Chapter 11

Integral use of *Nejayote*: Characterization, New Strategies for Physicochemical Treatment and Recovery of Valuable By-Products

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Abstract

In this research, an innovative physicochemical strategy is presented to address the problem of *nejayote*, from two perspectives: the first focusing on sanitation and reuse of *nejayote* using waste from shrimp shells, thereby adding value to the recovered solids of *nejayote*. Zeta potential measurements are a proactive electrochemical tool to define the strategy to allow integral use of *nejayote* in the industry nixtamalization. The treated water can be discharged from the municipal sewer system using a process of coagulation-flocculation, with an optimal dose of 1250 mg/L chitosan at pH 5, achieving removal of up to 80% of total suspended solids and turbidity. Moreover, zeta potential measurements show that the anionic biopolyelectrolyte obtained from *nejayote* has potential to be applied in the area of water treatment as a green chelating agent.

Keywords: nejayote, nixtamalization, biopolyelectrolytes, zeta potential, coagulation-flocculation

1. Introduction

Nixtamalized products such as maize tortillas originated in Mexico, are the main sources of energy, protein, calcium and other important nutrients and are considered the national breads and consumed with other fillings such as beans, meats, eggs and vegetables [1–3].

The ancient, laborious or traditional process (nixtamalization) to obtain tortillas is a process widely used by indigenous people in Mexico (41%), the Southern United States, Central America, Asia and parts of Europe, that consumes significant amounts of water, energy and time [2]. Traditional maize is lime-cooked in clay pots over a fire, followed by steeping for 8–16 h (generally overnight), the supernatant called maize wastewater or commonly known as "*nejayote*", derived from the Nahuatl word meaning "lime broth ashes" is discarded and then the nixtamal is hand-washed. Nixtamal is ground into a fine masa with a stone grinder called metate and then hand-molded, patted or pressed into disks, which are baked on both sides on a hot griddle [4–10].

Nixtamalization causes a loss of about 5% by weight dry basis of corn; 3% is suspended and the remaining 2% is dissolved. The suspended matter can be separated easily and inexpensively by sedimentation and the dissolved substance should "precipitate" to separate solids which is also done by sedimentation [2, 11–16].

A typical maize nixtamalization facility, processing 50 kg of maize everyday, uses over 75 L of water per day and generates nearly the equivalent amount of alkaline wastewater on a daily basis [4]. The estimated monthly volume of *nejayote* generated in Mexico is about 1.2 m^3 [17].

Nejayote is considered an environmental pollutant because it is an alkaline wastewater, with high chemical and biological oxygen demand [2, 9]. Due to the presence of lime in the process, the pH of the wastewater is very high (12–14), with a high temperature between 40 and 70°C), containing suspended solids (corn husks and broken grains) and a very high portion of dissolved material from the alkaline hydrolysis of corn components [14]. The *nejayote* with these physicochemical characteristics is thrown, often without treatment, into drainage systems and even directly to the soil and groundwater. Thus, alternatives for sanitation of *nejayote* and utilization are needed [14]. Among the solutions that have been reported, they are from biological treatment processes [9], membrane filtration, nixtamalization methods that minimize water use and the use of *nejayote* as a supplement in animal feed [17].

In this research, an innovative physicochemical strategy is presented to address the problem of *nejayote* from two perspectives: the first focused on remediation of *nejayote* and the second is on water reuse using biopolyelectrolyte (BPE) from waste shrimp shells. With the use of effluents generated by 20 tons of corn nixtamalized equivalent to one ton of corn or sorghum protein is obtained [2, 16]. Another benefit, both economic and social, which could have *nejayote* recovery is that wastewater could be recycled, either in nixtamalization industry itself or for any other use. The second is based on the use of *nejayote* for obtaining anionic BPE (maize gum) for treating wastewater from electroplating industry. In both cases, zeta potential (ζ) measurements as electrochemical parameters were used to develop the process of sanitation and water reuse and for the extraction and application of anionic BPE in the separation of heavy metals.

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2. Experimental

It is shown in **Figure 1** that zeta potential measurements were used to interconnect the physicochemical characteristics of *nejayote* and chitosan flocculant capacity to achieve sanitation and water reuse in nixtamalization industry. In the first stage, plots of ζ vs pH of *nejayote*, chitosan and maize gum were constructed to determine the behavior of surface charge and isoelectric point (IEP). Then the strategic dosage of chitosan was done in the process of coagulation-flocculation of *nejayote*. The coagulation-flocculation window was constructed by measuring the water-quality parameters of environmental interest (turbidity and total suspended solids) and zeta potential. Moreover, zeta potential measurements were used to to exploring the interaction capacity of maize gum obtained from *nejayote* with metal ions, frequently contained in wastewater from the electroplating industry.

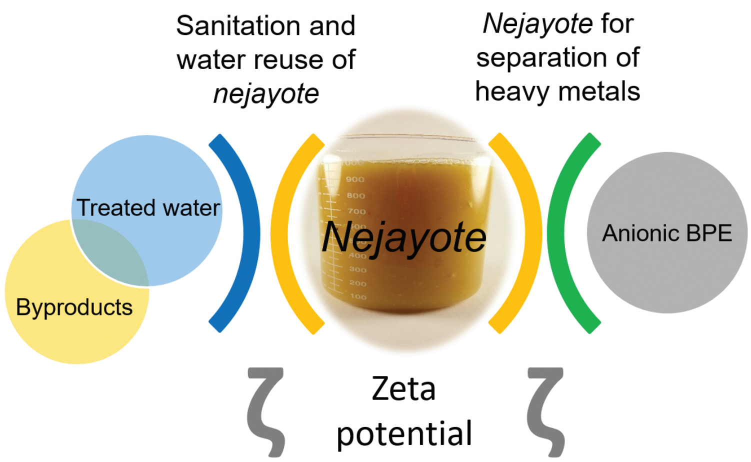

Figure 1. Using zeta potential measurements for *nejayote* sanitation and water reuse, and its use for obtaining a green flocculant for the separation of heavy metals.

2.1. Materials

Commercial testing water-quality reagents from HACH® were used. Milli-Q grade water was used in all the experiments. All other reagents were of analytical grade and were used without further purification.

2.1.1. Wastewater sampling in the nixtamalization industry

Nejayote was provided by a local tortilla-making industry. The wastewater sampling protocol was followed as recommended by Mexican sampling standard (NMX-AA-003-1980).

2.1.2. Chitosan extraction from waste shrimp shells

Chitosan is obtained from waste shrimp shells using the method proposed by the authors Goycoolea et al. [15].

2.1.3. Maize gum extraction of nejayote

Maize gum was obtained by fractional separation, using hexane, ethanol and hydrochloric acid, isopropanol, acetone, methanol formed by the steps of desalmidonado, deproteinization, delipidation, delignification which are proposed by the authors of [8, 18, 19].

2.2. Methods

2.2.1. Physicochemical characterization of nejayote

The main parameters of quality wastewater used in this research were performed following the Mexican standard procedures to determine the biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), total nitrogen (TN), the solids content, total organic carbon (TOC), total phosphorus (TP), and other parameter fields such as pH, electrical conductivity (EC) and temperature were carried out based on the Hach methods.

2.2.2. Profiles of $\zeta = f(pH)$ of nejayote, maize gum and chitosan

The charge density, isoelectric point and chitosan-dosing strategy for treating *nejayote* were determined in a $\zeta = f(\text{pH})$ plot. The zeta potential measurement was performed using the SZ-100 of Horiba Scientific equipment based on studies by López-Maldonado et al. [20, 21].

2.2.3. Nejayote treatability tests by coagulation-flocculation using chitosan

A sample of 20 mL of *nejayote* was taken in a vial and the pH was adjusted to 5. The chitosan dosage tests were performed in 20-mL-vials. Progressive additions of 0.1 g/L chitosan solution were done and after each one, the vials were shaken for 2 min at 250 rpm and 5 min at 50 rpm and allowed to settle for 5 more min. Finally the supernatant to a height of 2 cm from the vial was suctioned to determine the parameters of water quality in the supernatant.

2.2.4. Evaluation of the capacity of polyelectrolyte maize gum for decontaminating wastewater

The anionic BPE obtained from *nejayote* is characterized by Fourier Transform Infra-Red spectroscopy (FTIR), scanning electron microscopy (SEM) and measurements of zeta potential (ζ). FTIR spectra of maize gum were recorded using a Nicolet FT-IR spectrometer. The samples of maize gum were analyzed by SEM and X-ray microanalysis. The analysis was performed on SEM (ZEISS EVO-MA15), equipped with an EDS (energy dispersive spectroscopy) BRUKER detector microscope to observe the composition. The zeta potential measurement was performed using the SZ-100 of Horiba Scientific equipment based on studies by López-Maldonado et al. [20]. This was developed with the maize gum dispersion in a 0.1% solution, which took different levels of acidity and alkalinity in the range of 2–12 and injected into a cell with electrode graphite.

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3. Results and discussion

3.1. Physicochemical characterization of *nejayote*

In this investigation the *nejayote* generated by a tortilla factory in Mexico was taken as the object of study. A typical maize nixtamalization facility, processing 500 kg of maize every day, uses over 750 L of water per day and generates nearly the equivalent amount of alkaline wastewater on a daily basis. **Figure 2** shows the stages of the nixtamalization process used for the manufacture of nixtamal mass and the generation of *nejayote*.

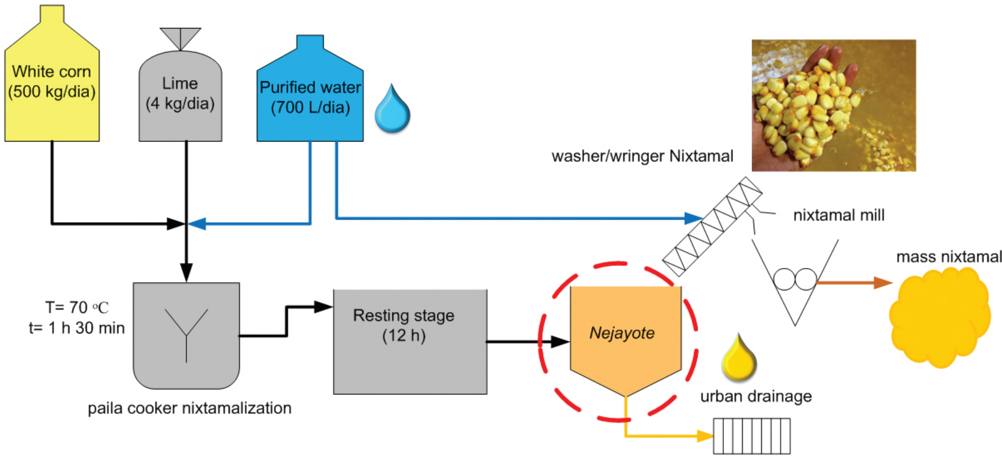

Figure 2. Diagram of the nixtamalization process and the point of generation *nejayote*.

As shown in **Table 1**, the physicochemical characteristics of *nejayote* concerning the content of organic matter determined by the parameters COD, TP, BOD_5 and TOC normed indicate that najeyote exceeds the maximum permissible limits of NOM-002-SEMARNAT-1996. The *nejayote* has a pH of 11.6 as already well known, is a wastewater alkaline by the use of lime in the nixtamalization.

Parameter	*Nejayote*	Maximum permissible limit
Suspended Solids, SS (mL/L)	800–900	1^b
Total Solids, TS (mg/L)	46,523.00	200^b
Total Dissolved Solids, TDS (mg/L)	46,339.70	NI
Total Suspended Solids, TSS (mg/L)	2000.00	NI
Turbidity (FAU)	690–1500	NI
Alkalinity (mg/L $CaCO_3$)	1020–1050	NI
Electric conductivity, EC (mS/cm)	4.29–6.42	NI
ζ (mV)	−10.5	NI
Particle size of the dissolved part (nm)	100–600	NI

Parameter	*Nejayote*	Maximum permissible limit
Temperature (°C)	30–39	40[b]
Color (Pt-Co)	5653–8580	NI
pH	11.61–12.1	5.5–10[a]
Chemical Oxygen Demand, COD (mg O_2/L)	9800–28,450	NI
Total Organic Carbon, TOC (mg C/L)	7337–9836	NI
Inorganic Carbon, IC (mg/L)	23–28	NI
Total Carbon, TC (mg C/L)	7360–9864	NI
Biochemical Oxygen Demand, BOD_5 (mg O_2/L)	2700	200[b]
Total Phosphorus, TP (mg P/L)	905–1321	30[b]
Total Nitrogen, TN (mg N/L)	303–418	60[b]
Biodegradability (BOD_5/COD)	0.27	NI

NI= Not included in the standard.
[a]NOM-001-SEMARNAT-1996.
[b]NOM-002-SEMARNAT-1996.

Table 1. Maize industry wastewater physicochemical composition.

For this research the measurement of other nonregulatory parameters was performed, and they are key to evaluate the performance of coagulation-flocculation process and determine the best operating conditions. $\zeta = -10$ mV (pH = 12) and particle size of the dissolved part of *nejayote* (100–600 nm), which indicates containing dispersed particles very stable. Considering the surface charge of the *nejayote* colloids and particle size to be separated by coagulation-flocculation, it requires the addition of a cationic BPE.

3.2. Profiles of $\zeta = f$(pH) of *nejayote* and chitosan

The zeta potential is a parameter by electrochemical nature that allows to study and predict the interactions occurring at the molecular level between the colloidal particles *nejayote* and the different ionic species of the medium, also it indicates the degree of stability of dispersion in an aqueous medium from the point electrically. The aim is to employ ζ measurements to know and understand the behavior of the BPE type chitosan in this kind of wastewater treatment (see **Figure 3**).

Surface charge of chitosan and *nejayote* colloids are pH-dependent and their behavior has great influence on coagulation-flocculation performance [22]. In addition, ζ measurements are required to characterize the colloidal system to understand repulsion and aggregation between colloidal particles.

In **Figure 4**, chitosan shows an amphoteric behavior, in the region of pH = 2–5.5 has a positive surface charge ($\zeta = 51.1$ mV) due to protonation of amine groups, at pH = 6–10 its surface charge remains neutral, this is due to the insolubilization phenomenon occuring at pH > IEP (pH = 5–6) of chitosan and increases their hydrophobicity.

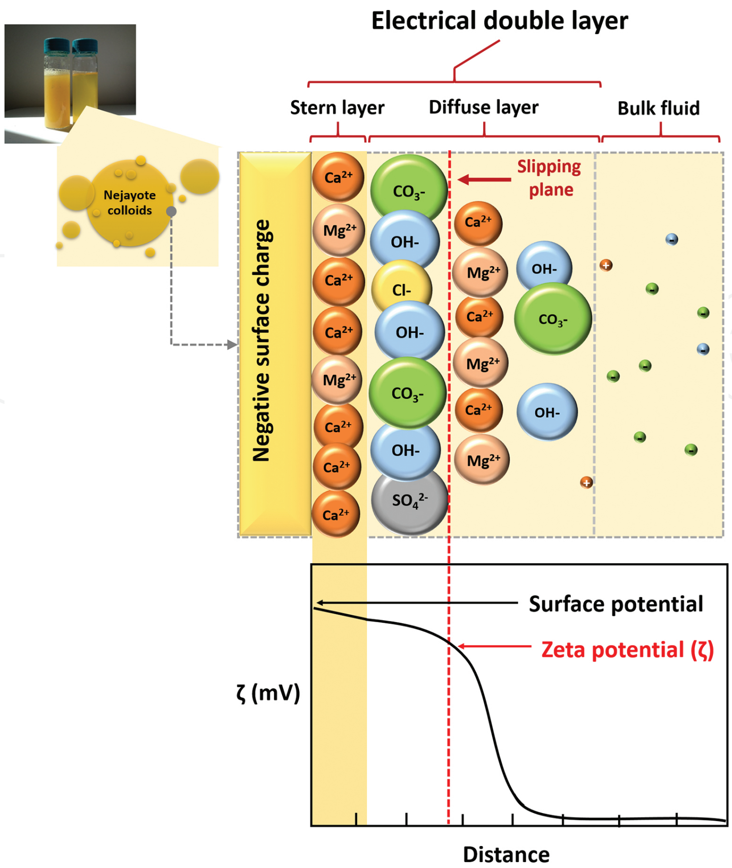

Figure 3. Model of the electrical double layer and zeta potential concept adopted for sanitation of *nejayote*.

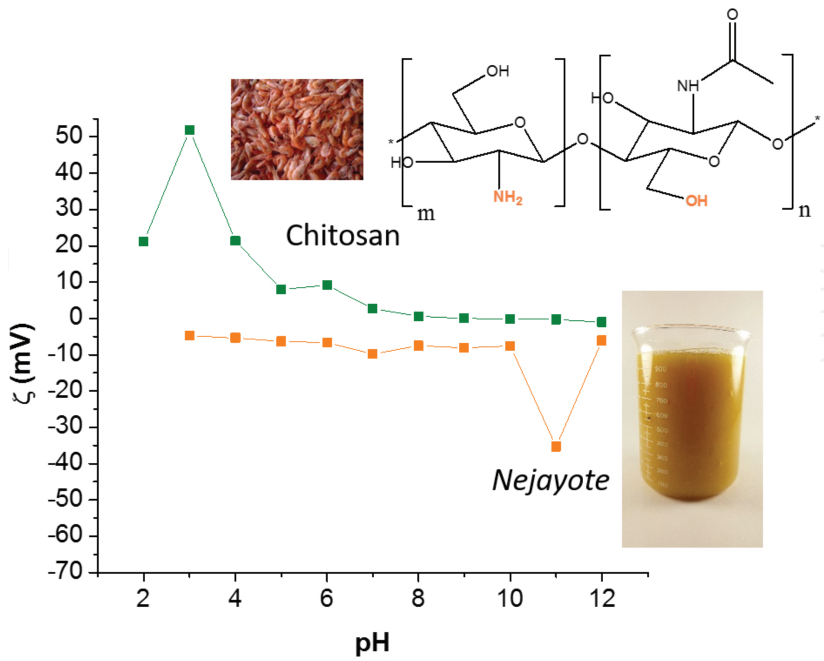

Figure 4. Electrokinetic properties of *nejayote* and biopolyelectrolyte type chitosan.

Moreover, the *nejayote* ($\zeta = 0$) has a negative surface charge throughout the pH range. From the electrical viewpoint, at pH = 5, the interaction between oppositely charged species chitosan-*nejayote* is ensured and therefore the strategic dosage cationic BPE was performed.

3.3. *Nejayote* treatability tests by coagulation-flocculation using chitosan

Dosing strategy for chitosan was determined by ζ of *nejayote* colloids and chitosan, and also by observing critical pH value of the IEP. In this study, charged chitosan purpose is to reduce the repulsion forces between particles by neutralizing the negatively charged molecules. In general, the electroneutrality zone for chitosan-*nejayote* system is below pH = 6 (see **Figure 4**), this has a practical application since higher charge density with less BPE concentration can be achieved.

Since the best wastewater clarification was at pH = 5.5 for chitosan, a turbidity-dosage profile was performed near the same pH to determine the optimal quantity of chitosan needed to flocculate *nejayote* colloids.

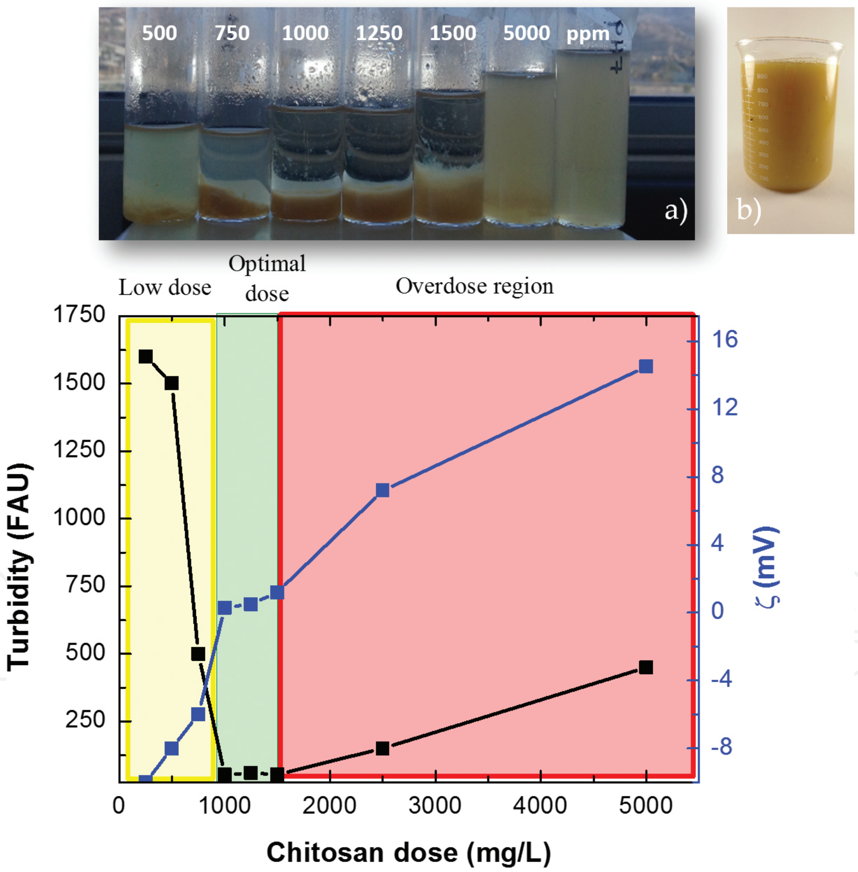

Figure 5. Turbidity and ζ of the supernatant in the coagulation-flocculation of nejayote at pH= 5 with chitosan: a) Nejayote and b) Nejayote visual appearance treated with chitosan.

The coagulation-flocculation window of *nejayote* using chitosan at pH = 5 was constructed based on the methodology reported by López Maldonado et al. [23].

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Figure 5 shows the behavior of the zeta potential and turbidity with respect to the concentration of chitosan. In the region of low doses (250 and 750 mg/L), a decrease in turbidity (1590–500 FAU) is achieved, and the variation of zeta potential ζ = −10 mV to more positive values (ζ = −5.4 mV) shows that the mechanism of destabilization of *nejayote* colloids occurs by charge neutralization [24]. At a dose of 1250 mg/L chitosan, point of zero charge was reached and the better quality of treated water (turbidity = 22 FAU, color = 315 Pt-Co, TSS = 12 mg/L) was obtained. At higher concentration (>1250 mg/L) the best dose, the restabilization processes occur due to excess chitosan adsorbed on the colloids of *nejayote*. In this region of overdose, the addition of chitosan had an adverse effect on the quality of wastewater, increasing turbidity and stability of the dispersed particles (ζ = 15 mV and turbidity = 450 FAU).

The coagulation-flocculation window was obtained from 1000 to 1500 mg/L chitosan with optimal dosage of 1250 mg/L chitosan, obtaining with this removal turbidity and suspended solids of about 80% (see **Figure 6**). At this dose, the surface charges of *nejayote* colloids were neutralized by chitosan molecules, resulting in a ζ value very close to zero.

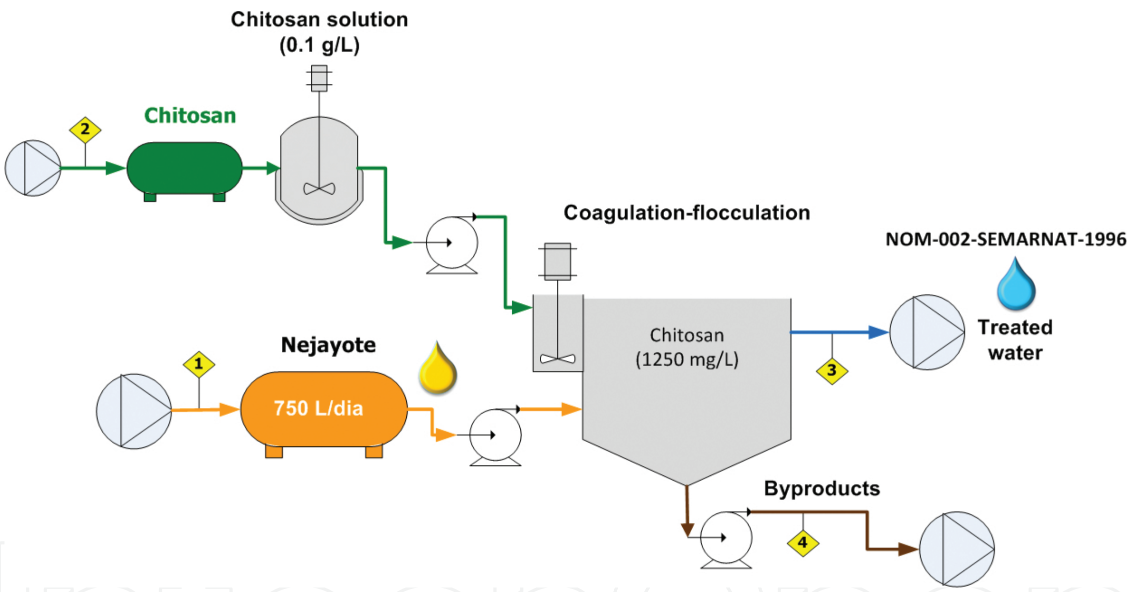


Figure 6. Diagram of the engineering for the sanitation process of *nejayote* using chitosan.

3.4. Evaluation of the polyelectrolyte capacity of maize gum for decontaminating wastewater

The behavior of zeta potential vs pH of anionic BPE obtained from *nejayote* is shown in **Figure 7**, which has a high negative charge density (−35 mV) in the pH range 6–12, having the isoelectric point close to pH = 2.

This negative surface charge is very interesting for the treatment of wastewater containing high concentration of heavy metal. In the FTIR spectrum (see **Figure 8**) shows that the BPE has the characteristic functional groups of a polysaccharide (3400 cm^{-1} corresponding to stretching of the OH groups and 2900 cm^{-1} corresponding to the CH_2 groups) which give the negative surface charge and that can interact with oppositely charged species, such as heavy metal ions [25].

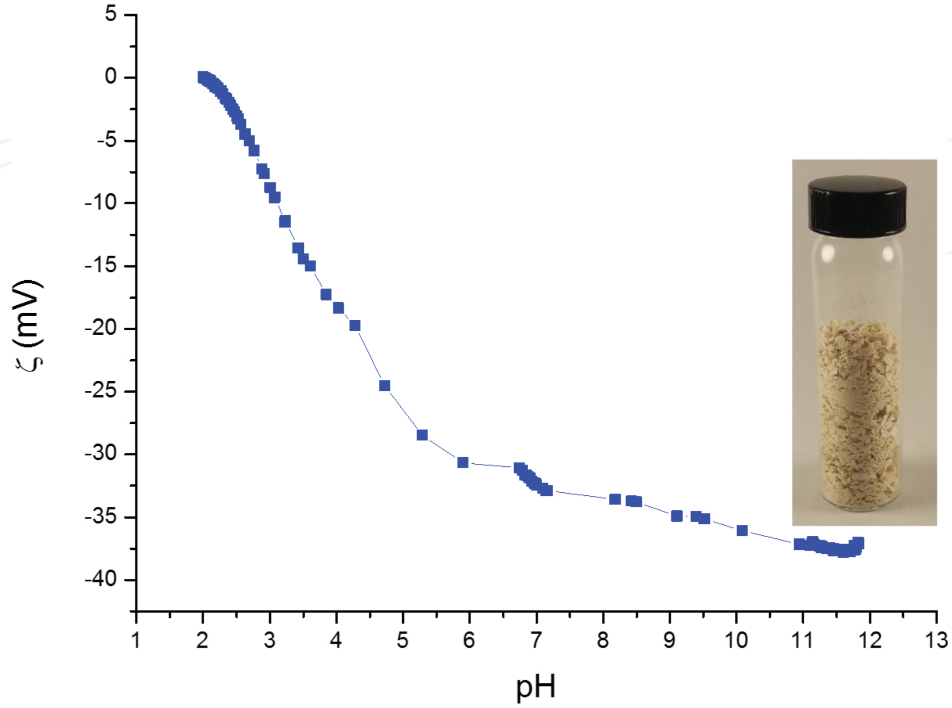


Figure 7. Zeta potential vs pH profiles of anionic BPE.

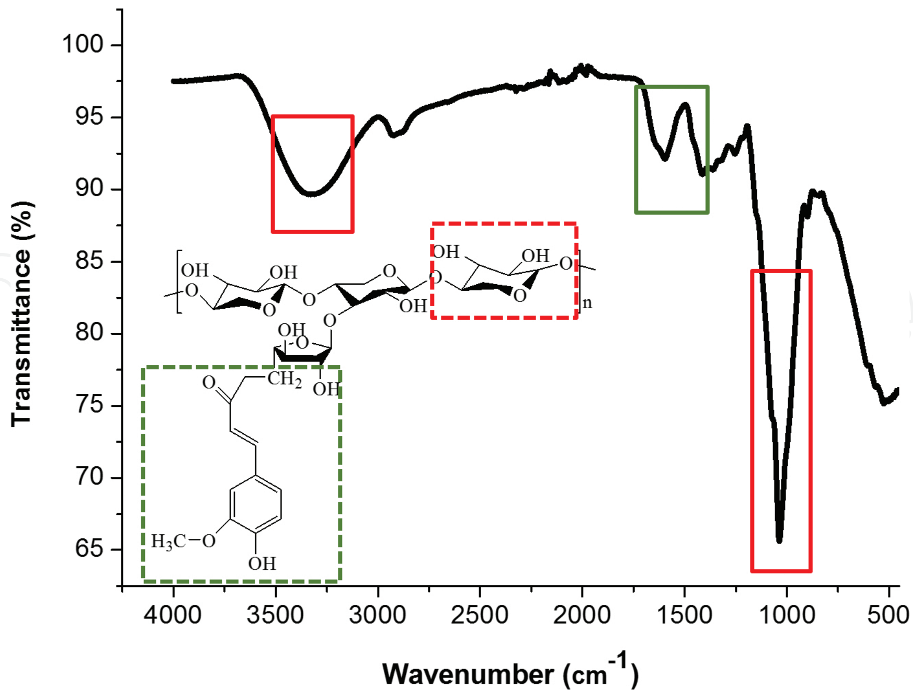
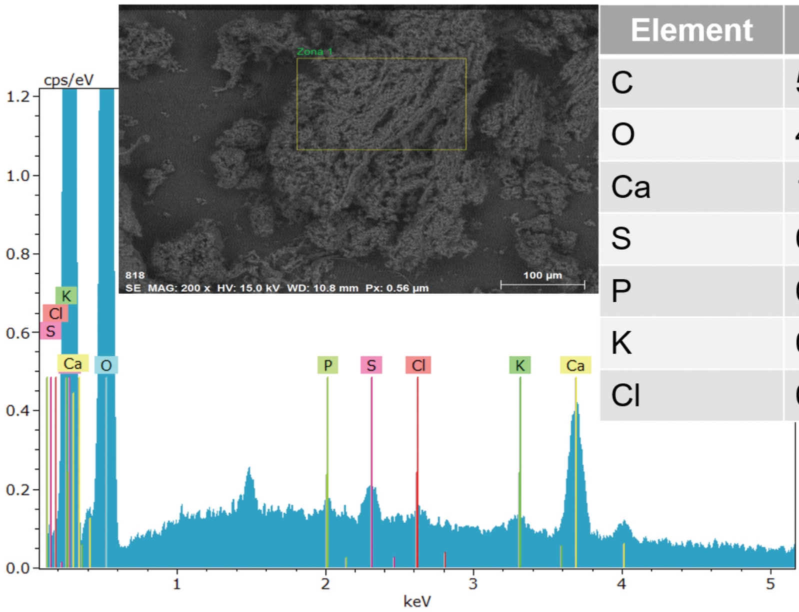


Figure 8. FT-IR spectrum of anionic BPE.

Figure 9 shows the morphology of anionic BPE and analysis of chemical composition, indicating that its content is primarily carbon, oxygen and calcium, because lime is used in the nixtamalization.



Element	% weight
C	50.92
O	46.82
Ca	1.69
S	0.23
P	0.07
K	0.19
Cl	0.09

Figure 9. SEM micrograph and EDS spectrum of the anionic BPE: Inset Table shows the composition analysis.

4. Conclusion

Zeta potential measurements are a proactive electrochemical tool to define the strategy of chitosan dosage that allows sanitation and water reuse industry nixtamalization. The use of chitosan allows the use and reuse of byproducts recovered from *nejayote* and it serves as a source of protein for animal feed. The treated water can be discharged into the municipal sewer system using an optimal dose of 1250 mg/L chitosan at pH = 5, achieving removal of up to 80% in the removal of total suspended solids and turbidity. This work evidenced the potential use of *nejayote* as a raw material for obtaining anionic biopolyelectrolyte in the treatment of wastewater with heavy metals of the electroplating industry.

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