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EVALUATION OF THEOBROMA CACAO POD HUSK EXTRACTS AS CORROSION INHIBITOR FOR CARBON STEEL

EVALUACIÓN DE EXTRACTOS DE CÁSCARA DE CACAO (Theobroma Cacao L.) COMO INHIBIDORES DE CORROSIÓN EN ACERO AL CARBÓN

AVALIAÇÃO DE EXTRATOS DE CASCA DE CACAU (Theobroma Cacao L.) COMO INIBIDORES DE CORROSÃO EM AÇO-CARBONO

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ABSTRACT

Cacao pod husks were used as raw material to obtain anti-corrosive extracts. The extraction was performed by adding 50 g of grinded husk to 300 mL of solutions of deionized water and ethanol, varying solvent concentration from 0 to 50% v/v, temperature from 28 to 50°C and extraction time from 2 to 5 hours. Then, the extracts were filtered and submitted to characterization tests. The anticorrosive activity was studied by weight loss analysis on A36 steel plates in 1M hydrochloric acid with variations of extract concentration (0, 1, 3, 7 and 10% v/v). A maximum corrosion inhibition efficiency of 91.13% was achieved with an extract concentration of 10% v/v. This extract was obtained with 16.1% v/v ethanol, at 50°C and during 5 hours of extraction time. The results proved that cacao pod husk is a suitable raw material for the production of corrosion inhibitors. Phenols were the predominant components in this extract and mainly account for its anticorrosive activity. The adsorption mechanism of the inhibitor on the metal surface was studied by Langmuir isotherm analysis and the results suggested the occurrence of a physisorption.

Keywords: *Cacao crop residue, Corrosion inhibitors, Weight loss method, Phenols, Langmuir isotherm.*

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RESUMEN

Cáscara de la vaina del cacao se utilizó como materia prima para obtener extractos anticorrosivos. La extracción se realizó adicionando 50 g de cáscara molida a 300 mL de soluciones de etanol en agua desionizada, variando la concentración de solvente entre 0 y 50 %v/v, la temperatura desde 28 hasta 50°C y el tiempo de extracción entre 2 y 5 horas. Luego, los extractos se filtraron y se sometieron a pruebas de caracterización. La actividad anticorrosiva sobre placas de acero A36 sumergidas en ácido clorhídrico 1 M se estudió mediante el método de pérdida de peso, variando la concentración del extracto (0, 1, 3, 7 y 10 %v/v). Se logró una máxima eficiencia de inhibición a la corrosión de 91,13 % con una concentración de extracto de 10 %v/v. Este extracto se obtuvo con 16.1 %v/v de etanol, a 50°C y durante 5 horas de tiempo de extracción. Los resultados demostraron que la cáscara de la vaina del cacao es una materia prima adecuada para la producción de inhibidores de corrosión. Los fenoles son los componentes predominantes en este extracto; razón por la cual, la actividad anticorrosiva se le atribuye principalmente a ellos. El mecanismo de adsorción del inhibidor sobre la superficie metálica se estudió mediante un análisis con isoterma de Langmuir, los resultados indicaron la ocurrencia de una fisisorción.

Palabras clave: *Cascarilla de cacao, Inhibidores de corrosión, Método de pérdida de peso, Fenoles; Isoterma de Langmuir.*

RESUMO

A casca da semente do cacau foi utilizada como matéria-prima na obtenção de extratos anticorrosivos. A extração foi feita pela adição de 50 g de casca moída a 300 mL de soluções de etanol em água desionizada, variando a concentração de solvente entre 0 e 50% v/v, a temperatura de 28 até 50°C e o tempo de extração entre 2 e 5 horas. Logo depois, os extratos foram filtrados e submetidos a testes de caracterização. A atividade anticorrosiva sobre chapas de aço A36 submergidas em ácido clorídrico 1 M foi analizada mediante o método de perda de peso, variando a concentração do extrato (0, 1, 3, 7 e 10 %v/v). Assim foi atingida uma máxima eficiência de inibição à corrosão de 91,13% com uma concentração de extrato de 10 %v/v. Esse extrato foi obtido com 16.1 %v/v de etanol, a 50°C e durante 5 horas de tempo de extração. Os resultados demonstraram que a casca da semente do cacau é uma matéria-prima adequada para a produção de inibidores de corrosão. Os fenóis são os componentes predominantes neste extrato; é por isso que atividade anticorrosiva é atribuída principalmente a esse componente. O mecanismo de adsorção do inibidor sobre a superfície metálica foi estudado mediante uma análise com isoterma de Langmuir, os resultados indicaram a ocorrência de uma fisisorção.

Palavras-chave: *Casca de cacau, Inibidores de corrosão, Método de perda de peso, Fenóis; Isoterma de Langmuir.*

1. INTRODUCTION

Carbon steel is one of the most widely used construction materials in water distribution, power production and chemical industries due to its cost effectiveness and mechanical properties (Fouda *et al*., 2013). Nevertheless, it has a low corrosion resistance in acidic media, which represents a major drawback for its applications since many industrial processes use acid solutions, e.g.: pickling, cleaning, descaling, oil wet cleaning (Kalaiselvi *et al*., 2010). Therefore, corrosion inhibitors are used to prevent the degradation of this material,. This commonly results in tremendous economic savings regarding equipment maintenance and safe operating procedures (Mourya, Banerjee & Singh, 2014). However, conventional inhibitors like chromates and nitrates have proved to exert toxic effects on the environment and human health (Abdel-Gaber *et al*., 2011). Thus, attention is being redirected to develop eco-friendly inhibitors commonly obtained from plant extracts and other natural products (Oguzie *et al*., 2010). These materials have many benefits such as low cost, high availability, renewability, non-toxicity, and their phytochemical composition, which presents a number of compounds frequently related to anticorrosive activity (Vrsalović, Kliškićand & Gudić, 2009). Among these substances, organic compounds containing N, O or S atoms, electronegative functional groups and π electrons in triple or conjugated double bonds are of special interest. Specific inhibition mechanisms are related with the interaction of such compounds with the metal surface via an adsorption process (Ikpi *et al*., 2012).

Phenols, saponins, tannins, oils and fats are some of the substances reported as corrosion inhibitors on steel, aluminum, zinc and other metals (Rajalakshmi, Prithiba & Leelavathi, 2012). These compounds can be found in the chemical structure of many plants and other natural resources (Yoo *et al*., 2012). Current research deals with the use of plant extracts as a source of green corrosion inhibitors that could efficiently replace and eliminate the negative impact caused by conventional anticorrosive products (Faustin *et al*., 2015).

Many of the aforementioned compounds are present in the composition of cocoa (*Theobroma Cacao*) (Yapo *et al*., 2013). A study conducted by Umoru, Fawehinmi, and Fasasi (2006) about the inhibitive effect of extracts from cocoa (*Theobroma Cacao*) and kolanut (*Cola Acuminata*) leaves on the corrosion of mild steel showed that the extracts from these plants are potential inhibitors of mild steel corrosion in seawater and marine environment. The highest inhibition efficiency was obtained when the concentration of the inhibitors was increased up to the optimum level (4% of each of the extracts).

The pod husk is a byproduct of cocoa crop, commonly disposed to rot on the plantations, causing foul odors and the spread of crop diseases such as black pod rot (Vriesmann, Amboni & De Oliveira, 2011). Around 39 million tons of pod husk are produced annually (International Cocoa Organization, 2015), therefore disposal alternatives need to be implemented in order to avoid environmental damages.

With the purpose of offering solutions for agricultural and industrial sectors, the main objective of this work was to obtain extracts from *Theobromona* cacao pod husk of the Colombian Caribbean Region and assess their potential corrosion inhibition activity on A36 steel in an acidic medium. This study was also intended to identify the active substances with anticorrosion properties present in extracts; establish the best extraction conditions that guarantee an extract with the highest efficiency, and define the adsorption mechanism of the inhibitor over materials.

Although, the properties of *Theobroma cacao* peel extracts as corrosion inhibitor have been studied before, the experimental conditions and methodology were different from those used in this work. The inhibition and adsorption properties of *Theobroma Cacao* peel polar extract (TCPE) on corrosion inhibition efficiency of 0.3%C mild steel in 1.5 M HCl solution for various exposure times, TCPE concentrations and operation temperatures were investigated by Yetri *et al*. (2014). Their results support the hypothesis of this work, which states that the addition of cacao peel extract in acidic media is effective to minimize corrosion effects on carbon steel. Similarly, the need to conduct more research on this topic also became evident in order to provide proper solutions for the industrial sector.

2. THEORY AND CALCULATIONS

Corrosion Inhibition Efficiency

Gravimetric calculations regarding the effectiveness of a corrosion inhibitor are based on the weight loss that the material undergoes when it comes in contact with the corrosive medium. A piece of the material is weighted before being exposed to degradation in an environment where no corrosion inhibitor has been added, and weight measurements are taken after a specified period of time. The same procedure is performed with samples containing different concentrations of the inhibitor. Then, Corrosion Inhibition Efficiency (CIE) is calculated by comparing the weight loss that was experienced by the protected materials with the one observed in the sample with no inhibitor (blank), as observed in *Equation 1:*

$$CIE\% = \frac{\Delta W_0 - \Delta W_i}{\Delta W_0} \times 100 \quad (1)$$

where ΔW_0 and ΔW_i are the weight losses underwent by the blank and the inhibited material, respectively (initial weight – final weight). It should be noted that this efficiency depends on a specific period of time which has to be clearly stated when reporting the result. Twenty-four hours is the most frequently used timeframe for these calculations (Mu & Li, 2005).

Adsorption Mechanism and Langmuir Isotherm

The organic compounds inhibit corrosion via adsorption on the area of the material exposed to the inhibitor (Bentiss *et al*., 1999). Commonly, this process takes place by two main mechanisms: a blocking in the reaction (corrosion) sites or the formation of a barrier that reduces the diffusion rate of corrosive species to the material surface. Many factors such as concentration of the inhibitor, its chemical structure, chemistry of the solution, nature and surface charge of the material, temperature and electrochemical potential have a bear on the adsorption process (Abbasov *et al*., 2013).

Langmuir adsorption isotherm expression (*Equation 2*) is one of the methodologies commonly used to obtain further information about this specific phenomenon of mass transfer. It relates to the surface coverage θ (which is defined as corrosion inhibition efficiency/100) and the inhibitor concentration C, allowing the calculation of the adsorption equilibrium constant K for different temperatures.

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (2)$$

This constant can then be used to give an insight between the two possible types of adsorption that could occur; physisorption or chemisorption, by calculating the standard heat of adsorption, according to van't Hoff *Equation 3*:

$$\Delta H = -RT(\ln K - C) \quad (3)$$

where R is the universal gas constant, T is the temperature at which the corrosion-inhibition reaction took place, and C is the molar concentration of water at standard conditions. Physisorption takes place at ΔH values lower than 48.2 kJ/mol, while chemisorption is attributed to ΔH values approaching 100 kJ/mol (Martinez & Stern, 2002).

3. METHODOLOGY

Reagents and Materials

Cacao pods from Criollo variety were grown and harvested after 4 months at a local farm in Magangue town of Bolivar (Colombia). 96% v/v ethanol and 37% v/v HCl from Sigma Aldrich were used. Deionized water was prepared at the Unit Operations Lab of the Chemical Engineering Department from the University of Cartagena. A36 steel plates (4 cm long, 3 cm wide, 4 mm thick) were provided by a local junkyard.

Preparation of Anticorrosive Extracts

The cacao pod husks were washed out with water and cut open to remove all the cocoa beans and mucilage from their interior. Then, the remaining husks were milled. The extracts were obtained adding 50 g of pod husk milled and undried (moisture content 84% w/w) to 300 mL of solvent, at constant temperature during a specific time. Then, the solutions were filtered. A complex experimental design of 2^3 was used, working with solvent concentration, temperature and extraction time as factors. The levels of these factors were set as follows: solvent concentration between 0% v/v (pure deionized water) and 50 %v/v ethanol; temperature between 28°C (room temperature) and 50°C; extraction time from 2 to 5 hours. Sixteen extracts were obtained in this stage. Table 1 shows the factors and levels of the experimental design, which were obtained using the software STATGRAPHICS® Centurion XVI. It was set as a complex 2^2 factorial design with central points and star points.

Table 1. List of the prepared extracts and their extraction conditions.

Extract #	Solvent concentration (% v/v)	Temperature (°C)	Extraction time (h)
1	25	39.5	3.4
2	10	33	2.5
3	25	39.5	3.4
4	0	39.5	3.4
5	40	46	2.5
6	40	46	4.3
7	25	28.5	3.4
8	40	33	2.5
9	10	46	4.3
10	50	39.5	3.4
11	25	39.5	1.8
12	40	33	4.3
13	10	46	2.5
14	10	33	4.3
15	25	39.5	5
16	25	50.5	3.4

Characterization of the Extracts

50 mL of each extract were characterized with the purpose of determining the presence of specific substances commonly related to anti-corrosive activity. Analyses were conducted by the Laboratory of Pharmaceutical Chemistry of the University of Cartagena. The methods applied were the AOAC 30.184 to determine tannins, Folin Ciocalteau reactive for phenolic compounds, AOAC 920.39C for oils and fats and visible spectrophotometry technique at 528 nm for saponins. Sixty four characterizations were performed in this stage.

Evaluation of the Corrosion Inhibition Activity

In order to test the corrosion inhibition properties of the extracts, analyses of weight loss were performed on A36 steel plates using 1M hydrochloric acid (HCl) solution as corrosive medium. Initially, the plates (4 cm × 3 cm × 4 mm) were polished using an electric polisher until the surface was smooth, without scrap metal, rust or dirt, so that no passivation (shielding of surface by a previous oxide layer) could occur. Then, the samples were immersed in 75 mL of the corrosive media with and without addition of the extract. The plate remained fixed vertically in the liquid, inside a closed container with tight lid. The inhibition extract was added directly to the HCl solution, and its concentration in the solution was varied (1, 3, 7 and 10% v/v). Once the corrosion process ran for 24 hours, each sample was lifted from the corrosion medium. The plate was washed carefully with distilled water and dried at room temperature. Finally, the weight of each sample was measured using analytical balance (Sensitivity 1 mg). This procedure was performed in spans of 24 hours during 14 days. The corrosion inhibition efficiency was determined using the *Equation 1*. The statistical analysis of data was performed with STATGRAPHICS® Centurion, and the extraction conditions rendering the highest corrosion inhibition efficiency were predicted.

This prediction was subsequently tested in an additional experiment. A Langmuir isotherm analysis was performed on the plate that exhibited the highest inhibition efficiency with the purpose of determining the adsorption mechanism through which the inhibitor molecules adhere to the surface of the metal. Sixty-nine samples were submitted to corrosion test in this stage.

4. RESULTS AND DISCUSSION

Characterization of the Extracts

Characterization tests proved the presence of tannins, phenols, oils and saponins in the extracts obtained. Table 2 shows the concentration of each chemical species according to the different extraction conditions. Due to the number of experiments performed, it is difficult to identify any trends in design; therefore, a Pareto chart analysis was developed using STATGRAPHICS® Centurion XVI (See Figures 1 to 4). Thus, the effect of extraction variables on concentration of chemical species in the extracts was assessed. Also, a quadratic regression model with 10 coefficients was considered.

As shown in Table 2, all of the target substances were present in the extracts. It is expected that a synergistic action among these compounds occurs when the corrosion on the plates is inhibited, according to the reported literature on this matter. The presence of oxygen heteroatoms, aromatic rings and electronegative functional groups in the structure of these substances makes it possible to hypothesize that cacao pod husk extracts could exert the desired anticorrosive activity (Zarrok *et al*., 2011).

Table 2. Phytochemical characterization of extracts from cacao pod husk.

Extract #	Oils And Fats (% w/w)	Phenols (% w/w)	Saponins (% w/w)	Tannins (% w/w)
1	0.004	0.114	0.005	0.32
2	0.015	0.02	0.004	0.06
3	0.003	0.11	0.01	0.52
4	0.033	0.126	0.007	0.49
5	0.005	0.09	0.011	0.49
6	0.052	0.1	0.01	0.39
7	0.006	0.02	0.006	0.07
8	0.012	0.05	0.011	0.16
9	0.003	0.128	0.004	0.492
10	0.003	0.121	0.007	0.5
11	0.006	0.13	0.007	0.51
12	0.005	0.124	0.004	0.51
13	0.008	0.13	0.006	0.52
14	0.008	0.105	0.004	0.28
15	0.004	0.111	0.002	0.254
16	0.011	0.08	0.008	0.41

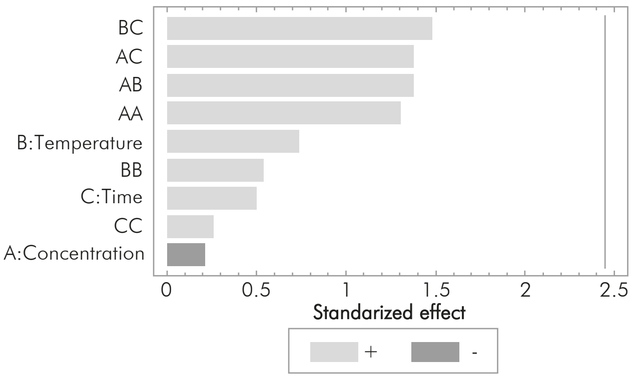

Figure 1. Standardized Pareto chart for the extraction of oils and fats.

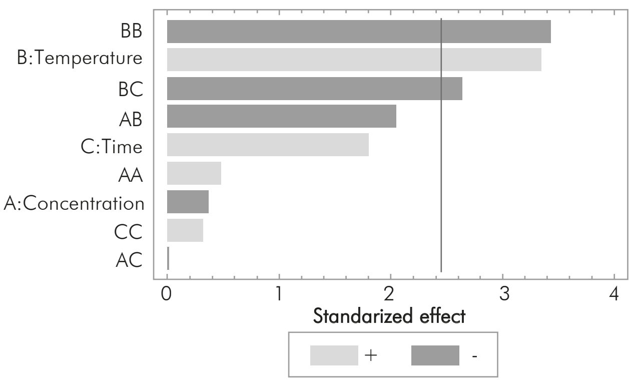

Figure 2. Standardized Pareto chart for the extraction of phenols.

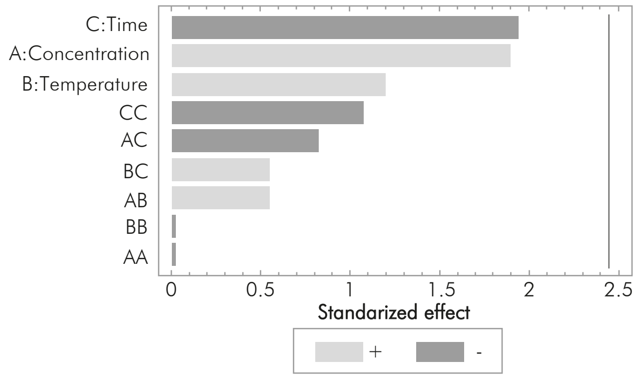

Figure 3. Standardized Pareto chart for the extraction of saponins

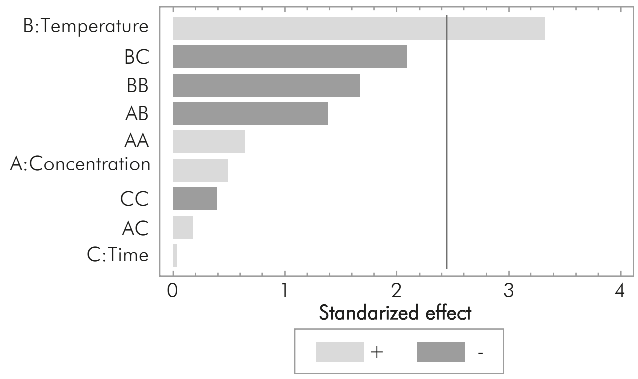

Figure 4. Standardized Pareto chart for the extraction of tannins.

Standardized Pareto charts indicated that only the temperature exerted a significant effect on the extraction of phenols and tannins. Likewise, the interaction between temperature and the extraction time has a slightly lower negative effect in the case of phenols, so that high temperatures during prolonged extraction time lead to low concentrations of phenols in the extract. According to the statistical analysis, no factor influenced the extraction of saponins, oils and fats. This is attributed to the range of the extraction conditions, which were established on the basis of an environmentally friendly and inexpensive methodology. A wider range of temperatures, ethanol concentrations and extraction times perhaps could evidence additional effects on the response variable.

Evaluation of the Corrosion Inhibition Activity

Corrosion inhibition efficiency was calculated using the values of weight loss in each plate after 24 hours, according to *Equation 1*. The results are shown in Table 3.

Table 3. Corrosion inhibition efficiency for different extract concentrations after 24 hours.

Extract #	Corrosion Inhibition Efficiency (%)			
	1% v/v	3% v/v	7% v/v	10% v/v
1	-101.03	-51.12	-18.90	-8.25
2	-107.90	-79.04	-27.49	36.77
3	-18.90	42.61	52.23	56.36
4	-106.87	-64.95	-30.58	-27.15
5	-77.66	-13.96	-4.47	-1.87
6	-13.40	7.90	8.93	16.49
7	12.37	12.71	14.47	14.78
8	-131.96	-125.43	-58.76	30.58
9	5.15	20.62	65.64	70.45
10	-126.12	-114.43	-54.76	-38.14
11	-96.22	-42.47	-31.62	-13.54
12	-120.62	20.62	46.05	59.97
13	-187.29	-134.36	-87.29	-75.26
14	-85.57	-46.05	8.45	43.44
15	-28.52	-21.31	-0.34	5.84
16	43.99	45.05	54.81	61.17

Many negative values of efficiency were obtained, which means that some of the extracts did not act as corrosion inhibitors, but rather accelerated the degradation process of the plates. This can be attributed to a possible decomposition of the organic compounds, which leads to the formation of acetic acid. This additional compound may induce a synergistic corrosive action along with the hydrochloric acid, accelerating the degradation rate of the plates (Amri, Gulbrandsen & Nogueria, 2008). Nevertheless, all of the extracts were proven to have higher efficiencies as their concentration increased in the corrosive medium. The highest inhibition (70.45%) was achieved by 10% v/v of extract # 9, which was prepared at 10% v/v of ethanol, 46°C and 4.3 hours of extraction time. Phenols and tannins were the substances with higher yield in this sample.

Data of corrosion inhibition efficiency were analyzed with the purpose of predicting the extraction conditions that would provide the highest corrosion inhibition efficiency. The response surface methodology was applied using STATGRAPHICS® Centurion XVI. The prediction was performed based on a quadratic regression model with ten coefficients. As a result, the following conditions were established: ethanol concentration: 16.1% v/v, operation temperature: 50.4°C; extraction time: 4.9 hours.

A final extract was prepared under these conditions. It was submitted to characterization tests (see Table 4) and its inhibition efficiency was assessed with the same methodology described above (See Table 5). Also, in order to determine the adsorption mechanism that describes the interaction between this organic compounds and the metal surface, an analysis by Langmuir isotherm of adsorption was carried out using the information of Table 5.

Table 4. Phytochemical characterization of the final extract (16.1 %v/v ethanol, 50.4°C, 4.9 h).

Compound	Yield (% w/w)
Oils and fats	0.006
Phenols	0.133
Saponins	0.006
Tannins	0.513

Both phenols and tannins were obtained around their highest proportions, while the yields of saponins, oils and fats remained at relatively low-intermediate values.

Table 5. Corrosion inhibition efficiency of final extract after 24 hours and Langmuir adsorption isotherm parameters.

C (% v/v)	CIE (%)	Inhibitor concentration C (mL/L)	Surface coverage θ	C/θ
1	17.73	10	0.1773	5.63
3	41.55	30	0.4154	7.22
7	75.81	70	0.7580	9.23
10	91.13	100	0.9113	10.97

As predicted, higher corrosion inhibition efficiencies were attained with the final extract. The highest efficiency was achieved with the highest extract concentration. The anticorrosive activity is mainly attributed to the presence of phenols and tannins (Rajalakshmi *et al.*, 2012), since these were the chemical species with the highest yield in the extract (see Table 4). Table 6 presents the corrosion inhibition efficiency reported for extracts of different natural species. The results indicated that cacao pod husk extracts present a high corrosion inhibition efficiency when compared to similar natural products, and therefore, the use of this agricultural residue as raw material for producing corrosion bio-inhibitors could be a viable alternative.

Table 6. Corrosion inhibition efficiency reported for natural species extracts

Extract	Inhibitor concentration	Corrosive medium	CIE (%)
Artemisia pallens[1]	40 g/L	HCl 4N	96.5
Ruta graveolens[2]	2 g/L	HCl 1M	94.34
Artemisia pallens[1]	1.5g/L	HCl 4N	93.48
Justicia gendarussa[3]	150 ppm	HCl 1M	93
Theobroma cacao	10% v/v	HCl 1M	91.13
Bifurcaria bifurcata[4]	50% v/v	HCl 1M	80
Tinospora crispa[5]	800 ppm	HCl 1M	78.14
Tinospora crispa[5]	1000 ppm	HCl 1M	73.33
Occimum viridis[6]	10% v/v	HCl 1M	66.89

[1]Kalaiselvi *et al.* (2010); [2]Mahir, Abdul-Wahab & Hussein (2014); [3] Satapathy *et al.* (2009); [4]Abboud *et al.* (2009); [5]Hazwan *et al.* (2011); [6]Oguzie (2006).

Likewise, the inhibition efficiency attained in this study was similar to the efficiency of *Theobromona* cacao peel polar extract obtained by Yetri *et al*. (2014). Although the extraction conditions and the metal subject to analysis in both studies were different. Table 7 summarizes the experimental conditions of each study.

Yetri *et al*. (2014) obtained a polar extract using methanol as solvent and other organic compounds to fractionate it, generating a solution rich in phenolic, aromatic rings and ether compounds, while the methodology applied in this study only uses an aqueous solution of ethanol, which renders this procedure more environmentally friendly and cheaper. On the other hand, although the metal used in this study is more prone to oxidation, the extract appears to be less stable as the achieved inhibition corrosion efficiency proved to be lower than the polar extract for a shorter exposure time. This is an assumption that could be tested later through electrochemical impedance spectroscopy.

Figure 5 shows the lineal regression of the Langmuir isotherm, obtained from the data of Table 5. An adsorption equilibrium constant K of 0.1906 L/mL was calculated according to *Equation 2*. Likewise, a standard heat of adsorption of -13.1680 kJ/mol was obtained with van't Hoff *Equation 3*. This value suggests that the inhibitor adheres to the metal surface by physisorption, which matches the results obtained for Yetri *et al*. (2014).

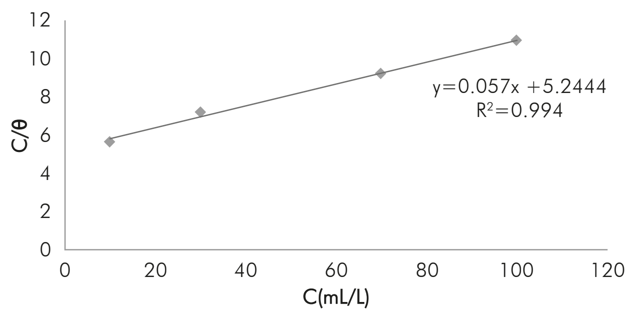

Figure 5. Langmuir isotherm of adsorption for the extract that showed the highest corrosion inhibition efficiency.

Table 7. Experimental conditions and results of studies about corrosion inhibition efficiency of extracts from *Theobroma cacao* pod husk.

Study	Extraction conditions				Corrosion test conditions			
	Solvent	Time	Chemical compounds	Metal	Media	Extract concentration	Exposure time	CIE (%)
Yetri et al., 2014	70% Methanol Hexane and ethyl acetate for fractionation	4 days	Phenols, aromatic rings and ethers	Mild Steel (0.3%C)	1.5M HCl	2.5%	768 h	96.03
This one	16.1% Ethanol	4.9 h	Phenols and tannins	A36 Steel (0.18%C)	1M HCl	10%	24 h	91.13

5. CONCLUSIONS

- Green corrosion inhibitors can be obtained from cacao pod husk by means of an extraction with ethanol and relatively low temperatures and extraction times. This represents an advantage regarding the implementation of an economic, environmentally friendly process, since neither expensive materials, nor toxic substances were required or produced. The anticorrosive activity of the extracts is related to the presence of antioxidants and substances of natural origin in the chemical composition of husks. Phenols and tannins were the predominant compounds in the extract that exerted the highest inhibition efficiency: thus, inhibitive action can be mostly attributed to these components. Analysis by Langmuir isotherm suggests that the inhibitor molecules adhered to the metal surface through physisorption.

- This work is one of the few studies conducted in the world about extracts from *Theobromona cacao* pod husk and their use as corrosion inhibitors. It represents a significant contribution as it provides scientific information related to the behavior of extract on A36 steel plates. Moreover, optimal operation conditions were determined based on a relation between the extraction conditions and corrosion inhibitor efficiency. However, more studies on this topic are required in order to settle the technical and economic viability of this alternative.

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