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VALORIZATION OF CASHEW NUT PROCESSING BY-PRODUCT: DEVELOPMENT OF A CARDOL/STARCH BIOPOLYMER COMPOSITE WITH ELECTROCHEMICAL PROPERTIES AND TECHNOLOGICAL POTENTIAL

The problem of food agro-industry residues represents a growing concern in our society, therefore its use as a raw material to obtain biopolymers of technological interest is an attractive alternative. The objective of this work was to assess the viability of utilizing cardol, derived from cashew nut shell liquid, in the production of a biopolymer composite by combining it with cassava starch. The biopolymer composite was prepared by thermochemical method using different cardol concentrations and varying the synthesis pH. The results allowed us to demonstrate the formation of cardol/starch biopolymeric films. The infrared spectra showed possible interactions by hydrogen bonds between the cardol and the glucose units of the starch. The impedance behavior showed a similar conduction mechanism in all cases, allowing the establishment of a single equivalent circuit. The electrochemical parameters showed that the presence of cardol and the lower pH increased the values of the electrical resistance and the double layer capacitance in the biopolymers. In addition, the values of the CPE/Rre system, related to the electractivity, were not affected by the pH, but by the presence of cardol. The biodegradability tests showed a complete decomposition of the biopolymer composite films in three stages in a period of 17 to 19 days. It could be concluded that it is possible to use the cardol extracted from the cashew nut shell liquid to elaborate a biopolymer composite with electrochemical properties when combined with cassava starch. The electrical properties of the biopolymer can be modulated by varying the synthesis pH and the amount of cardol used. The composite cardol/starch biopolymer could be used as a biopolymeric solid electrolyte in the manufacture of batteries, capacitors, etc.

Keywords: cardol, cassava, biopolymer, electrochemistry, composite, waste, cashew, nut, shell, starch

Alvaro Angel Arrieta
Corresponding author
Doctor in Advanced Chemistry, Professor
Department of Biology and Chemistry*
E-mail: alvaro.arrieta@unisucre.edu.co
Jorge Alberto Ducuara
Biologist, Master's student in Environmental Sciences*
Enrique Miguel Combatt
Doctor en Ciencia de Suelos, Profesor
Department of Agricultural Engineering and Rural Development
Universidad de Cordoba
ave., 6, 77-305, Montería, Colombia, PC 230002
*Research Group in Development and Innovation
in Advanced Materials
University of Sucre
ave., 28, No. 5-267, Red Door neighborhood-Sincelejo,
Colombia, PC 700001

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1. Introduction

Carrying out research on the use of residues from the food agribusiness to produce new biopolymers is of the utmost importance. These investigations allow the development of innovative technologies that promote the efficient use of resources, the reduction of waste and the generation of sustainable materials. In addition, by turning waste into value-added products, the circular economy is fostered and the transition towards a greener and more environmentally friendly industry is promoted.

Materials made from biological resources with renewable, biodegradable and low-cost properties have attracted the attention of research centers and industry, allowing new alternatives to replace non-renewable products to be explored. In addition, the sources of raw material for the new bio-based materials are concentrated in agro-industrial products, waste or by-products, thus reducing post-harvest residues and generating added value in production [1–4]. Among the agro-industrial waste is the shell of the cashew nut, which is a by-product of obtaining the almond. Annually its world production of this fruit exceeds 4.1 million tons [5]. This residue is rich in an oil called cashew nut shell liquid (CNSL), it presents a reddish-brown color due to carbonization and chemical changes, CNSL constitutes about 20–25 % of the weight of the cashew [5, 6].

The main components of CNSL are long chain substituted phenolic compounds at the meta position. These compounds can be used as a basis for the production of polymeric substances widely used in industry. CNSL has an attractive cost-benefit ratio and can replace some phenolic compounds in many applications. The most recognized components of CNSL are anacardic acid, cardanol, and cardol. These substances have been used in several applications, among the most prominent uses are their applications as additives for resins, plastics, biodiesel, antioxidants, and antimicrobials [7–9]. It has been reported on the use of cardanol in a cardol-formaldehyde composite resin [10], anacardic acid in a biopolymer composite for active packaging [11], epoxidized cardanol as an antioxidant in biodiesel [12], among others.

Cardol is the less studied component of CNSL, chemically it presents substituted resorcinols with 15 carbon chains, in which the side chains mainly contain a mixture of one, two and three double bonds [13, 14]. This compound, being a resorcinol and having an unsaturated alkyl chain, could provide interesting physical properties to different polymers, especially since it is a low-cost renewable resource, making it attractive for research and exploration of new alternatives to replace additives and polluting polymers. Cardol has been used in combination with cardanol to generate anticorrosive coatings [15], prepare biobased epoxy resins, cardol polyesters [13], nanoparticles for drug delivery [16], etc.

On the other hand, starch is one of the most common carbohydrates in nature and is mainly found in the seeds and tubers of various plants as carbohydrate reserves. In addition to being widely used in the food industry, it also has applications in the non-food sector [17–19]. Starch is made up of two glucose macromolecules (amylopectin and amylose). Amylose is a linear biopolymer composed of approximately 250 to 2500 glucose units linked by α-1,4 bonds, amylopectin is a branched glucose biopolymer with α-1,4 bonds in the linear chain and the branching units occur every 20 to 30 glucose units with α-1,6 bonds. The proportions of amylose and amylopectin are approx. 20 % and 80 %, depending on the original plant species [20]. The most commonly used plant species for starch extraction are corn, cassava, potato, rice, yam and plantain. Unmodified and modified starch has been used to develop various biopolymers for food packaging, artificial muscles, pharmaceuticals, water treatment, among others [19, 21–24].

Although cardol has been little studied and research has been found regarding combinations with other polymers, there are no reports of its combination with starch-based biopolymers. Therefore, carrying out research on the use of cardol extracted from the cashew nut shell in the elaboration of a compound cardol/cassava starch biopolymer will allow exploring a new sustainable alternative in the bioplastics industry, taking advantage of agricultural waste and combining it with a renewable source such as cassava starch. In addition, this approach would promote the reduction of waste, the use of resources and the development of biodegradable materials with low environmental impact.

2. Literature review and problem statement

Several researches have been carried out on the use of CNSL derived compounds in the production of biomaterials. These studies have demonstrated the potential of this resource as a versatile and sustainable raw material for the production of bioplastics and other biodegradable materials.

The use of anacardic acid in obtaining biomaterials has been the subject of research in recent years. This natural compound, extracted from cashew nut shell liquid, has shown promising properties in the manufacture of biopolymers, coatings and composite materials: An inclusion complex of hydroxypropyl-β-cyclodextrin (HP-β-CD) with anacardic acid has been developed to improve its aqueous solubility and antimicrobial activity [25]. In this work, the formation of the anacardic acid Inclusion complex with HP-β-CD was carried out to allow anacardic acid solubility and improve the eradication of S. aureus. However, in this work there were no tests to determine the limits of acid concentration required for the eradication of S. aureus and the mechanism by which anacardic acid improves eradication.

Polyurea nanocapsules based on anacardic acid (A.A) were designed by interfacial polymerization using the inverse mini-emulsion technique with 2,4-toluene diisocyanate (TDI) [26]. The study presents an interesting approach to the controlled release of AA. However, more research is required to evaluate its therapeutic efficacy in vivo models and its viability as nanotransporters. In addition, it would be beneficial to perform more exhaustive tests in various bacterial systems to validate its antimicrobial potential.

Electroactive biopolymer composite was developed by combining anacardic acid and cassava starch [27]. The work provides relevant information on the influence of pH on the electrochemical and mechanical properties of cassava starch electrolyte films. However, it would be useful to include more details about the conditions of the experiments and the quantitative results for a better understanding of the effects of pH. Anacardic acid is the most abundant and most researched component of CNSL and the previously mentioned studies demonstrate the potential of anacardic acid as a versatile component in the field of biomaterials. However, it is necessary to determine its potentiality in conductive solid electrolytes and its potentiality in electroactive materials.

Cardanol is the second most abundant component in CNSL, after anacardic acid. This compound has also been used for the production of biopolymers, resins and composite materials: Through a poly-condensation process, a cardanol biopolymeric resin was synthesized from cashew shell nut liquid using coconut shell fiber as reinforcing material [28]. It would be beneficial to have more details about the characterization techniques used and perform mechanical tests for a more complete evaluation of biocomposites. In addition, more research is needed to better understand the effect of alkaline treatment on the properties of the compounds and determine the effect of the size of the coconut shell particles used.

Cardanol oil extracted from CNSL was used in the synthesis of biocomposite films prepared with polylactic acid (PLA)-polybutylene adipate-co-terephthalate (PBAT) by solution casting method [29]. The paper highlights the improved properties of plans composed of PLA/PBAT with the addition of cardanol oil and presents a wide range of characterization techniques and properties evaluated for the mixture of bio-base polymers. However, there is no detailed discussion on synthesis methods or an experiment design where the different mixtures and interactions of the components in the results and properties of the resulting material are studied.

The chemical compound present in the CNSL, which occupies the third position in abundance, is cardol. Although in recent years some research has been carried out aimed at the use of cardol in the production of biomaterials, it is important to mention that it is the least explored component of CNSL. Some of the works found in the literature on the use of cardol are: Diglycidyl ether de cardol (DGEC) was prepared by reacting cardol with epichlorohydrin in the presence of sodium hydroxide and cured with commercial amine hardeners to produce cardol epoxy compounds [13]. The results obtained on the thermal and mechanical properties are consistent and are supported by appropriate analysis techniques. However, a more detailed discussion on the potential applications of these materials and their comparison with other similar materials is lacking. In addition, the possible electrochemical activity of the materials due to the cardol presence, which is a material with antioxidant properties and electroactivity, is not explored. The work does not give a more detailed explanation about the curing mechanisms and the chemical interactions that occur during the polymerization process.

Biomaterials with episulfide groups (CCES) and epoxy groups (CCEO) were synthesized from cardol/cardanol and mixed with commercial epoxy resins bisphenol-A diglycidyl ether (DGEBA) to be used as an anticorrosion coating [15]. The results obtained show a significant improvement in the corrosion resistance properties of the CCES-DGEBA mixtures compared to the pure DGEBA and the CCEO-DGEBA mixtures. However, a more detailed discussion on the interaction mechanisms between the different components and how cardol and cardanol contribute to the anti-corrosion properties is lacking. In addition, the long-term stability and durability of the developed coatings and in conditions of salinity or corrosive environment were not studied.

Most cardol applications in the production of biomaterials are focused on the production of resins, so the research literature aimed at using cardol in biopolymers or biopolymer composites is very scarce, the only related work on its use in a cardol/starch biopolymer composite was recently reported [30]. The results obtained reveal interesting electroactive properties and reversible electrochemical processes. However, the information presented is mainly focused on the voltammetric characterization of biopolymers and does not explore the electrochemical parameters and impedance behavior, in such a way that it is possible, from values such as capacitance and resistance, to elucidate the applications and practical impact of these materials. Additional aspects could be explored, such as the biodegradability of the materials and their stability. Overall, it is an interesting study that could be expanded to address more applied and practical aspects of the biopolymers developed. Despite the potentiality shown in previous studies, cardol has not been explored for its potential to provide electroactivity in composite materials, its impedance behavior, and its electrochemical parameters. Therefore, this research constitutes a contribution to the application of cardol in the field of composite biopolymers and promotes the development of new research on this subject.

3. The aim and objectives of the study

The aim of this work is to evaluate the potentiality of cardol extracted from cashew nut shell liquid to be used in the elaboration of a biopolymer composite from its combination with cassava starch.

To achieve this aim, the following objectives are accomplished:

– to evaluate the electrochemical behavior of biopolymer composite films and the effect of the amount of cardol used and the synthesis pH;

– to evidence the possible interactions established between the starch molecules and cardol in the biopolymer composite;

– to evaluate the biodegradability of the biopolymer composite, the biodegradation time and the structural changes registered by FTIR.

4. Materials and methods

4. 1. Object and hypothesis of the study

The object of the study is cardol, derived from cashew nut shell liquid, in the production of a biopolymer composite elaborated with cassava starch.

It is hypothesized that the development of a biopolymer composed of cardol and starch from the by-product of cashew nut processing will result in a material with outstanding electrochemical properties and high potential for use in various technological applications. This study assumes that cardol can generate hydrogen bond-type interactions with cassava starch and generate a stable material. In addition, the antioxidant properties of cardol can contribute to the generation of electrochemical activity in the compound biopolymer.

4. 2. Materials

The reagents used in the procedures were of analytical grade. Sodium hydroxide (NaOH), hydrochloric acid (HCl), methanol (CH_3OH), ammonium hydroxide (NH_4OH), ethyl acetate ($C_4H_8O_2$), hexane (C_6H_{14}), anhydrous sodium sulfate (Na_2SO_4), glycerol ($C_3H_8O_3$), polyethylene glycol ($C_{2n}H_{4n+2}O_{n+1}$), and glutaraldehyde ($C_5H_8O_2$). Cardol and starch were extracted from natural CNSL and cassava tubers, respectively. All solutions were prepared with ultrapure water.

4. 3. Cardol and starch extraction

The natural CNSL was extracted from cashew shells of the *Anacardium occidentale* Yucao Ao3 variety. The shells were ground and passed through a press mill at room temperature. The cashew nut shells were supplied by the association of local producers Asopromarsab.

Cardol was synthesized from CNSL by solvent extraction following the method reported by [31]. The starch was extracted from commercial cassava tubers of *Manihot esculenta* (Crantz variety) by the wet method that consists of washing, peeling and liquefying the tubers. For 500 g of crushed tuber, 1 L of water was added and filtered through a muslin cloth, the filtrate was allowed to settle for 24 hours, the sediment was dried at 40 °C in an oven and macerated and sieved.

4. 4. Synthesis of cardol/starch biopolymer composeite films

3 g of starch were scattered by stirring in 100 ml of pH-adjusted water: three types of pH (3, 7, and 11) were used, which were adjusted with NaOH (0.1 M) or HCl (0.1M) as required. The mixture was heated at 70.0±5.0 °C until its complete dissolution and was allowed to cool to room temperature. Then, the plasticizers (3 g of

glycerol, 3 g of glutaraldehyde and 1.5 g of polyethylene glycol) and cardol (films are prepared with 2.0 g, 1.0 g and 0.0 g of cardol) were added at room temperature and with constant stirring. The solutions were heated at 70.0 ± 5.0 °C for 15 min. The solutions were poured into Teflon Petri boxes and heated for 48 h at 70.0 °C.

4. 5. Characterization of cardol/starch biopolymer composite films

Biopolymer composite films were characterized by FTIR-ATR spectroscopy performed with a Perkin-Elmer Spectrum-two spectrometer. The spectra were recorded with a resolution of 4 cm^{-1}, wavenumber range from 400 cm^{-1} to 4000 cm^{-1} and 100 scans were recorded.

For the measurement of the electrochemical properties, a Gamry 1010 E potentiostat/galvanostat with a dry cell formed by two sheets of stainless steel (1×1 cm) was used, the properties were characterized by electrochemical impedance spectroscopy (EIS) in a range of frequencies from 2.0 MHz to 10.0 mHz with 10 mV rms AC. The reference potential used in both techniques was the open circuit potential (OCP) with a value of 0.15 V. The biodegradability of the films was measured by soil burial test, the soil mixture was prepared using silty silt (23 %), organic matter/cow manure (23 %), and (23 %), and distilled water (23 %). The test samples were weighed before being buried 10 cm deep at 25 (±5) °C, previously packed in perforated bags. The monitoring consisted of digging up the samples every two days and recording the weight loss. The experiments were performed in triplicate and the average value was reported.

5. Results of the research on the development of a cardol/starch biopolymer composite

5. 1. Synthesis of cardol/starch biopolymer composite films

Fig. 1 shows an image with the biopolymer films cardol free and with cardol prepared at different pHs.

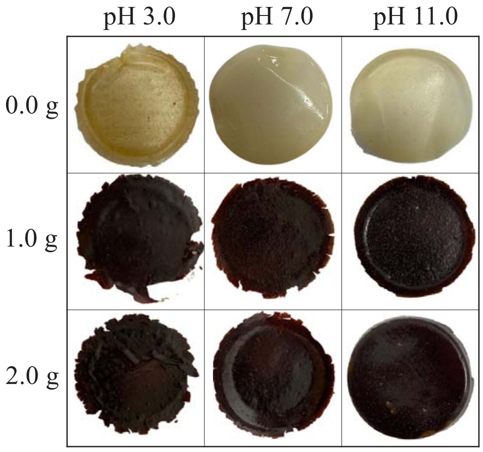


Fig. 1. Image of starch biopolymer and cardol/starch biopolymer composite films prepared at different pH values and different amounts of cardol

The starch biopolymer films (cardol free) presented a yellowish-white color that darkened as the pH was lower. The biopolymer composite films (with cardol) presented a dark brown color that was more intense in the films with a higher amount of cardol and a lower pH.

5. 2. Characterization of the cardol/starch biopolymer composite by FTIR spectroscopy

In Fig. 2, the infrared spectra of cardol, the starch biopolymer, and the cardol/starch biopolymer composite can be observed. The synthesized biopolymeric films were easily peeled from the Petri dishes due to their consistency and resistance to manual traction and presented an average thickness of 0.6 mm. However, there were slight differences regarding the mechanical stability of the films; the films elaborated at a higher pH and with a greater amount of cardol presented greater stability and resistance to manual traction.

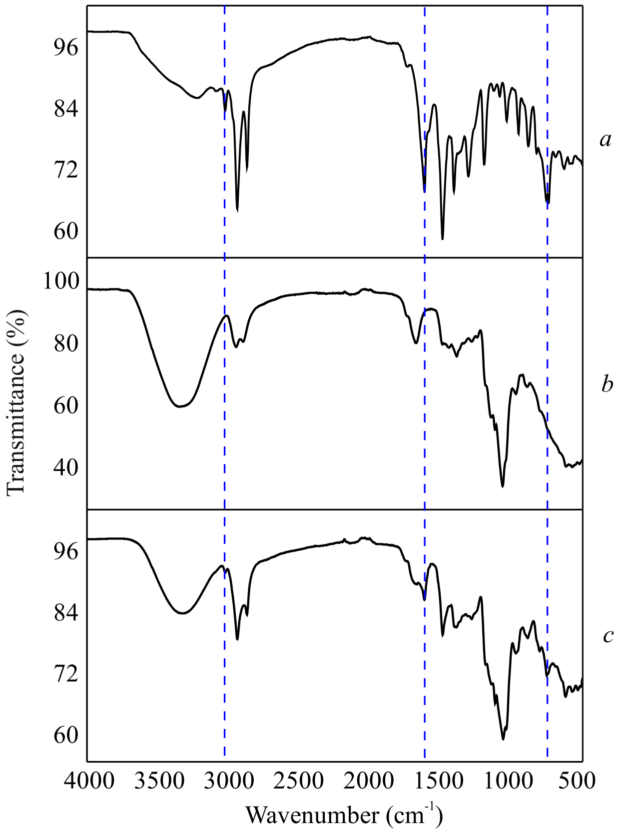


Fig. 2. Infrared spectra of: *a* – cardol; *b* – starch biopolymer film; *c* – cardol/starch biopolymer composite film

In the spectrum recorded with cardol, the characteristic peaks of this compound were observed (Fig. 2, *a*), showing a broad band at 3,415 cm^{-1} typical of OH bond stretching, a band at 3,010 and 750 cm^{-1} shows the presence of CH bond stretching attached to an aromatic group or double bond, and symmetric and asymmetric tension vibrations for a C-O bond at 1,218 cm^{-1} and 1,145 cm^{-1}. In the region from 1,100 to 650 cm^{-1}, several intense peaks were observed due to the presence of an aromatic ring and C-H vibrations out of plane. Table 1 shows the bands assigned to the FTIR vibrations of cardol, cassava starch biopolymer without cardol, and cardol/starch biopolymer composite.

The infrared spectrum of the starch biopolymer films (Fig. 2, *b*) showed the corresponding peaks consisting mainly of the vibration of the OH groups at 3,412 cm^{-1}, the stretch assigned to the CH at 2,911 and 2,878 cm^{-1}, the bands of the fingerprint region between 1,490 and 800 cm^{-1}, with the peaks attributed to C-O, C-OH, and C-O-C. The cardol/starch biopolymer composite films showed in their infrared spectrum the characteristic bands of starch and cardol bands (Fig. 2, *c*), also allowed to observe evidence of the establishment of possible interactions by hydrogen bond due to changes in the relationships of the intensities in the bands corresponding to OH.

Table 1

Assignment of FTIR vibrations of the spectra of cardol, cassava starch biopolymer without cardol (CSB), and cardol/starch biopolymer composite (C/SBC)

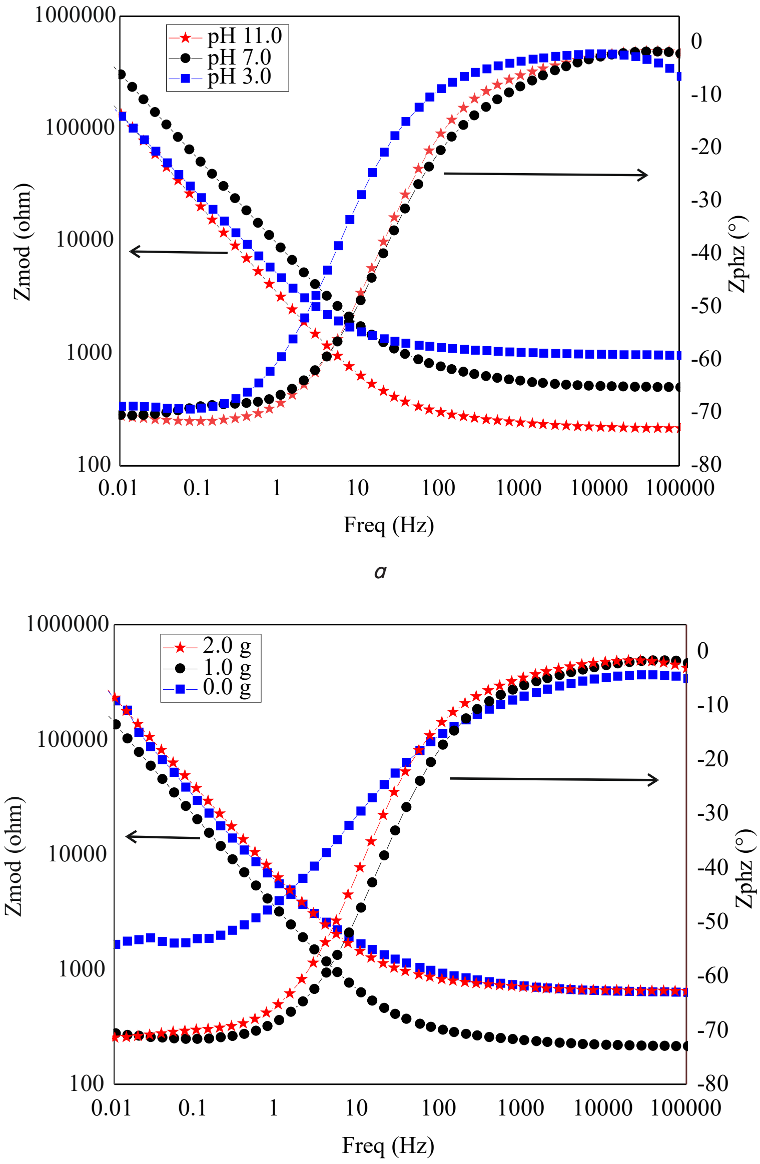
Assignments	Wavenumber (cm^{-1})		
	Cardol	CSB	C/SBC
O-H stretching	3,415	3,412	3,413
C-H stretching	3,010–2,958	2,991–2,878	2,985–2,893
O-H (water) bending	–	1,649	1,648
C-H bending	1,457	1,456	1,456
O-H bending	–	1,407	1,407
COH bending	1,359	1,350	1,350
CH_2OH related modes	–	1,247	1,247
COH deformation	1,218	1,201	1,203
COC antisymmetric bridge stretching	1,145	1,146	1,146
COH asymmetric stretching in ring plane	–	1,103	1,105
Ar C=CH in plane	1,048	–	1,050
C-OH bending	–	1,077	1,075
COH solved	–	1,018	1,019
COC ring vibration of carbohydrate	–	995	995
C-H bending modes	–	844	844
ArC=CH deformation	779–695	–	778–696
CH_2 rocking	750	757	757

5. 3. Characterization of the cardol/starch biopolymer composite by electrochemistry impedance spectroscopy

The electrochemical impedance spectroscopy of the films allowed us to evaluate their electrical conductivity. In Fig. 3, *Zmod* (impedance modulus) is plotted on a logarithmic scale on the *y*-axis (first ordinate) and *Zphz* (phase shift) on the second ordinate versus frequency on a logarithmic scale on the abscissa (*x*-axis), this type of graphs is known as Bode plots.

In the Bode plots of all samples, regardless of pH or cardol content, the impedance modulus at low frequencies was markedly higher than at high frequencies; with values close to 1 MHz at low frequencies and values close to 500 Hz at high frequencies.

A similar variation could be observed between the values of impedance phase shift (*Zphz*); the phase shift was close to 0° at high frequencies and between –50° and –80° at low frequencies. This tendency could be due to the fact that at low frequencies the films are less conductive and their behavior is more capacitive, resulting in a negative impedance phase shift typical of capacitors. While at high frequencies the impedance phase shift tends to 0° evidencing the flow of current through the films.



a

b

Fig. 3. Bode diagrams of the films elaborated: *a* – with 1.0 g of cardol at different pH values; *b* – elaborated at pH 11.0 with different cardol concentrations

It was possible to appreciate that all the films presented a close behavior in the Bode diagrams, which could indicate that the biopolymers elaborated with and without cardol and at different pH conduct electric current through a similar mechanism. The equivalent circuit that corresponds to the Bode diagrams recorded in the biopolymer films is presented in Fig. 4.

The circuit is composed by a resistance Rf that corresponds to the resistance of the biopolymer film, a capacitance *Cdl* that is due to the double layer formed at the biopolymer/metal (electrode) interface connected in parallel to a resistance *Rct* due to the resistance in the charge transfer from the metal (electrode) to the biopolymer and a parallel system formed by a *CPE* (constant-phase elements) and a resistance (*CPE/Rre*) generated by the diffusion of electrons in electrochemical reactions (oxidation/reduction).

Table 2 shows the values of the electrochemical parameters of the films represented in the components of the equivalent circuit. The values of the electrochemical parameters determined from the impedance spectra showed that the presence of cardol in the films increased their electrical resistance (*Rf*). The pH also affected the resistance of the films, showing an increase as the pH was higher. Similar behavior could be observed in the resistance to charge transfer between the metal (electrode) and the biopolymer (*Rct*), which was consistent with those observed for *Rf*.

On the other hand, the double layer capacitance (*Cdl*) was higher in the biopolymer films elaborated at pH 11.0, while the films made at pH 3.0 and pH 7.0 presented little differentiation between them; showing a tendency to slightly higher values at pH 7.0.

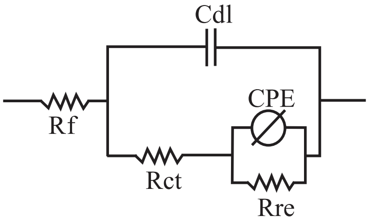


Fig. 4. Equivalent circuit obtained from the impedancemetric behavior of starch biopolymer films and biopolymer composite synthesized at different pH

The electrochemical parameters related to the oxidation-duction reactions (*CPE*/*Rre*) did not show a significant affectation in the biopolymer films made without cardol. However, in the cardol/starch biopolymer composite films higher values were observed in the system (CPE/*Rre*).

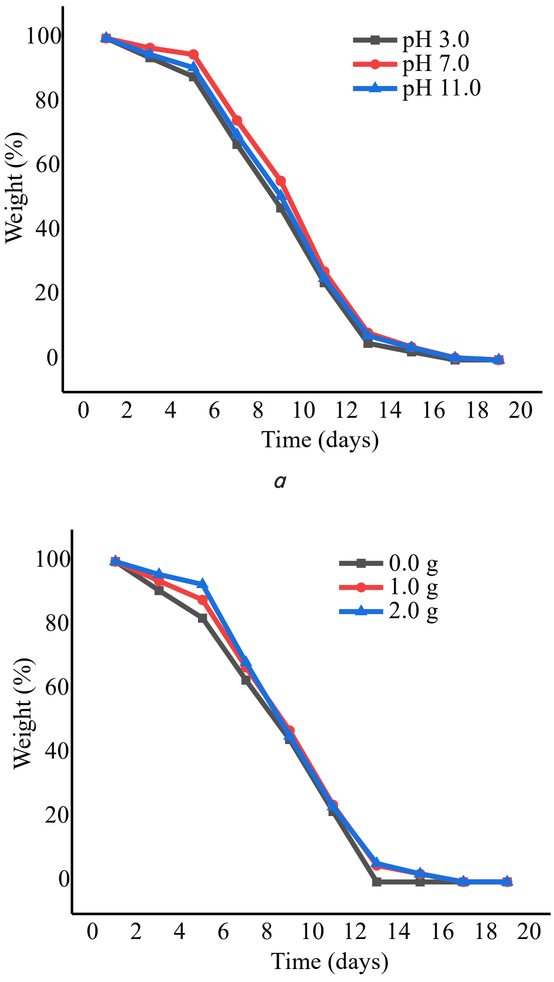
Table 2

Values of the electrochemical parameters of the biopolymer films

Cardol	pH	Electrochemical parameters				
		Rf, ohms	*Rct*, ohms	*Rre*, ohms	*CPE*, S*s^a	*Cdl*, F
0.0 g	3	1.59e-03	593.89	2.83e+06	1.26e-04	2.73e-09
	7	1.55e-03	698.94	2.12e+06	4.62e-05	1.46e-09
	11	6.11e-02	817.10	4.85e+11	3.21e-05	1.26e-05
1.0 g	3	1.61e-02	1008.46	6.05e+06	5.84e-05	1.44e-09
	7	1.87e-02	1.41e+11	6.63e+09	2.73e-03	9.39e-05
	11	2.21e-01	1.32e+11	1.80e+08	2.41e-03	6.96e-05
2.0 g	3	4.92e-01	875.59	2.66e+06	7.31e-05	1.40e-09
	7	4.28e-01	1.41e+11	1.79e+08	0.13e-03	7.80e-05
	11	6.424	1.36e+11	6.66e+08	7.72e-03	3.72e-05

Fig. 5 shows the biodegradability results of starch biopolymer films synthesized with 1.0 g of cardol at different pH values (Fig. 5, *a*) and films synthesized at pH 3.0 with different cardol concentrations (Fig. 5, *b*). In all cases, it was possible to appreciate a biodegradability process with three stages of well-marked weight loss.

The first stage was between days 1 to 5 in which the films lost between 10 and 20 % of weight. This first biodegradation process can be associated with the leaching of plasticizers (glycerol, polyethylene glycol and glutaraldehyde). The second process was evidenced approximately between day 5 and 13, at this stage there was a weight loss in the range of 75 % to 85 %, which represents most of the weight of the films. The weight loss in this stage can be associated with the biological degradation produced by the microorganisms present in the soil.



a

b

Fig. 5. Biodegradability recorded by weight loss of: *a* – films synthesized with 1.0 g of cardol at different pH; *b* – films synthesized at pH 3.0 with different concentrations of cardol

The third stage, the shortest and slowest, occurred approximately between days 13 and 19 and represented a weight loss of about 5 %. At this stage, the biopolymer films disappeared almost completely. In addition, it was observed that the differences in weight loss are not significant and occur mainly in the first stage of biodegradation, which may be due to possible differences in the crystallinity of the films. Additionally, the biodegradability process was monitored using FTIR spectroscopy. Fig. 6 shows the FTIR spectra of the biopolymer composite films synthesized at pH 7.0 with 1.0 g of cardol, in three different stages of the biodegradation process.

It was clearly observed that on day 5 (Fig. 6, *b*), at the end of the first stage of degradation, the intensity of the bands decreased significantly when compared with the intensity of the bands at the beginning of the process (Fig. 6, *a*), by approximately 40 %. This loss of intensity was more notable in the broad band corresponding to the OH vibration located between 3,730 and 3,150 cm^{-1} and the band at 1,649 cm^{-1}.

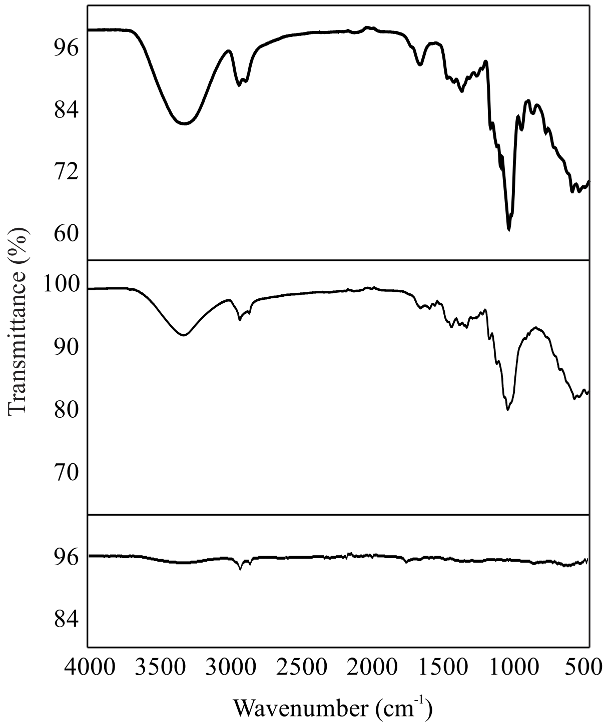


Fig. 6. FTIR spectra of a biopolymer composite film synthesized at pH 7.0 with 1.0 g of cardol at different stages of biodegradation: *a* – 0 days; *b* – 5 days; *c* – 13 days

At the end of the second stage, in the final phase of the biodegradation process, the bands are practically negligible, with a practically linear spectrum (Fig. 6, *c*). However, the bands at 2,991 and 2,878 cm^{-1} can be very faintly noted, corresponding to the C-H stretching vibrations.

6. Discussion of experimental results of the development of a cardol/starch biopolymer composite with electrochemical properties

Through this research it was found that cardol extracted from cashew nut shell liquid can be used to make a biopolymer composite when combined with cassava starch (Fig. 1). The mechanical stability of the films was affected by the pH used in the synthesis, this behavior could be due to the fact that when the retrogradation of the starch occurs, the acid used to adjust the acidic pH, influences the amorphous zones of the starch polymer chains, causing a decrease in crystallization, forming a less stable film [29]. Infrared spectroscopy (Fig. 2) made it possible to show that in addition to the substances used to adjust the pH, the cardol present in the biopolymer composite films could affect the crystallinity of the films by establishing hydrogen bonds between its hydroxyl (OH) groups and those of the starch.

The observed impedance behavior of the films (Fig. 3) could be due to the fact that since they are solid polymer electrolytes, the films conduct current through the movement of ions [32], in such a way that at low frequencies their conductivity decreases and it behaves like a condenser module. While when the frequency is increased, the current can flow through the movement of the ions present in the matrix of the biopolymers.

The differences in the values of the electrical resistance (*Rf*) and the charge transfer between the metal (electrode) and the biopolymers (*Rct*) shown in Table 2 could be due to the fact that cardol molecules have an aliphatic chain that could decrease ionic mobility ionic in the polymeric matrix and to the fact that at basic pH, the crystallinity of the films is greater, therefore, the mobility of ions could be less. Additionally, the trend of double layer capacitance (*Cdl*) to be higher at basic pH could be due to the differences in crystallinity that could be generated by the pH, since at a higher pH the crystallinity is greater and the generation of double-layer charges tends to increase due to the molecular organization of the biopolymers. On the other hand, the effect of cardol on the parameters related to the oxidation-duction reactions (*CPE/Rre*), which may be related to a higher electractivity caused by the presence of cardol. This fact could be due to the fact that cardol is an antioxidant compound that can be easily oxidized and reduced.

The biodegradability results presented in Fig. 5 showed a three-stage process where initially a weight loss occurs due to the leaching of plasticizers, a second process of weight loss at a higher speed, due to fragmentation and therefore to the increase of the contact surface with the degrading bacteria and a third process where the complete degradation of the films occurs.

Once the potential of using cardol to make a biopolymer composite by combining it with cassava starch has been evidenced, it would be important to carry out other work aimed at optimizing this process and evaluating other physicochemical, thermal, and mechanical properties, which would allow us to better understand the effect of cardol on the biopolymer composite.

The results of this work allow evaluating the potential of cardol in the valorization of the by-products of cashew nut processing through the development of a cardol/starch biopolymer composite. The scope of the results is to provide insights into the synthesis, characterization, and evaluation of the electrochemical properties.

The findings of this research can enhance the application of cardol in new materials with electrochemical activity. The cardol/starch biopolymer composite can find applications in energy storage systems, such as batteries and supercapacitors, where improved conductivity, charge storage capacity, and stability are crucial. Additionally, the composite may have potential uses in the development of sensors, electronic devices, and other technologies that benefit from biocompatible and environmentally friendly electroactive materials.

The limitations of this study include the lack of discussion about the driving mechanism given in the biopolymer composite obtained. Although the formation of biopolymeric films from cardol and cassava starch was demonstrated, the characterization of the physical and mechanical properties of these materials was not included. Furthermore, the electrochemical evaluation was mainly focused on the characterization of electrical parameters without exploring their relevance in specific applications, such as batteries or capacitors. Furthermore, the degradability of the biopolymers was evaluated only through laboratory tests and their behavior under real decomposition conditions was not addressed.

Despite the positive conclusions of the paper, there are some disadvantages that must be taken into account. First of all, the relationships between the synthesis conditions and the physical and mechanical properties of biopolymers and the relationship between these properties and the electrochemical behavior are not studied. Furthermore, although possible interactions between starch and cardol were mentioned, a detailed characterization of the structure and nature of these interactions would be desirable. Finally, although the biodegradability of the films was evaluated, the degradation products and their impact on the environment were not addressed. A more comprehensive analysis of the degradation and resulting by-products would be important to assess the sustainability and environmental safety of the biopolymer.

The development of this research holds significant potential due to the growing concern surrounding food agro-industry residues and the need for sustainable alternatives. The use of cardol derived from cashew nut shell liquid, combined with cassava starch, to produce biopolymer composites offers an attractive solution. The demonstrated formation of cardol/starch biopolymeric films and the observed interactions between the components provide a foundation for further exploration. The ability to modulate the electrical properties of the biopolymer through synthesis parameters enhances its applicability. Moreover, the biodegradability of the composite supports its potential as an environmentally friendly material. This research opens doors for the utilization of the cardol/starch biopolymer as a solid electrolyte in the manufacture of batteries, capacitors, and other technologies.

7. Conclusions

1. The evaluation of the electrochemical behavior of biopolymer composite films, and the effect of the amount of cardol used and the synthesis pH, provides valuable information on the electrochemical properties of this material. It was evidenced that the pH and the amount of cardol can allow variations in the conductivity of the biopolymer that can range from values of 1.55e-03 ohms for films elaborated without cardol at pH 7.0 up to 6.424 ohms for films elaborated at pH 11.0 with 2.0 g of cardol, representing an increase in resistance of three decimal places. Regarding the capacitance of the double layer, it can vary from 1.40e-09 F in the films elaborated with 2.0 g of cardol at pH 3.0 up to 7.80e-05 F in the films elaborated at pH 7.0 with 2.0 g of cardol, representing a variation of four decimal scales. The results allowed us to understand how these manufacturing parameters affect the performance and electrochemical behavior of the biopolymer composite, which is essential to optimize its application in electrochemical devices and technologies.

2. The results obtained show the possible interactions established between the starch molecules and the cardol in the biopolymer composite. The bands corresponding to the OH groups of starch in the biopolymer composite showed variations in intensity and position in the spectra with respect to the starch biopolymer without cardol, which may show possible interactions by hydrogen bonding between starch and cardol molecules. The analysis of these interactions provides information about the structure and properties of the material, and their understanding is crucial to determine the efficacy and stability of the compound in different applications. This evidence supports the feasibility and potential of using the biopolymer composite as a sustainable and functional alternative.

3. The evaluation of the biodegradability of the biopolymer composite, the biodegradation time and the structural changes registered by means of FTIR offers a comprehensive vision of the material's response to the biological environment. The biopolymers are completely degraded after 19 days, showing three well-differentiated stages of degradation; the first stage between day 0 and 5, the second stage between day 6 and 13 and the third stage between day 14 and 19. These findings are critical to determining the sustainability and environmental impact of the biopolymer composite throughout its life cycle. The information obtained allows informed decisions to be made and promotes the development of more environmentally friendly materials, which contributes to reducing waste and promoting more sustainable practices.

Conflicts of interest

The authors declare that they have no conflict of interest in any of the technical or financial aspects related to this work.

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Data availability

The manuscript has no associated data.

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