M. Panizza, G. Cerisola, Direct and mediated anodic oxidation of organic pollutants, Chem. Rev., 109 (2009) 6541–6569.
- [30] E. Brillas, C.A. Martínez-Huitle, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods, Appl. Catal., B, 166–167 (2015) 603–643.
- [31] S. Garcia-Segura, J.D. Ocon, M. Nan Chong, Electrochemical oxidation remediation of real wastewater effluents a review, Process Saf. Environ. Prot., 113 (2018) 48–67.
  [32] Y. Feng, D.W. Smith, J.R. Bolton, Photolysis of aqueous free
- [32] Y. Feng, D.W. Smith, J.R. Bolton, Photolysis of aqueous free chlorine species (HOCl and OCl<sup>-</sup>) with 254 nm ultraviolet light, J. Environ. Eng. Sci., 6 (2007) 277–284.
- [33] F. Bonfatti, S. Ferro, F. Lavezzo, M. Malacarne, G. Lodi, A. De Battisti, Electrochemical incineration of glucose as a model organic substrate. II. Role of active chlorine mediation, J. Electrochem. Soc., 147 (2000) 592–596.
- [34] D.T. Moussa, M.H. El-Naas, M. Nasser, M.J. Al-Marri, A comprehensive review of electrocoagulation for water treatment: potentials and challenges, J. Environ. Manage., 186 (2017) 24–41.
- [35] Q.H. Nguyen, T. Watari, T. Yamaguchi, Y. Takimoto, K. Niihara, J.P. Wiff, T. Nakayama, COD removal from artificial wastewater by electrocoagulation using aluminum electrodes, Int. J. Electrochem. Sci., 15 (2020) 39–51.
- [36] S. Capasso, S. Salvestrini, V. Roviello, M. Trifuoggi, P. Iovino, Electrochemical removal of humic acids from water using aluminum anode: influence of chloride ion and current parameters, J. Chem., 2019 (2019) 5401475, doi: 10.1155/2019/5401475.
- [37] Ch. Wang, Q. Zhang, L. Jiang, Z. Hou, The organic pollutant characteristics of Lurgi coal gasification wastewater before and after ozonation, J. Chem., 2018 (2018) 1461673, doi: 10.1155/2018/1461673.