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Inhibitory action of rice husk extract (RHE) on the corrosion of carbon steel in acidic media

O Olawale[1*], A A Adediran[2], T Oyinbo[1], and O Kalawole[1]
[1]Department of Chemical Engineering, Landmark University, Omu-Aran, PMB 1001, Kwara State, Nigeria.
[2]Department of Mechanical Engineering, Landmark University, Omu-Aran, PMB 1001, Kwara State, Nigeria
*Corresponding author email: olawale.olamide@lmu.edu.ng/lamstock2@yahoo.com

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Abstract – The study investigates the inhibition characteristics of rice husk extract (RHE) on the corrosion of mild steel in 1M acidic media. Mass loss, Fourier Transform Infrared Spectroscopy (FTIR), phytochemical analysis were used as basis for studying the corrosion inhibition behaviour of the extracts. The analyses of the results showed that as concentration increases, there was increase in the inhibitor while increase in temperature reduces the inhibition respectively. Moreover, the highest inhibition efficiency was 94.24 % at 40 °C and 0.25 g/l inhibition concentration in sulfuric acid medium while inhibition efficiency of 89 % at 60 °C and 0.20 g/l inhibition concentration in hydrochloric acid. The thermodynamic parameters revealed that the adsorption of extract onto the metal surface was spontaneous. Langmuir isotherm best fits the data obtained suggesting physical adsorption as the adsorption mechanism between the extract and the mild steel substrate. The results from the FT-IR spectroscopy showed that the organic compounds found in Rice husk made it a good inhibitor.

Keywords: Rice husk, Adsorption mechanism, Corrosion, Inhibition, Weight loss, Phytochemical constituents.

Introduction

Inhibitors are commonly used to prevent metal dissolution as well as acid consumption and retard the corrosive attack on metallic materials. The electronic characteristic of the asdorbate molecules , the solution of chemical composition, the Nature of metallic surface, the temperature of the reactions, the immersion time and the electrochemical potential at the metal –solution interface determine the adsorption degree and hence the inhibition efficiency (Zarrouk *et al.*, 2010). Furthermore, corrosion inhibitors gives the benefits of longevity of process vessels, installations and facilities, reduced maintenance and replacement, and significantly reduced failure rates (Alaneme *et al.,* 2016).

Corrosion inhibitors are generally divided into inorganic and organic substances. Inorganic substances suitable as metal corrosion inhibitors must easily oxidise the metal to form an impervious layer which direct ions-metal interaction and hence retard the rate of metal dissolution in the medium. The presence of heteroatoms and/ or double bonds, large surface area and active centre; which upon adsorption on the metal surface will blanket a large area of the metal are features of the organic substances. Previously, authors such as Chidiebere *et al.*, (2012); Fouda *et al.*, (2006) and Achary *et al.*, (2008) have reported the use of inorganic (silicates, nitrates, nitrites, molybates, phosphates and borates) and organic (predominantly those with O, N, S and P heteroatoms) compounds as metal inhibitors in different corrosive environment. This has led the search to use of green chemistry as corrosion inhibitors that must be cheap, non-toxic, readily available and environmentally friendly (Lebe *et al.,* 2016).

Currently, research activities are geared towards finding a replacement for inorganic and organic metal corrosion inhibitors. Plants, however, are one of the sources for replacement of inorganic and organic inhibitors. Plant products are inorganic in nature and contain certain phytochemicals like: tannins, flavonoids, saponins, organic and amino acids, alkaloids and pigments which could be extracted by simple less expensive procedures. Extracts from different plants had been widely reported as effective and goo metal corrosion inhibitors in various environments.

The use of inhibitors has been widely explored to decrease corrosion of mild steel used in acidic environments because they form various types of films in several ways: by adsorption, by formation of bulky precipitates, and/or by the formation of passive layer on the metal surface (Karim *et al.*, 2016). However, due to limited solubility and toxic properties of the inorganic salts or organic compounds which are proven as good inhibitors because they contain nitrogen, salts or nitrogen, awareness of their ecological and health risks has drawn

researchers to explore more environmentally friendly inhibitor sources. These sources are natural products which are non-toxic, cheaply processed, biodegradable and readily available in plenty and are sometimes regarded as agro-waste. The yield of these compounds as well as the corrosion inhibition abilities vary widely depending on the part of the plant and its geographical location while its efficiency is justified by the phytochemical compound present there in with molecular and electronic structures bearing close similarity to conventional organic inhibitor molecules.

In this regard, plant based inhibitors such as elephant grass (Alaneme *et al.*, 2016); tobacco leaves (Bhawsar *et al.*, 2015); Jatropha stem (Olawale *et al.*, 2016); coconut shell (Daramola *et al.,* 2015); cashew waste (Olawale *et al.*, 2015); Lebe *et al.*, (2016) Pentaclethra Macrophyla Benthsm Roots; among many others had recorded varied levels of success while research efforts are still ongoing to source for greener inhibitor alternatives. Mild steels are industrially important especially in water transportation as conveying tanks, marine vessels, petrochemical septic tanks and oil well oxidizing system. However, it has low corrosion resistance especially in acidic medium (Alaneme *et al.*, 2016). The disadvantages of corrosion has been found to cause plant shutdowns during important processes in industries, loss of products through leaking of pipes, loss if efficiency; contamination of finished products thereby shortening the life; and hazardous to human, animals and biological life; collapse of buildings and contamination of waterbodies. It has brought about the staggering cost in maintenance of automobiles, aircrafts, concrete, gas and liquid transformation in pipelines as well as aging and deteriorating infrastructures (Ahmed, 2006). Hence, the present work investigates the inhibitory effect of rice husk extracts (RHE) as corrosion inhibitor for mild steel in H_2SO_4 and HCl acid media.

Materials and Methods

Materials

Rice husk (RH) was obtained from Igbemo Ekiti, Ekiti State, Nigeria and mild steel of composition: C 0.2, P 0.024, Si 0.003, Mn 0.35, bal Fe. The mild steel was mechanically cut into coupons of dimensions 50 mm × 40 mm × 2 mm. the surface treatment was done by degreasing the coupons suing absolute ethanol, followed by drying in acetone. An analytical grade of HCl and H_2SO_4 was used, the prepared samples were stored in the desiccator.

Preparation of Extract

RHE first was pulverized, about 20 g of the husk was weighed and soaked in 100 ml of 1 M H_2SO_4 and 1 M HCl for 3 h in a water bath at temperature of 40 °C and 90 °C respectively. The mixture was then left to cool overnight and then filtered to obtain the extract. The filtrates obtained represents the extract stock solution.

Inhibitor Concentration Preparation

The analytical grade HCl and H_2SO_4 respectively were diluted with distilled water for the preparation of the electrolytes. The stock of the RHE obtained was used in preparing different concentrations of the extract by dissolving 0, 10, 15, 20 and 25 ml /100 ml for both 1 M H_2SO_4 and HCl respectively.

Weight loss measurement

The method involves exposing a specimen of metal (the coupon) to a process environment for a given period. The weight loss taking place over the period of exposure being expressed as corrosion rate (Olawale et al. 2016). The weight of the samples were recorded using an electronic weighing balance (HX

302T with 0.01g accuracy). After weighing, the mild steel was placed inside the 250 ml capacity beakers containing 100 ml of the inhibitor solutions maintained at 40 °C (313 K) and 60 °C (333 K) in the water bath respectively. The coupons were placed in the solutions for 3 h and covered with aluminum foil after which the coupons were retrieved from the solution, cleaned with ethanol and then reweighed. The experiments was carried out in duplicates to ensure reproducibility. The corrosion rate and inhibition efficiency were calculated using equation 1 and 2.

$$\boldsymbol{CR} = \frac{\boldsymbol{\Delta W}}{\boldsymbol{A.T}} = \frac{\mathbf{W_1 - W_2}}{\mathbf{A.T}} \qquad (1)$$

$$\boldsymbol{I.E}(\%) = \left(\frac{CR_1 - CR_2}{CR_1}\right) \times 100\% \qquad (2)$$

where W_1 is the weight of mild steel before immersion.
W_2 is the weight loss of mild steel after immersion.
A is the surface area of the coupon in cm^2.
T is the period of immersion in h.
I.E (%) is inhibition efficiency
CR_1 is corrosion rate of mild steel coupons in the absence of inhibitors
CR_2 is the corrosion rate of mild steel coupons in the presence of concentration of inhibitors

Surface Analysis

Analysis was carried out on RHE using a Fourier Transform Infra-red (FT-IR) spectrophotometer. The FT-IR was used to evaluate the molecular structure and active group of the inhibitor. This is to observe the reaction between the adsorbed inhibitor and mild steel surface in acidic environment (Karim et al., 2016).

Results and Discussion

Phytochemical analysis Result

The result of the phytochemical analysis showed that RHE contained some organic substances which are responsible for the inhibitive ability. According to Deng and Xianghong (2012) the inhibitive property is due to the presence of these complex organic species. Phytochemical constituents of RHE are as shown in Table 1.

Table 1. Phytochemical test For Rice Husk

Constituents	Alkaloids	Saponins	Tannins	Flavonoids
Presence	-	+	+	+
Indication	Turbidity of the resulting precipitate	The formation of stable foam ,	The formation of a green precipitate	The formation of a yellow precipitate

Evaluation of corrosion parameters

The use of RHE in H_2SO_4 at 40 °C showed that inhibitor efficiency increases from 0 % to 94.24 % while there was decrease in corrosion rate from 0.035 (g/cm^{2-} h) to 0.023 (g/cm^{2-} h) on the coupon from 0.10 g/l to 0.25 g/l inhibitor concentration. Furthermore, similar trend was also observed at temperature of 60 ^{o}C with increase in inhibitor efficiency as the concentration increases. Moreover, a decrease in corrosion rate from 0.0578 (g/cm^2 h) to 0.0147 (g/cm^2 h) was also observed within the aforementioned temperature regime. The inhibitor efficiency at 40 °C from 0.10 g/l to 0.25 g/l inhibitor concentration was significantly greater than that of 60 ^{o}C which demonstrated that increase in temperature increases corrosion rate and decreases inhibitor efficiency. The use of rice husk in HCl at 40 °C gave inhibitor efficiency increases up to 82.65 % with a decrease in corrosion rate from 0.182 (g/cm^2 h) to 0.032 (g/cm^2 h) on the coupon from 0.10 g/L to 0.25 g/L inhibitor concentration. However, at temperature of 60 °C, it was observed that there was an increase in inhibitor efficiency from 0 % to 89 % while decrease in corrosion rate from 0.372 (g/cm^2 h) to 0.046 (g/cm^2 h) on the coupon respectively. A fluctuation in the inhibitor efficiency was observed as 0.10 g/L and 0.25 g/L inhibitor concentration gave efficiency of 87.5 % and 0.20 g/L inhibitor concentration gave 89 % inhibition.

Table 2. Comparison of the concentration of RHE in HCl, mass loss, corrosion rate and inhibition efficiency during the corrosion of mild steel.

Concentration of RHE, g/l	Mass loss, g		Corrosion rate, (g/cm^2 h)		Inhibition efficiency,%	
	40 °C	60 °C	40 °C	60 °C	40 °C	60 °C
0	0.98	2.0	0.1823	0.372	0	0
0.10	0.32	0.25	0.0595	0.0465	67.35	87.5
0.15	0.23	0.31	0.0428	0.0577	76.53	84.5
0.20	0.29	0.22	0.0353	0.0409	80.61	89
0.25	0.17	0.25	0.0316	0.0465	82.65	87.5

Table 3. Comparison of the concentration of RHE in H_2SO_4, mass loss, corrosion rate and inhibition efficiency during the corrosion of mild steel.

Concentration of RHE, g/l	Mass loss, g		Corrosion rate, (g/cm^2 h)		Inhibition efficiency,%	
	40 °C	60 °C	40 °C	60 °C	40 °C	60 °C
0	0.0405	2.0	0.0405	0.0578	0	0
0.10	0.0035	0.25	0.0035	0.0160	91.36	72.33
0.15	0.003	0.31	0.03	0.01567	92.59	72.91
0.20	0.0025	0.22	0.025	0.0150	93.83	74.06
0.25	0.00233	0.25	0.00233	0.0147	94.24	74.64

Corrosion rate and mass loss were found to increase up to a concentration of 0.15 g/L of RHE, while the inhibition efficiency was found to increase as the concentration of the media increased. It could be inferred from Table 2 and 3 that the corrosion inhibitors solution strength was influential in promoting corrosion. It appears as the concentration of RHE increased, there were more species in the solution to corrosively attack the substrate surface, thus increasing the corrosion rate. The reduction observed in the inhibition efficiency as the concentration reduces may be attributed to the reduction in active sites created by the species, thus, resulting in less effective adsorption. As presented in Table 2 and 3, the variation in concentration, corrosion rate, inhibition efficiency and mass loss. From the results, it is evident that the inhibition efficiency increased, while the corrosion rate reduced with increase in concentration of RHE. As previously reported, the decrease in corrosion rate may be due to the ability of inhibitor to be absorbed on the substrate. Researchers have noted that the inhibitive mechanism of most organic compounds is based on their adsorption at the corroding metal surface (Elewady et al., 2008; Ebenso et al., 2010; Obot et al., 2011).

Adsorption behaviour

Model such as Langmuir, Frumkin, Flory-huggins, Temkin, Bockris-Swinkles and Freundlich among other adsorption isotherm are usually used to describe adsorption (Oguzie, 2007). However, Langmuir adsorption fits the interaction between the metal surface and the inhibitor used in the present study.

The degree of surface coverage (□) was obtained from equation (3), I.E = □ × 100. The evaluated values from the ratio of inhibitor concentration to surface coverage was used by the Langmuir adsorption isotherm which can be expressed as:

$$\frac{C}{\theta} = \frac{1}{\text{Kads}} + C \tag{3}$$

From equation (3), C is the inhibitor concentration, θ is the surface coverage and Kads is the equilibrium constant of the inhibitor adsorption process. Langmuir adsorption model operates on the assumption that adsorption takes place only at specific homogeneous sites of metal surface and that the adsorption forms a monolayer (Langmuir, 1917). The representative values of the adsorption is presented in Figure 1 and 2 showing the plot of $\frac{C}{\theta}$ versus C. the plot gave a straight line with a room mean square values of 0.979 at 313 K and 0.999 at 333K for the sulfuric medium while 0.999 at 313K, and 0.999 at 333K for HCl medium, all these describes the linearity of the plot.

The free energy ΔGads was related to the Kads using the equation in (4) as reported by researchers (Obiukwu et al., (2013); Rani and Basu, 2012)

$$Kads = (1/55.5)\ \mathrm{Exp}\ (-\Delta Gads/RT) \tag{4}$$

From equation (4), the free energy of adsorption showed a negative value. The negative values of ΔGads suggest that the adsorption of RHE onto the steel surface is a spontaneous process. Thus, the data in Table 4 corroborate this.

Table 4. Variation in concentration and heat of absorption

Concentration of RHE, g/L	Q_{ads} H_2SO_4	Q_{ads} HCl
0.1	-60.46	-52.89
0.15	-66.46	-22.24
0.20	-72.36	-52.97
0.25	-74.23	-16.65

Effect of Temperatures

Further analysis was done on the temperature dependence of the inhibitor efficiency as well as comparison of heat of adsorption in order to understand the possible mechanism of inhibitor adsorption. It was reported by Popova et al., (2003) that a rise in temperature leads to a decrease in the inhibition efficiency resulting in a corresponding increase in corrosion activation energy in the presence of an inhibitor. This trend was reported to be physical absorption. Equation (5) gives the relationship between heat absorption with respect to surface coverage and temperature respectively.

$$Q_{ads}=2.303R\left[\log\left(\frac{\theta 2}{1-\theta 2}\right)-\log\left(\frac{\theta 1}{1-\theta 1}\right)\right]\frac{T1T2}{T2-T1} \tag{5}$$

where θ_2 and θ_1 are the surface coverage at temperature 333 K and 313 K respectively. It was found that the adsorption of RHE species on the steel surface is an exothermic process attributed to a negative value of heat adsorption. Hence, the earlier proposed physical adsorption mechanism is valid.

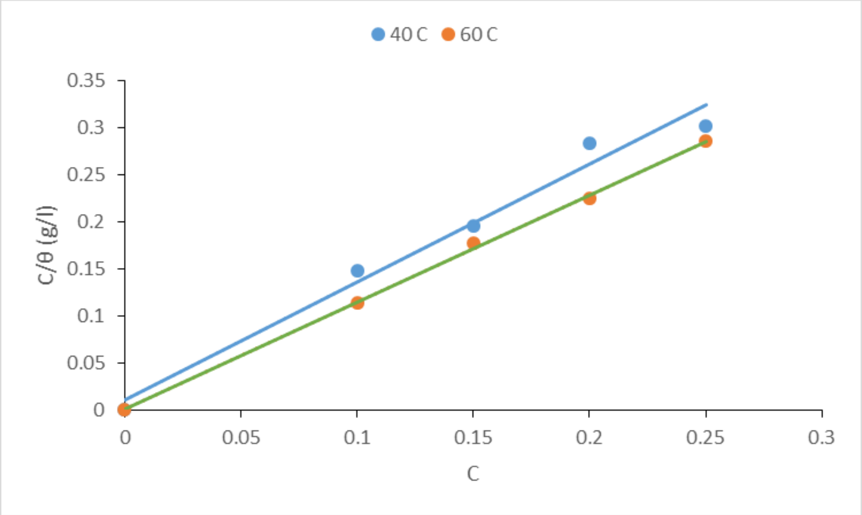

Figure 1. Langmuir adsorption plot for mild steel in 1M HCl containing RHE at 40 °C and 60 °C

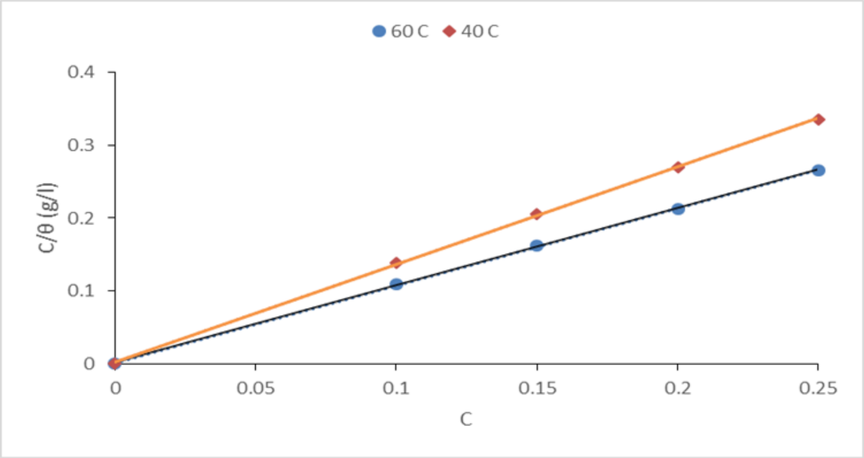

Figure 2. Langmuir adsorption plot for mild steel in 1M H_2SO_4 containing RHE at 40 °C and 60 °C

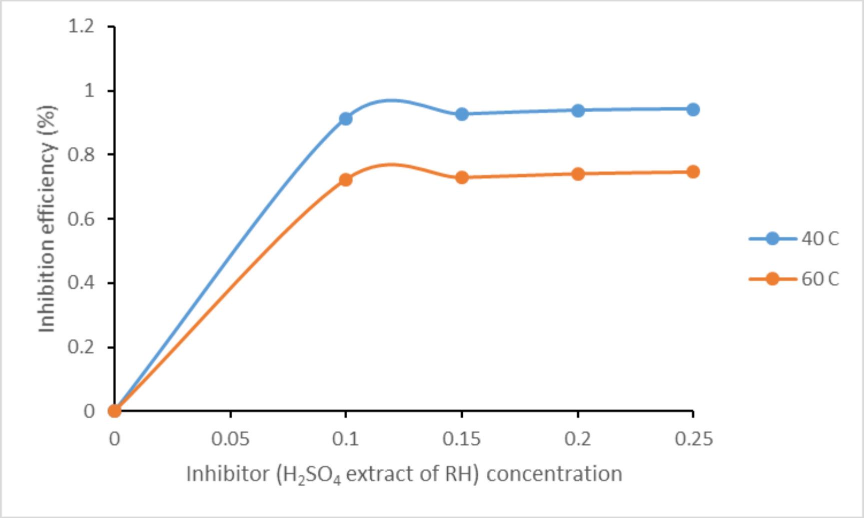

Figure 3: Variation of inhibition efficiency (%) against inhibitor concentration in H_2SO_4

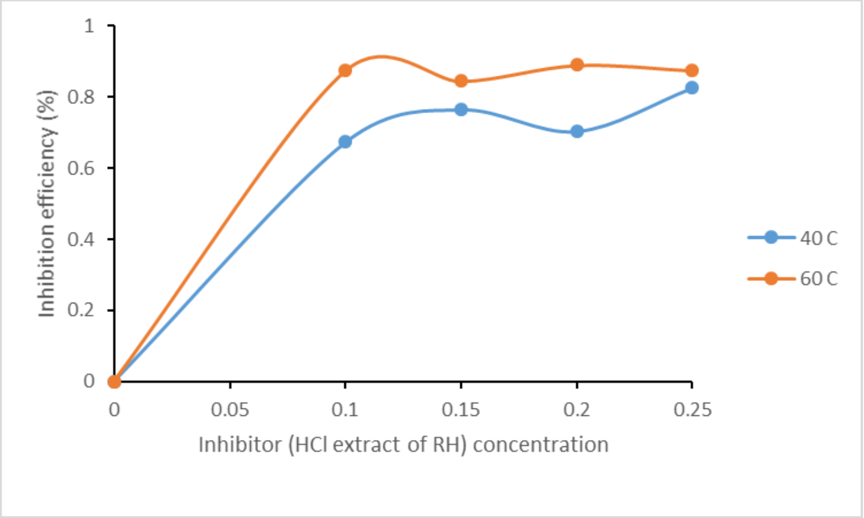

Figure 4: Variation of inhibition efficiency (%) against inhibitor concentration in HCl

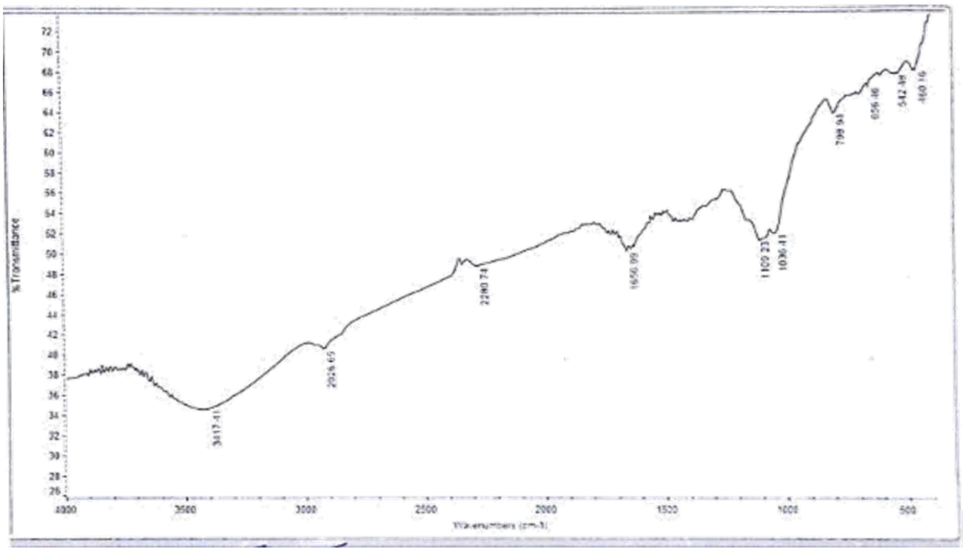

Figure 5. FTIR spectrum of RHE

A representative spectrum of the rice husk extract (RHE) is as presented in Figure 5. From the Figure, the peak showing the stretching vibration of hydroxyl (-OH) group at 2926.65 cm^{-1} observed. Also, the peak for group -CO stretching vibrations at both 1100.23 and 1036.41 cm^{-1}, and finally a small peak attributed to group C=C stretching vibration at 2926.65 cm^{-1} was revealed in the IR spectrum. These ranges have been identified rice husk as a phenolic compound, a similar result was reported by Saratha and Vasudha (2010). From their findings, they concluded that the adsorption of the compounds present on the metal surface creates a barrier for charge and mass transfer leading to a decrease in the interaction between the metal and the corrosive environment.

Conclusions

This study investigated the inhibitory action of rice husk extract on the corrosion of carbon steel in acidic media. From the result, the inhibition efficiency increases with a corresponding increase in concentration of the RHE. A spontaneous process was the adsorption of the extract onto the substrate as confirmed by the thermodynamic parameters. Langmuir models best fitted into the results obtained and the IR spectrum corroborate the functional groups present in the extract

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