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Corrosion rate of canned green corn packaging studied by linear polarization

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Abstract. Tinplate is highly resistant, malleable and has good weldability. It is also easily recycled, making it ideal for packaging food and beverages, however, a major disadvantage is its susceptibility to corrosion. In acid food, the interaction between packaging and food leads to the dissolution of metals such as iron and tin that compose the packaging. In this study, brine of canned green corn was characterized in terms of its pH value (6.3), Brix degree (5.0 ºBrix), Cl^- concentration (1.2 g/L) and density (1.1 g/mL). Samples of the three parts of the can (lid, body and bottom) with and without varnish were studied for electrochemical corrosion using Tafel curves in different pH, Cl^- and temperature conditions. Statistical analysis was also used to study the influence of these factors on the corrosion rate (CR) via a 2^3 factorial design with a triplicate central point. The study showed that the factors studied had a significant influence on the corrosion rate (CR) only for the sample without varnish. The varnish was characterized as a phenolic epoxy resin according to attenuated total reflectance for Fourier Transform Infrared (FTIR/ATR) spectroscopy measurements. The corrosion inhibition efficiency promoted by the varnish was confirmed by comparing the activation energy values for the corrosion process, which were 154.3 kJ/mol and 42.97 kJ/mol for samples with and without varnish, respectively. Thus, in this work, the main elements in tinplate corrosion were quantified in order to contribute to the use of this important type of packaging.
Key words: Tinplate, green corn, electrochemical corrosion, linear polarization.

Introduction

Packaging is essential for preserving the quality of a product, protecting and preserving the food.

Among the packaging used in the food industry is tinplate. This material has high mechanical strength, malleability and good weldability, and is also easily recycled, making it ideal for packaging food and drink(DANTAS, 1999;

VAIREANU, 2018). On the other hand, one of the disadvantages of metal packaging is its susceptibility to corrosion. In acidic foods, the interaction between the packaging and the food leads to the dissolution of the metals that make up the packaging (oxidation reaction), mainly iron and tin from the tinplate, as well as the evolution of hydrogen (cathodic reaction), limiting the shelf life of the product, as well as causing damage to health or losses to the food industry.In the case of food packaged in brines, in addition to their acidic nature, the salts present in the medium, especially NaCl, can accelerate the process and encourage pitting corrosion due to the presence of chloride ions (Cl^-) (COSTA, 2016; EUZUBER, 2014).Tinplate food packaging has a protective layer of varnish on the inside to minimize the metal's interaction with the products inside(JORGE, 2013; ROBERTSON, 2005). The varnishes must be resistant to mechanical deformation and heat treatment and must not present any risk of toxicity or transmit any taste or odor to the food. Its thickness and quality have a direct influence on corrosion(JORGE, 2013; SALAS, 2016; VAIREANU, 2018). The basic resins that make up varnishes can be oleoresinous, phenolic, epoxyphenolic, epoxyanhydride, vinyl polyester or acrylic organosols. The characteristics of each one, such as chemical, physical or sulphur resistance, mean that they have different uses. Epoxy-phenolic resins are one of the most widely used in the food industry. They are commonly used in vegetable, meat and fish packaging and have been used in many types of food (DANTAS, 1999; CERRATO, 2017). It is important that the consumer buys the product in perfect condition, as any damage to the protective layer exposes the metal to the environment, which favors corrosion. Corrosion of food packaging can be affected by factors such as pH, packaging temperature, salt concentration and the integrity of the varnish layer. It is therefore important to study the influence of these factors on corrosion as well as the evolution of this oxidative process over time (SALAS, 2016; VAIREANU, 2018; TAROCO, 2020; RAMANA, 2009). In this context, the aim of this study was to evaluate the corrosion rate of canned green corn via linear polarization under different conditions, as well as to study the influence of these parameters on the corrosion rate via statistical analysis.

Material and Methods

Physico-chemical characterization of the preserves

The preserves were characterized in terms of pH and °Brix. The Brix degree was measured using an Abbe refractometer and the pH was obtained using a Hanna peagameter (model HI5222). The chloride content was obtained by argentimetric titration; all measurements were taken in triplicate.

Characterization of green corn can varnish

The body, bottom and lid of the can of green corn from the brand studied were subjected to Fourrier transform infrared spectroscopy using Perkin Elmer Spectrum 100 equipment.

Electrochemical measures

Cans of canned green corn from the same manufacturer and the same batch were used. Working electrodes were prepared using different parts of the can (lid, body and bottom) with an active area of 1 cm². Linear polarization measurements were carried out in the potential range of potential range from -1.0 V to 1.0 V with a scan rate of 10 mv/s. The Tafel curves were processed using NOVA software (Metrohm) to determine the corrosion rate (CR), based on the corrosion current and the equation:

Where:

$$CR = \frac{icMM}{ZFd} \qquad \text{(Equation1)}$$

c: corrosion current density (A/cm^2)
MM: molar mass
Z :ion electric charge
F : Faraday constant (96500 C/mol)
d : density of the material

The measurements were carried out in a 20 mL electrochemical cell consisting of three electrodes: the reference electrode, Ag/AgCl, and the auxiliary electrode, platinum,as shown in figure 01.

The working electrodes (with and without varnish) were immersed in a canning medium in order tocheck the susceptibility to corrosion of each part of the can. The varnish on the inside of the can was removed using concentrated sulphuric acid.

Effects of pH and chloride concentration

The electrodes of the three parts of the can (with and without varnish) were immersed in model solutions to study the effect of pH and NaCl on corrosion. The pH was controlled using sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH). For the chloride concentration study, the body electrodes were used, lid and bottom electrodes were used (with and without varnish) and the NaCl solutions were 1g/L; 3.4 g/L; 7.0 g/L and 14 g/L.

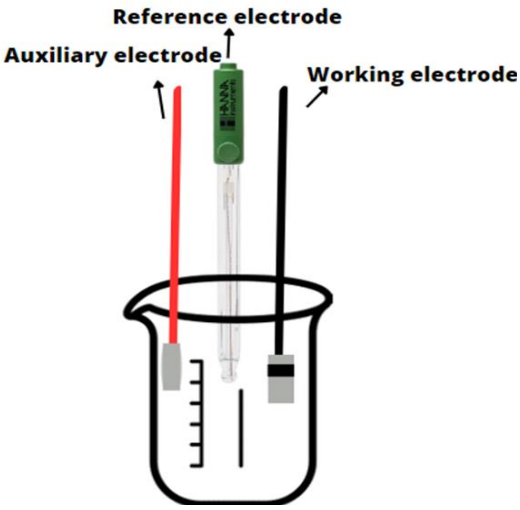


Figure 01. Representative diagram of the three-electrode cell used in the electrochemical measurement.

Temperature effect

To adjust the temperature, the lid, body and bottom electrodes (with and without varnish) were immersed in a solution of NaCl 1.2 g/L and pH= 6.1 (a value close to that of the cannedanalyzed). A water bath was used to control the temperature.

Characterization of the green corn can varnish

The body, bottom and lid of the green corn can were subjected to Attenuated total reflectance with Fourier transform infrared spectroscopy (ATR/FTIR)using Perkin Elmer Spectrum 100 equipment.

Statistical analysis

To evaluate the influence of the factors temperature, chloride concentration and pH on the corrosion rate, a 2^3 factorial design was used in triplicate at center point.The use of the central point makes it possible to add a third level for each factor, which makes it possible to study the factorial using the Response Surface Methodology (RSM), as well as quantifying the significance of possible curvature and errors associated with individual effects and interactions (MONTGOMERY, 1997).

The factors explored at two levels (low, high) and their coded values are shown in Table 1.

Analysis of variance (ANOVA) was carried out to determine which factors (and their effects) are statistically significant at a 5% significance level. The statistical analyses were carried out using Statistica software (JPZ804I376009FA-9), version 13.

Table 01. Factors and levels used in the factorial design.

Factors	Low level (-)	Central Point (0)	High level (+)
pH	6.1	7.05	8.0
Cl^- (g/L)	1.2	2.0	2.8
T (°C)	25	35	45

Results and discussion

Physico-chemical characterization of the canned food

Table 02 shows the values of some of the physical and chemical parameters of canned green corn. The pH of the canning food was approximately 6.28, which could be aggressive to the metallic material of the packaging (DANTAS, 2011). This acidic value was also obtained by other authors such as Costa et al. (2016) who found a pH of 5.88 for canned peas.The Brix and density values are close to those obtained by Reis et al.(REIS, 2018). The concentration of chloride in canned green corn can vary depending on the manufacturer and the preservation process used. Controlling the concentration and content is essential to ensure compliance with regulations and provide correct product information to the consumer.

Characterization of the can varnish

There is a similarity between the three infredspectra of the parts of the can in figure 02. The result obtained is in agreement with that observed by Dantas et al (1999), with the protective layer being of the type epoxy phenolic type. The OH band is observed between 3600 and 3200 cm-. This peak is short due to the smaller number of OH groups in the phenolic resin. The presence of the C=C group at 1600 $cm^{-1}$and also the C-O group at 1200 cm^{-1} is evident. Fernandes et al. showed different C-H groups between 600 and 1100 cm^{-1} for phenolic resin, which is also observed in this spectrum (CERRATO, 2017; FERNANDES, 2018)

Electrochemical measurements

Figure 03 shows the corrosion rate (CR) for the different parts of the can in a canning environment.

The rate of corrosion is influenced by various factors, such as the time the packaged food is stored, the storage temperature and pH. The presence of NaCl in the canned solution contributes to the corrosion process and can have different values for each part of the can. This may be due to the different compositions of the parts of the packaging.

The body showed the highest CR (0.0858 mm/year) without varnish. On the other hand, the bottom showed a CR of approximately 0.0275 mm/year with varnish. This is possibly due to the acidified brine having greater contact with the body of the can. Costa et al (2016) also highlighted the unvarnished body with the highest corrosion rate, around 1.7 mm/year.

Table 02. Physical-chemical characterization of canned green corn

pH	°Brix (%)	Cl^- (g/L)	Densidade (g/L)
6.28	5.0	1.2	1.1

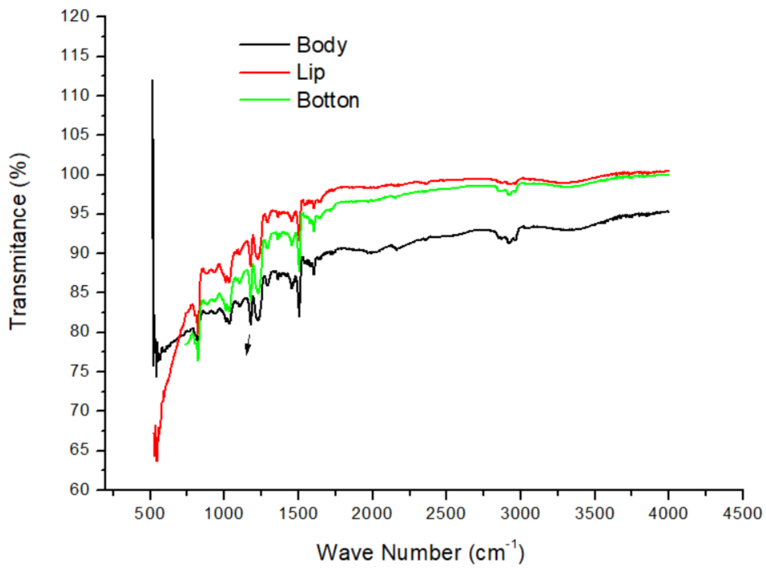


Figure 2. FTIR/ATR three parts of the green corn can

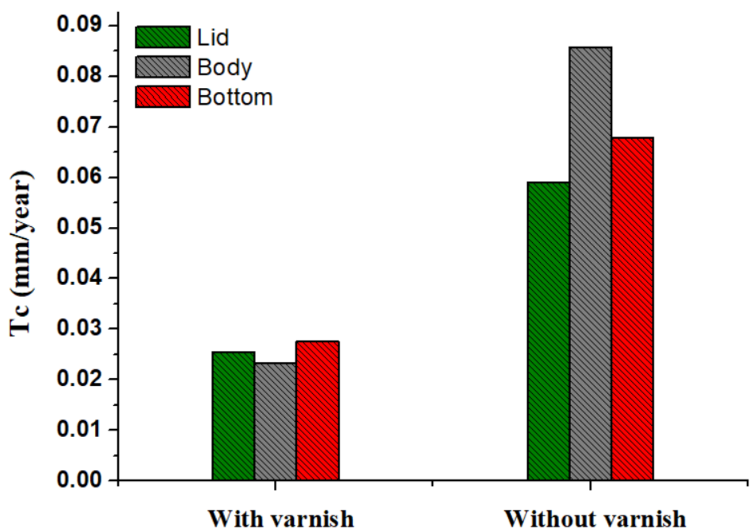


Figure 03. Corrosion rate of the different parts of the can with varnish and without varnish in the middle of canned green corn.

Effect of NaCl

Figure 4 shows the corrosion rate (CR) of the three parts of the can with and without varnish in NaCl solution at different concentrations.

For all parts of the can, the corrosion rate was higher without the presence of the varnish, as expected, since its essential function is to minimize the interaction of the metals in the packaging with the products inside.

The use of the organic coating (varnish) when applied internally to the packaging prevents the tinplate from coming into contact with the packaged product, thereby minimizing the corrosive process of the packaging. The varnish in this case protected the can by approximately 99.8% considering the body in the 7 g/L NaCl solution. NaCl favors the corrosion process, especially pitting corrosion (PARDO, 2000). The mechanism of corrosion of tinplate steel iron in chloride has been proposed by Rengaswamy et al (1998)

$$Fe\,(s) \rightarrow Fe^{2+}\,(ions) + 2e^- \qquad \text{(Equation2)}$$

$$Fe^{+2} + 2Cl^- \rightarrow FeCl_2 \qquad \text{(Equation3)}$$

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + 2Cl^- \quad \text{(Equation4)}$$

$$6\,FeCl_2 + O_2 + 6H_2O \rightarrow 2Fe_3O_4 + 12H^+ + 12Cl^- \quad \text{(Equation5)}$$

First there is the oxidation of Fe (equation 2). The Fe^{2+} ions react with the chloride ions present in the canned food to form $FeCl_2$(equation 3), which in turn produces hydroxide and iron oxide in the presence of O_2 and H_2O, according to equations 4 and 5. Due to the acidification of the interface promoted by the release of H^+ ions, there is a decrease in pH at the interface, further favoring corrosion. This is a feedback process in which chloride ions can be considered as catalysts for the corrosion reaction. A representative diagram of this process is shown in figure 05.

It is expected that the higher the concentration of chloride, the higher the corrosion current, the more negative the corrosion potential and consequently the higher the corrosion rate.

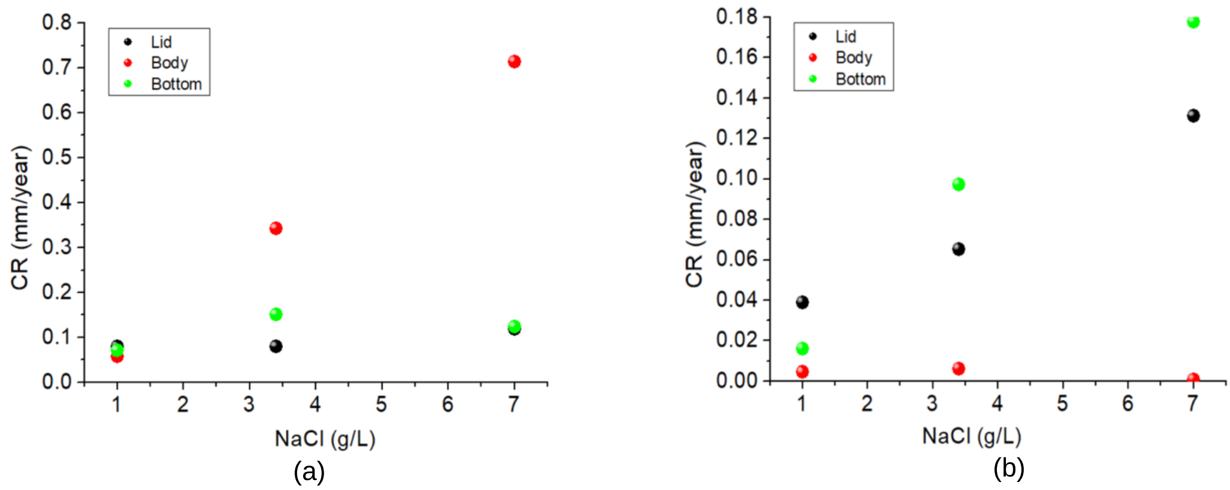


Figure 04. Corrosion rate of can parts as a function of NaCl concentration for samples (a) with varnish (b) without varnish.

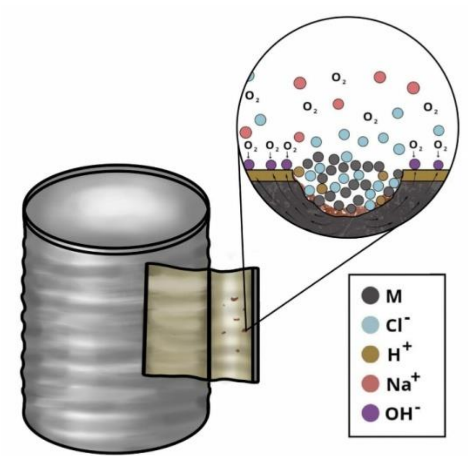


Figure 05. Representative diagram of pitting corrosion suffered by tinplate cans.

Effect of pH

Figure 06 shows the effect of pH on the can body at different pH levels.

The CR has a higher value at acidic pH, due to the facility with which the metal dissociates in this medium(REIS, 2018; RAMANA, 2009). For the study in question, the highest CR, shown in figure 06, was for the body of the can at pH = 2.2.

Effect of temperature

Figure 7 shows the CR of the varnished and unvarnished parts of the can in a solution of NaCl 1.2 g/L and pH 6.1 at different temperatures. There is an increase in CR with temperature. Corrosion increased linearly, following the Arrhenius equation (AL JUHAIMAN, 2012) according to equation 7:

$$\ln K = \ln A - \frac{Ea}{RT} \qquad \text{(Equação 7)}$$

From the linear coefficient of the curves in figure 07 and equation 7, the parameters shown in table 3 and the corrosion activation energy for each of the samples analyzed were obtained.

A higher CR is observed with increasing temperature, while the corrosion rate increased sharply when the varnish was missing, showing the importance of this protective layer.

According to the Arrhenius equation, the activation energy is higher in the varnished sample, which is to be expected, since the function of the varnish is to protect the metal against corrosion, making the metal oxidation process less favorable. Other authors have also observed an increase in steel corrosion with temperature (RAMANA, 2009; BENETISS, 2005).

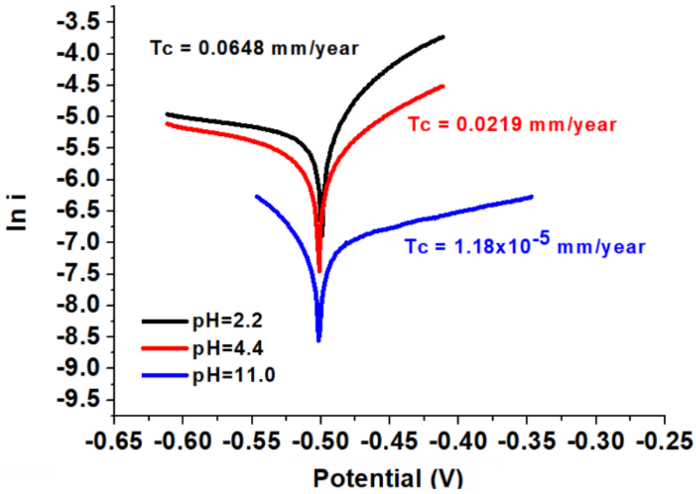


Figure 06: Tafel curves for the can body at different pH values for the can body with varnish.

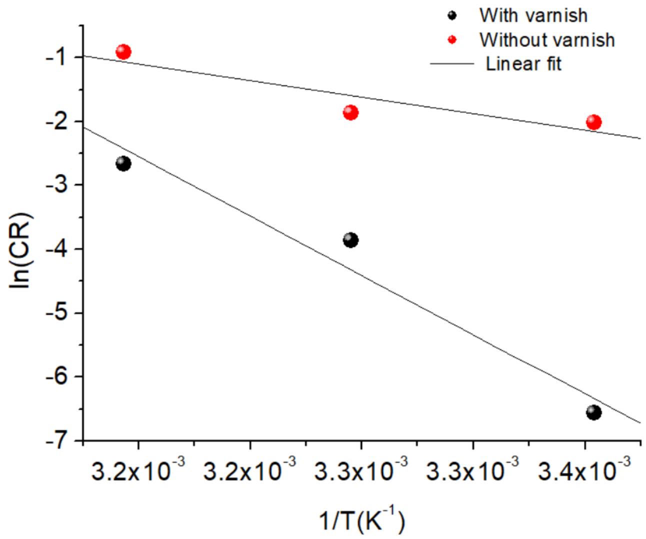


Figure 7. Ln (CR) of the can body at different temperatures for samples with and without varnish, in a 1.2 g/L NaCl solution at pH 6.

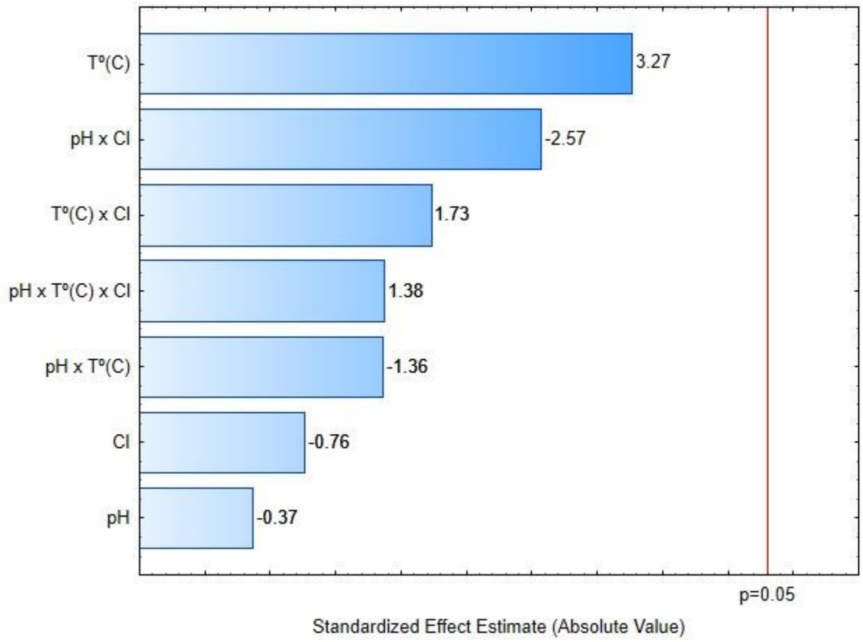
Table 3. Activation energy and parameters obtained from the regression of the curves in figure 7.

	Angle coefficient	Activation energy (kJ/mol)	R^2
With varnish	-18560.214	154.3	-0.98008
Without varnish	-5168.885	42.97	-0.91334

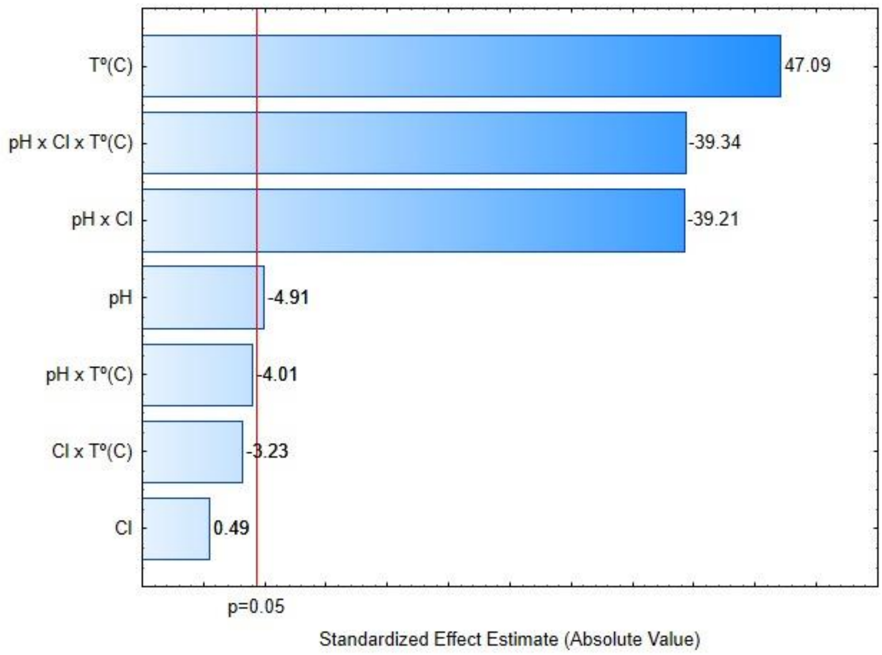
Statistical analysis

Figure 8 shows the Pareto chart for the samples with and without varnish. It can be seen that for the sample with varnish there is no significant influence of the parameters studied on the corrosion rate, which shows the effect of the varnish on the packaging. For the sample without varnish, temperature and pH have a significant influence on the corrosion rate of green corn packaging, in which case temperature is the factor with the greatest magnitude.

Figure 9 shows that for temperatures above 36^{o}C, the complete pH range studied has a significant influence on CR. This shows the care that must be taken when storing or transporting in regions with a hot climate.



(a)



(b)

Figure 8. Effect of pH, temperature and chloride concentration and their interactions on the corrosion rate for samples (a) with varnish and (b) without varnish.

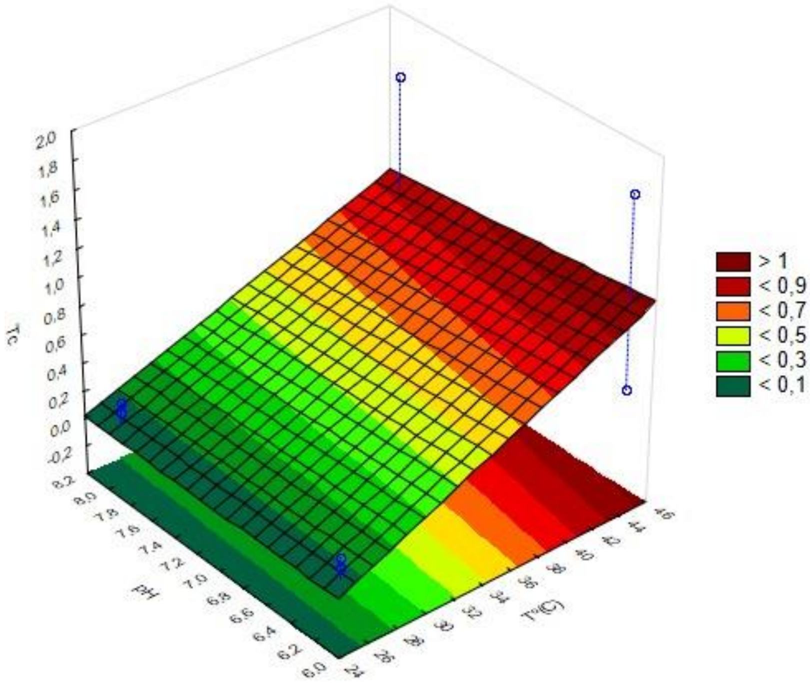


Figure 9. Response surface for the corrosion rate variable as a function of pH concentration and temperature for the unvarnished can body.

The composition of the tinplate material or even the varnish differs according to the origin of the packaging and the food for which it is intended. This leads to different results, such as that observed by Taroco et al. who showed higher CR for temperatures above 20°C and pH below 4.0 for tinplate corrosion of tomato extract.

Conclusion

In this study, canned green corn proved to be a favorable medium for tinplate corrosion. The brine solution was characterized in terms of its pH value (6.3) °Brix (5.0), Cl^- concentration (1.2 g/L) and density (1.1 g/mL). The study showed that the varnish had an effective protective effect, as expected, on cans of canned green corn. The parts of the can that showed the greatest corrosion, in the middle of canning, were the body (0.0858 mm/year) and the bottom (0.0275 mm/year) for samples without and with varnish, respectively. In relation to chloride, the CR was higher for the body of the can (0.7135 mm/year) and the lid (0.11928mm/year) for samples without and with varnish, respectively. The statistical results showed that pH and chloride concentration have a significant influence on CR only for the sample without varnish. The varnish proved to be effective in protecting against corrosion, a fact also evidenced by the activation energy whose values were 154.3 kJ/mol and 42.97 kJ/mol for the can body with and without varnish respectively. In this study, the protection efficiency of the varnish layer was quantified via electrochemical measurements, highlighting the importance of purchasing products in good conditions.

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