PHYTOCHEMICALS AND INHIBITIVE PROPERTIES OF CASHEW EXTRACT AS CORROSION INHIBITOR OF ALUMINIUM IN H_2SO_4 MEDIUM

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***Abstract*— This work studied the phytochemicals and inhibitive properties of cashew extract as corrosion inhibitor of aluminium in H_2SO_4 medium. Qualitative and quantitative analyses of the cashew extract were carried out to identify and quantify the phytochemicals for the corrosion inhibition process. Thermometric and gravimetric techniques were employed in the study of corrosion inhibition of aluminium in H_2SO_4 medium. The inhibition efficiency of the cashew extract was modeled using Response Surface Methodology (RSM) of Design Expert Software 9. It was revealed that phytochemicals of alkaloids, cardiac glycosides, flavonoids, phenolics, phytates, saponins and tanins were present in the cashew extract at various degrees. The cashew extract is predominantly made of flavonoids (425.0mg/100g) followed by alkaloids (221.7mg/100g).Adsorption of the cashew extract on the Al surface obeyed physical adsorption mechanism. Thermometric and gravimetric techniques are in agreement of recording high inhibition efficiencies of 83.7% and 82.5% respectively. The phytochemicals of the cashew extract are good inhibitive agents for the corrosion control process. A quadratic model is adequate for the description of the inhibition efficiency of the cashew extract as a function of inhibitor concentration, temperature and time.**

***Keywords*— Aluminium, Cashew, Corrosion, H_2SO_4, Phytochemicals**

I. INTRODUCTION

Corrosion inhibition of metals by eco-friendly phytochemicals of plant extract is a viable corrosion control technique. Phytochemicals can be correlated to the antioxidant capacity of plant (Mello and Kubota, 2014; Azari *et al.*, 2015). Corrosion control of aluminium is of great importance because of its high technological value and industrial applications. Aluminium is used for the construction of reaction vessels, pipes, machinery and chemical batteries because of its advantages of low cost, lightness and good corrosion resistance at moderate temperatures (Refat and Ishaq, 2013; El-Maghraby, 2009). Passive oxide film formed on aluminium surface is responsible for its resistance to corrosion, but the surface film is amphoteric and dissolves substantially when the metal is exposed to high concentrations of acids or basses (Li and Deng, 2012; Aggarwal, 2010). Aluminium structure corrodes as a result of electrochemical reaction with its environment. Pickling, descaling and cleaning operations are often carried out in industries to prolong the life span of the aluminium structures. Acid medium such as H_2SO_4 used for such maintenance operations often corrodes the structures.

Previous corrosion inhibition studies of aluminium include the examination of the influence of three selected polyacrylic acids on the corrosion inhibition of aluminium (Amin *et al*, 2009). The measurements were conducted under different conditions using chemical and electrochemical techniques, complemented with energy dispersive x-ray examinations of the electrode surface. The inhibition efficiencies of the inhibitors increased with increase in concentration, molecular weight and immersion time. Corrosion inhibition of aluminium in hydrochloric acid by anionic polyeletrolyte pectates as water-soluble natural polymer polysaccharide was investigated (Refat and Ishaq, 2013). Weight loss and gasometric techniques were used in the study. It was observed that inhibition efficiency increased with increase in inhibitor concentration and decreased with increase in temperature. From the review of previous reports, there is need to employ inhibitor of plant origin with suitable phytochemicals and inhibitive properties as additive in the maintenance operations. The aim of this work is to study the phytochemicals and inhibitive properties of cashew extract as corrosion inhibitor of aluminium in H_2SO_4 medium.

II. METHODS

Analytical grade of 1.0 M H2SO4 was used in this study. Leaves of cashew (Anacardium occidentale) were obtained from Akpugo, Enugu State, Nigeria. The cashew leaves were sun-dried for three days. The dried leaves were ground to increase the surface area and stored in closed containers. 30 grams of the ground cashew leaves (fineness; particle size of 0.85mm) were measured and soaked in 1000ml of ethanol (99.7% v/v) for 48 hours. At the end of the 48 hours, the mixture was filtered. The cashew leaves extract was obtained by evaporating the ethanol from the filtrate. The extract was used for the corrosion inhibition study. The Al coupons with chemical composition of Si (0.25%), Fe (0.02%), Zn (0.05%), Mn (0.04%) Mg (0.03%), V (0.04%), Ti (0.02%), Cu (0.03%), Cr (0.02%) and Al (99.5%) were cleaned followed by polishing with emery paper. The coupons were degreased with acetone and finally washed with distilled water, dried in air and then stored in desiccators.

A. Phytochemical Analysis of the Cashew Extract

Methods used by Marcano and Hasenawa (1991) and Mayuri (2012) were adopted for the qualitative and quantitative analyses of the cashew phytochemicals. The solvent free extract obtained was subjected to qualitative test for the identification of various constituents of the sample. For the alkaloids detection, small portion of solvent free cashew extract was transferred in to test tube. Few drops of dilute hydrochloric acid were added and stirred. It was then filtered. The filtrate was tested carefully with alkaloid reagents; Mayer´s reagent (Cream ppt), Dragendorf´s reagent (Orange-brown ppt). In the detection of cardiac glycosides, 1ml of the extract, 5ml water and 2ml glacial acetic acid were mixed in a vessel. One drop of $FeCl_3$ was added. Then, 1 ml conc. H_2SO_4 was added. There was appearance of brown ring. For the determination of flavonoids, 25 ml water was added to 1g of sample. It was put in oven at 100ºC for 15 min. 5ml of NH_4OH was added to 2ml of the extract. Then 1ml conc. H_2SO_4 was added. There was appearance of yellow colour.

The presence of phenolics was determined by adding a few drops of 1% (w/v) solution of ferric chloride followed by 1% (w/v) gelatin in sodium chloride of the same concentration. The formation of a precipitate indicated the presence of phenolics. For the determination of saponins, 1 g of sample was boiled in 40ml of water, and it was filtered. 10 ml of the filtrate was shaken vigorously. Formation of froth was noticed. 3 drops of oil were added, and the mixture was shaken. Emulsion of the oil was noticed. For the determination of tannins, 1g of the sample was added to 25 ml of water. It was then put in oven at 100ºC for 15 min. To 1 ml of the extract, 10 ml water was added and then boiled. A few drops of 0.1% $FeCl_3$ were added. A green colour appeared.

B. Thermometric method of study

In the thermometric method of study, the aluminium samples were immersed in beakers containing inhibited and uninhibited H_2SO_4 medium. The beakers were placed in thermostat set at 30ºC. The progress of the corrosion reaction was monitored and the temperatures of the system containing the aluminum and the test solution were regularly recorded until a steady temperature value was obtained. Equations (1) and (2) were used for the determination of the reaction number and inhibition efficiency (Mabrouk *et al*., 2011; Eddy *et al*., 2012; Omotioma and Onukwuli, 2016).

$$RN = \frac{T_m - T_i}{t} \quad (1)$$

where T_m and T_i are the maximum and initial temperatures (in ^{0}C) respectively, and t is the time in minutes elapsed to reach T_m.

$$IE\% = \left(1 - \frac{RN_{add}}{RN_{free}}\right) * 100 \quad (2)$$

where RN_{free} and RN_{add} are the reaction numbers for the Al dissolution in free and inhibited H_2SO_4 medium, respectively.

C. Gravimetric method of study

Gravimetric method of study was carried out using one factor at a time and response surface methodology. Thermodynamic parameters of activation energy, heat of adsorption and free Gibbs energy of the corrosion inhibition process were determined. Central composite design of Design Expert Software was employed in the response surface methodology. The weight loss (Δw), corrosion rate (CR), inhibition efficiency (IE) and degree of surface coverage were calculated using standard equations of (3), (4), (5) and (6) respectively.

$$\Delta\omega = \omega_i - \omega_f \quad (3)$$

$$CR = \frac{\omega_i - \omega_f}{At} \quad (4)$$

$$IE\% = \frac{\omega_0 - \omega_1}{\omega_0} * 100 \quad (5)$$

$$\theta = \frac{\omega_0 - \omega_1}{\omega_0} \quad (6)$$

where ω_i and ω_f are the initial and final weight of Al samples respectively; ω_1 and ω_0 are the weight loss values in presence and absence of inhibitor respectively. A is the area and t is the time.

III. RESULTS AND DISCUSSION

A. The Qualitative and Quantitative Results of the Cashew Phytochemicals

The qualitative and quantitative analyses of the cashew extract are shown in Table 1. Phytochemicals of alkaloids, cardiac glycosides, flavonoids, phenolics, phytates, saponins and tanins were present in the extract at various degrees. The extract is predominantly made of flavonoids (425.0mg/100g) followed by alkaloids (221.7mg/100g). The presence of these phytochemicals is an indication that the extract can inhibits corrosion of aluminium in the H_2SO_4.

B. The Results of the Thermometric Method

The results of the thermodynamic measurements are presented in Table 2. Increase in concentration increases the inhibition efficiency of the cashew extract. The inhibition

Table 1: Analyses of the cashew extract.

Phytochemicals	Qualitative analysis	Quantitative analysis
Alkaloids (mg/100g)	+	221.7
Cardiac glycosides (mg/100g)	-	10.0
Flavonoids (mg/100g)	+++	425.0
Phenolics (GAE/g)	++	38.0
Phytates (mg/100g)	++	78.3
Saponins (mg/100g)	++	36.7
Tannins (mg/100g)		86.7

+++ (highly concentrated), ++ (concentrated), + (in traces), - (absence or too little to be observed qualitatively).

Table 2: Effect of concentration of the cashew extract on the IE (%) of Al in H_2SO_4 Medium

C (g/l)	RN (0C/minutes)	IE (%)
0.0	0.0267	
0.2	0.0129	51.6
0.4	0.0105	60.8
0.6	0.0071	73.4
0.8	0.0054	80.0
1.0	0.0043	83.7

C = Inhibitor (cashew extract) concentration,
RN = Reaction number, IE = Inhibition efficiency

Table 3: The inhibition efficiency (*IE*) of Al in H_2SO_4 with cashew leaves extract.

C (g/l)	*IE* (%) at 303K	*IE* (%) at 318K	*IE* (%) at 33 K
0.2	50.0	45.0	44.4
0.4	57.5	55.0	47.8
0.6	75.0	61.7	55.6
0.8	82.5	66.7	58.9
1.0	82.5	71.7	63.3

C = Inhibitor (cashew extract) concentration, *IE* = Inhibition efficiency.

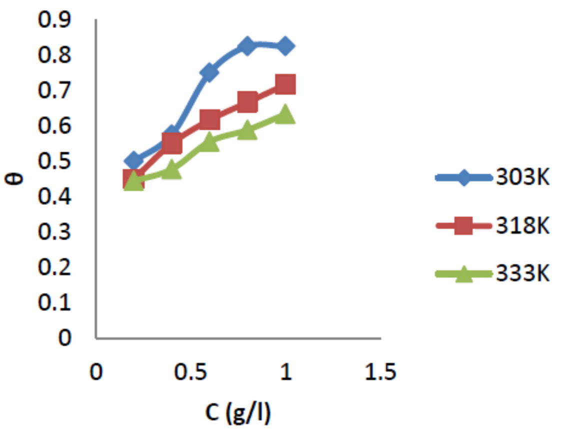

Figure 1: Degree of surface coverage (θ) versus inhibitor concentration (C).

efficiency is a function of the reaction number in absence and presence of the cashew extract. Highest inhibition efficiency of 83.74% was obtained, indicating that cashew extract is a suitable inhibitor for corrosion control of Al in H_2SO_4 Medium.

C. The Results of the Weight Loss Method

Inhibition efficiency as a function of concentration and temperature is presented in Table 3. Inhibition efficiency increases with increase in concentration of the extract, but decreases with increase in temperature. Similar trend is exhibited in the plot of degree of surface coverage versus concentration of the inhibitor (Fig. 1). The degree of surface coverage increases with increase in concentration but decreases with increase in temperature. It should that adsorption of the extract on the aluminium surface is concentration and temperature dependent.

D. Thermodynamic Parameter for the Adsorption Process

The activation energy and heat of adsorption for the corrosion inhibition of Al in H_2SO_4 with cashew extract are presented in Table 4. Linearized Arrhenius model of Eq. (7) was used to determine activation energy, E_a ($kJmol^{-1}$), while Eq. (8) was employed to evaluate the heat of adsorption, Q_{ads} ($kJmol^{-1}$) (Octave, 2003; Orubite-Okorosaye and Oforka, 2004; Nwabanne and Okafor, 2011; Nnanna *et al.*, 2013). The negative sign in the values of the heat of adsorption indicate an exothermic reaction process.

$$ln\left(\frac{CR_2}{CR_1}\right) = \left(\frac{E_a}{2.303R}\right)\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \quad (7)$$

$$Q_{ads} = 2.303R\left[log\left(\frac{\theta_2}{1-\theta_2}\right) - log\left(\frac{\theta_1}{1-\theta_1}\right)\right] + \frac{T_2T_1}{T_2-T_1} \quad (8)$$

Table 4: The E_a and Q_{ads} for the corrosion inhibition of Al in H_2SO_4 with cashew extract.

C (g/l)	E_a (kJ/mol)	Q_{ads} (kJ/mol)
0.2	58.39	-6.246
0.4	66.31	-10.94
0.6	88.50	-24.48
0.8	105.3	-33.31
1.0	98.27	-28.08

C = Inhibitor (cashew extract) concentration, E_a = Activation energy, Q_{ads} = Heat of adsorption.

where corrosion rates of the Al at T_1 and T_2 are CR_1 and DR_2, R is the gas constant, θ_1 and θ_2 are the degree of surface coverage at temperatures T_1 and T_2, respectively.

The data obtained for the degree of surface coverage were used to test the suitability of adsorption isotherms of Langmuir, Frumkin, Temkin and Flory-Huggins isotherms expressed in Eqs. (9), (10), (11) and (12), respectively (Nwabanne and Okafor, 2011; Li and Deng, 2012; Alinnor and Ejikeme, 2012; Patel *et al*, 2013; Omotioma and Onukwuli, 2016). The free energy of adsorption (ΔG_{ads}) was calculated using Eq. (13).

$$log\left(\frac{C}{\theta}\right) = logC - logK \quad (9)$$

$$log\left((C) * \left(\frac{\theta}{1-\theta}\right)\right) = 2.303logK + 2\alpha\theta \quad (10)$$

$$\theta = -\frac{2.303logK}{2\alpha} - \frac{2.303logC}{2\alpha} \quad (11)$$

$$log\left(\frac{\theta}{C}\right) = logK + xlog(1-\theta) \quad (12)$$

$$\Delta G_{ads} = -2.303RT\ log(55.5K) \quad (13)$$

where K is the adsorption equilibrium constant, C is the concentration of the inhibitor, θ is the degree of surface coverage, α is the lateral interaction term describing the interaction in adsorbed layer, a is the attractive parameter, R is the universal gas constant and T is temperature.

The values of the correlation of determination (R^2) suggest that the adsorption of the extract is a physical adsorption process. The isotherm properties indicate that there was attraction between the extract and the aluminium surface. From the Temkin adsorption isotherm, the attractive parameter values (a) were negative, -2.2 and -4.2 at temperatures of 303K and 333K respectively. This is an indication that repulsion exists in the adsorption layer (Nnanna *et al.*, 2013). The layer of the extract is bulky because of positive values of the size parameter (x); 0.8 and 2.7 at temperatures of 303K and 333K respectively. The free energy of adsorption is less than -40 kJ/mol. It showed that the adsorption of the cashew extract on the Al surface obeyed physical adsorption mechanism. These findings are in agreement with previous report (Omotioma and Onukwuli, 2016).

E. The Results of the Response Surface Methodology (RSM)

The RSM results of weight loss, corrosion rate and inhibition efficiency as function of concentration, temperature and time are presented in Table 6. The weight loss, corrosion rate and inhibition efficiency were concentration, temperature and time dependent. Highest inhibition efficiency of 82.5% was obtained at *1g/l*, 303K and 24h period of immersion. It shows that the phytochemicals of

Table 5: Parameters for the corrosion inhibition of Al in H_2SO_4 by cashew extract.

AI	*T*	R^2	*K*	ΔG_{ads}	*IP*	
Langmuir	303	0.996	0.77	-9.5		
	333	1.000	0.59	-9.6		
Frumkin	303	0.985	0.08	-3.6	α	1.9
	333	0.972	0.05	-2.8		2.6
Temkin	303	0.932	41.2	-19.5	*a*	-2.2
	333	0.937	182	-25.5		-4.2
Flory-Huggins	303	0.830	3.54	-13.3	*x*	0.8
	333	0.879	8.72	-17.1		2.7

AI = Adsorption Isotherm, *T* = Temperature (K), R^2 = Correlation of determination, *K* = Equilibrium constant, ΔG_{ads} = free energy of adsorption (kJ/mol), *IP* = Isotherm property, α = lateral interaction term describing, *a* = attractive parameter, *x* = size parameter.

Table 6: The RSM result of the corrosion inhibition of Al in H_2SO_4 by cashew extract.

S	*R*	*IC*	*T*	*t*	Δw	*CR*	*IE* $\pm$0.01
1	1	0.2	303	8	0.01	0.08	35.0
15	2	0.6	318	16	0.02	0.06	53.5
10	3	1.0	318	16	0.01	0.04	69.8
9	4	0.2	318	16	0.03	0.08	37.2
19	5	0.6	318	16	0.02	0.06	53.5
18	6	0.6	318	16	0.02	0.06	53.5
3	7	0.2	333	8	0.03	0.17	27.0
4	8	1.0	333	8	0.02	0.11	54.0
6	9	1.0	303	24	0.01	0.02	82.5
7	10	0.2	333	24	0.05	0.10	44.4
13	11	0.6	318	8	0.01	0.08	43.5
8	12	1.0	333	24	0.03	0.07	63.3
5	13	0.2	303	24	0.02	0.04	50.0
20	14	0.6	318	16	0.02	0.06	53.5
17	15	0.6	318	16	0.02	0.06	53.5
16	16	0.6	318	16	0.02	0.06	53.5
12	17	0.6	333	16	0.03	0.09	52.4
14	18	0.6	318	24	0.02	0.05	61.7
2	19	1.0	303	8	0.01	0.04	65.0
11	20	0.6	303	16	0.01	0.02	74.1

S = standard (Std), *R* = Run, *IC* = Inhibitor concentration (g/l), *T* = Temperature (K), *t* = Time (hr), Δw = Weight loss (g), *CR* = Corrosion rate (mg/cm2hr), *IE* = Inhibition efficiency (%).

the cashew extract are good inhibitive agents for corrosion control of aluminium in H_2SO_4 medium. The plot of predicted versus actual inhibition efficiency is shown in Fig. 2. The points clustered along the line of best fit, indicating high level of correlation between the predicted and the actual values.

Effects of the considered factors on the inhibition efficiency of the cashew extract were further analyzed using three-dimensional (3-D) diagrams. The interactions between inhibitor concentration and temperature, concentration and time, and temperature and time are shown in Figs. (3), (4) and (5) respectively. 3-D plot and numerical optimization tools of the design expert software were used to obtain the optimum inhibition efficiency of 79.1±0.01% at optima inhibitor concentration of 0.94g/l, temperature of 305.3K and time of 23.5hrs. With the optimum parameters, adequate repulsive force exists at the adsorption layer, which prevents dissolution of any kind.

The mathematical model (in coded form) of the inhibition efficiency as a function of concentration (A), temperature (B) and time (C) is expressed in Eq. (14):

$$IE = +54.9 + 14.1A - 6.5B + 7.7C - 2.1AB - 0.7AC - 0.7BC - 3.5A^2 + 6.2B^2 - 4.4C^2 \quad (14)$$

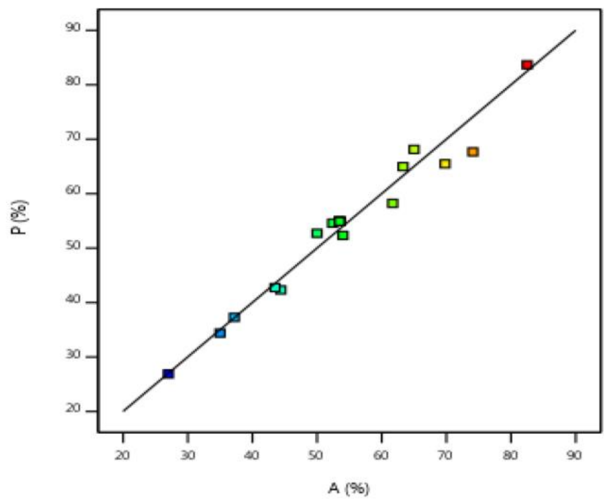

Figure 2: Predicted (P) versus Actual (A) Inhibition Efficiency.

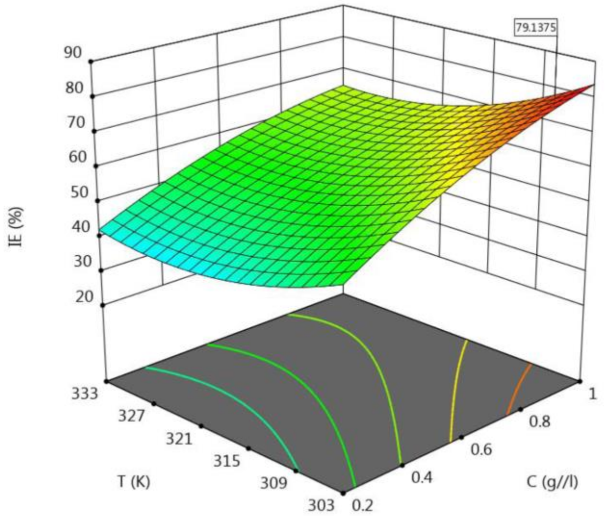

Figure 3: Inhibition efficiency (*IE*) versus inhibitor concentration (*C*) and temperature (*T*).

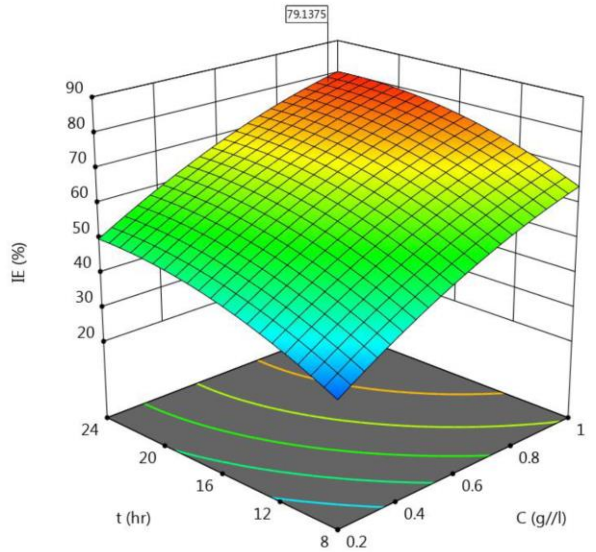

Figure 4: Inhibition efficiency (*IE*) versus inhibitor concentration (*C*) and time (*t*).

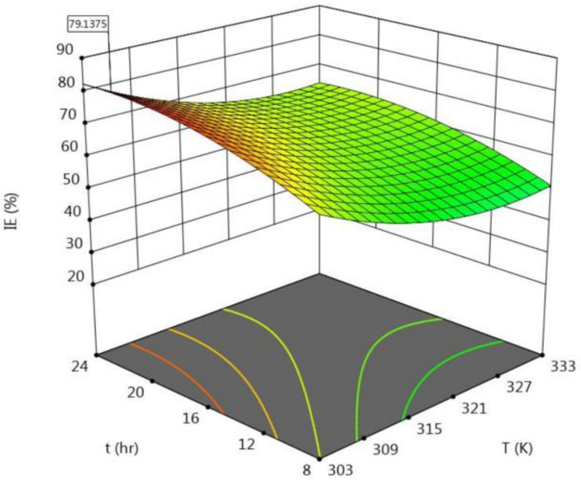

Figure 5: Inhibition efficiency versus temperature and time.

It is a quadratic model. All the considered factors were responsible for the quadratic nature of the model. The positive and negative signs of the coefficients debit synergetic and antagonistic tendencies respectively.

IV. CONCLUSIONS

From the analysis of the experimental data, the following conclusions can be drawn:

- Phytochemicals of alkaloids, cardiac glycosides, flavonoids, phenolics, phytates, saponins and tanins were present in the cashew extract at various degrees. The cashew extract is predominantly made of flavonoids (425.0mg/100g) followed by alkaloids (221.7mg/100g).
- The adsorption of the cashew extract on the aluminium surface obeyed physical adsorption mechanism.
- The thermometric and gravimetric techniques are in agreement of recording high inhibition efficiencies of 83.7% and 82.5% respectively.
- The phytochemicals of the cashew extract are good inhibitive agents for the corrosion control of aluminium in H_2SO_4 medium.
- A quadratic model is adequate for the description of the inhibition efficiency of the cashew extract as a function of concentration, temperature and time.

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