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Investigation of the Adsorptive And Inhibitive Properties Of *Cucurbita Maxima* Peel Extract And Halide Ions As Inhibitors For Stainless Steel in 1m H_2so_4 Solution

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Abstract: In consideration of the need to populate the research database with information on green corrosion inhibition, the present study investigated the corrosion inhibition efficiency of various concentrations of *Cucurbita maxima peel extract on Grade 304 austenitic stainless steel in 1 M H_2SO_4 using two basic analytical methods, namely gravimetric and electrochemical methods. The extract showed a progressive increase in inhibition efficiency with an increase in concentration but with a decrease in temperature, the efficiency was observed to decline. employment of synergistic combination of the extract with iodide ions extended the maximum inhibition efficiency from 88.27 to 90.20 % for PCM with KI at 0.7 g/L extract concentration for 3 hours' immersion time and an efficiency of 90.43% at 0.7 g/L concentration with KCl at 30 ºC. Evidences from the polarization curve indicated that C. maxima peel functions as a mixed-type inhibitor. The inhibition action of the peel extract is due to the adsorption of the extract compounds on the stainless-steel surface. The presence of the extract increased the activation energy of the corrosion reaction. The evaluated range for the ΔG_{ads} values confirmed that the adsorption is spontaneous and operated through a physical adsorption mechanism that best fitted the Langmuir adsorption model. . The scanning electron micrograph of the metal surface shows a smooth surface compared to the surface obtained for the control experimental set-up. The greatest efficiency was achieved using the peel extract with KI halide ion which shows that the peel of C. maxima is a very effective corrosion inhibitor on stainless steel in an acidic medium.*

Keywords: Metal, degradation, ptotection, *Cucurbita maxima waste,*

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1.0 Introduction

stainless steel is a class of versatile materials, whose composition can be variedto exhibit a wide range of engineering features through alloy design and controlled mechanical treatments. Due to their adaptability, stainless steel is now more in demand for a wide range of applications, including the manufacture of small pins, nuclear power plants, ships, petrochemical plants, and vehicles. Also, its biocompatibility, enablescertain grades of stainless steel to be employed in the production of biomedical implants (Dhruv 2017). However, several operations involving the contact of this valuable metal and some aggressive medium has consistently been realized as a major setback to the durability of stainless steel. For example, some industrial operations, such as pickling, cleaning, and descaling, use diluted acid solutions to remove unwanted scales and rust from steel surfaces (Wang *et al.,* 2012) and the consequence may involve electrochemical degradation of the metal through corrosion

The efficiency of corrosion inhibitors is determined by several factors including their molecular structure, hetero atom content, the presence of pi-electron, system conjugation, etc. According to (Rani and Basu 2012; Preethi *et al.,* 2014; Ebenso *et al.,* 2008), organic corrosion inhibitors have heterogeneous atoms like O, N, S, and P that help to inhibit the corrosion of metals and alloys due to their high basicity and electron density. Since many corrosion inhibitors threaten the environment with their toxicity even though they possess high corrosion inhibition efficiency (Ramesh and Rajeswari 2004), this sparked an interest among corrosion engineers and scientists chemists, and polymer chemists and engineers to develop a new class of inhibitors that does not or pose minimal threat to the environment and the inhibitors should have high corrosion efficiency.

Plant extracts are a remarkably rich source of natural chemical compounds that may be obtained through a simple process at a minimal cost and are essentially biodegradable. The organic compounds included in the natural plant extract, which serves as a healthy substitute for harmful and dangerous substances, include amino acids, alkaloids, steroids, flavonoids, proteins, and tannins. In addition, these substances have developed into corrosion inhibitor substitutes that are affordable, readily accessible, and renewable (Deghani *et al.,* 2019; Chaubey *et al.,* 2018; Jokar *et al.,* 2016; Deghani *et al.,* 2020).

The corrosion-inhibitive properties of *Cucurbita maxima* (also known as pumpkin) peel were studied on stainless steel in a sulphuric acid medium. All the parts of *Cucurbita maxima,* a monoecious plant of *Cucurbita* species have medicinal properties. Peels from fruits and vegetables, which are typically thrown away during preparation and consumption, are a good source of nutrients. In the subcontinent, pumpkin is a widely cultivated and consumed vegetable. Pumpkin peel, which contains substantial amounts of vital nutrients, is seen as trash and discarded. Pectin from pumpkin peels, for example, is a dietary fibre that has been shown to slow down the digestion of starch and treat diet-related disorders like diabetes (Bai *et al.,* 2020). Due to its cool and wet character, pumpkin fruit peel is beneficial for hot and dry illnesses like burn wounds, and various formulations of the pumpkin fruit peel are recommended for burn wound healing (Bahramsoltani *et al.,* 2014).

Therapeutically, pumpkin peel, flesh and seeds contain useful active compounds that work well as antioxidants and antimicrobials. All components of the pumpkin fruit should be utilized because they have good phytochemistry and may possess a positive impact on one's health. To isolate and define bio-actives and employ them as therapeutic agents in the food and pharmaceutical industries, all of these components of pumpkin can be used as powders or extracts. Technology should be exploited to create novel and revolutionary nutraceuticals and pharma foods from the health-beneficial components of pumpkin rather than consuming it raw (Hussain *et al.,* 2022). The phytochemical components of the *Cucurbita maxima* plant have been studied and flavonoids, alkaloids, carotenoids, steroids, saponins, carbohydrates, and amino acids have all been discovered in *Cucurbita* species. The majority of phytochemicals with functional groups like NH_2, CO, and CHO are responsible for the qualities that inhibit corrosion. These compounds adhere to the surface of the metal to form a protective layer. Numerous organic compounds are present in *C. maxima* peel extract, which can be utilized as a green corrosion inhibitor (UdayaPrakash *et al.*, 2013). *Cucurbita maxima* peel has been utilized as a corrosion inhibitor for different metals (Anbarasi and Mini 2016; Anbarasi and Vasudha 2014). However, it is yet to be studied as a potential inhibitor for stainless steels in a highly corrosive environment such as 1 M H_2S0_4. This study, therefore, investigated the corrosion inhibitory potential of *Cucurbita maxima* peel extract on stainless steel in 1M H_2S0_4 under varied conditions.

2.0 Materials and Methods

2.1 Materials

The materials and reagents used are *Cucurbita maxima* peel and stainless steel, ethanol, acetone, sulphuric acid (H_2SO_4), potassium chloride (KCl), potassium iodide (KI), and distilled water.

2.2 Preparation of specimens

The commercially available stainless steel was cut into coupons having dimensions of 9 x 3 cm. The coupons were polished using emery paper of grade 400 and degreased in ethanol then washed with distilled water, rinsed with acetone, and dried at 45 ºC for 15 mins. These plates were used for weight loss studies (Anbarasi and Vasudha 2014).

2.3 Preparation of C.maxima peel extract

C. maxima pumpkins were selected and acquired from a commercial market in Kaduna State. The fresh pumpkins were cut by a sharp knife and peeled and the peel was sliced into pieces. The sliced samples were dried for 48 hours at 100 °C in a hot air oven before being ground into a powder with a grinder. The fine powder of the pumpkin peel was packed in low-density polyethylene (LDPE) bag and kept in a refrigerator until analysis.

The extract from the peel was obtained by soaking 150 g of pulverized *C. maxima* peel in 500 ml of 95 % v/v ethanol for 48 hours. The mixture was first sieved using a muslin cloth and the resultant liquid was subsequently filtered using Whatman No 1 filter paper. The filtrate was then concentrated using a rotary evaporator until a semi-solid extract was left. The semi-solid extract obtained was oven-dried to a solid residue at 45 ºC for 15 mins, weighed, and stored in a Bama bottle for use (Madu *et al.*, 2019).

2.4 Weight loss method

Varying concentrations (0.3, 0.5, and 0.7 g/L) of the solid plant extract which contains alkaloids, tannins, saponins, carbohydrates, and phenolic compounds were prepared in 1M H_2SO_4. The study was executed at varying temperatures of 303K, 333K, and 363K. The weight loss was measured at an immersion time of 3 hours. During the measurements, the metal coupons were removed from the solutions, washed with ethanol, cleaned with acetone, and thoroughly dried using paper towels. The weights were obtained and used to estimate the changes that occurred during the experiment (Madu *et al.*, 2019).

The following equations were used in evaluating the effect of the extract: weight loss (Equation 1), corrosion rate (Equation 2), surface coverage (Equation 3), and percent inhibition efficiency (% IE) of the inhibitors (Equation 4).

$$\Delta W = W_2 - W_1 \quad (1)$$

$$CR(mmy) = \frac{87.6 \times W}{\rho A t} \quad (2)$$

$$\theta = \frac{CR2 - CR1}{CR2} \quad (3$$

$$\%IE = \left(\frac{CRblank - CRinh}{CRblank}\right) \times 100 \quad (4)$$

where ΔW is the change in mass in mg, W_1 and W_2 are initial and final masses, respectively. In Equation 2, CR represents the corrosion rate in mm/y, ρ is the density of stainless steel in g/cm^3, A is the area of the stainless steel bars in cm^2, and t is the time in hours. The weight loss of the coupon in the electrolyte with the *C. maxima* inhibitor is W_1 and W_2 is the weight loss of the coupon in the electrolyte without the inhibitor. The surface coverage of the inhibitor on the surface of the steel is θ, CR_1 and CR_2 (equation 4) are the change in mass of stainless steel in solution with inhibitor and without inhibitor, respectively (Madu *et al.,* 2019).

2.5 Electrochemical measurements

The electrochemical experiment was carried out using computer-controlled Parstat 2273. Power Suite software and ZsimpWin (version 3.21) were used to obtain data and evaluate it. A three-electrode setup was used, with a saturated calomel electrode serving as the reference electrode and platinum foil serving as the auxiliary electrode. The stainless steel coupon with surface prepared according to the weight loss experimental method served as the working electrode. The potentiodynamic polarization curves were recorded using the cell setup. The potentials were scanned at the rate of 1.66 mVs^{-1} (Gunavathy and Murugavel 2013). The inhibition efficiency (IE) was obtained from the measured I_{corr} using the following relationship:

$$IE_p = \frac{Icorr - I'corr}{Icorr} \times 100 \qquad (5)$$

where I'_{corr} and I_{corr} are the corrosion current density values of stainless steel in the presence and absence of inhibitors, respectively (Gunavathy and Murugavel 2013).

2.6 SEM analysis

The Supra 40VP model was used to examine the metal surfaces using a Scanning Electron Microscope (SEM) to understand the changes that occurred before and after corrosion in the presence and absence of the extract and halide ion (KI) (Madu *et al.,* 2019).

3.0 Results and Discussion

3.1 Weight loss method

The weight loss method was carried out with the concentration ranging from 0.3 g/L, 0.5 g/L, and 0.7 g/L. The weight loss data are listed in Table 1. The results show that with a rise in the concentration of peel of *C. maxima* extracts, the inhibition efficiency increased. At an optimum concentration of 0.7 g/L plus KI in the peel of *C. maxima* extract, it has a maximum inhibition efficiency of 95.21%. This result indicates that *Cucurbita maxima* peel extract with halide ion acts as an excellent corrosion inhibitor. This is attributed to the absorption of nutrients of the extracts on the surface of the stainless steel which makes a barrier for mass and charge transfer and prevents further corrosion and are relatable to works done by (Anbarasi 2016; Madu *et al.,* 2019; Jovine and Joseph 2021).

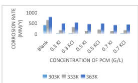
The data in Table 1 indicates that the peel extract with potassium iodide is effective as an inhibitor for stainless steel in 1 M H_2SO_4 at 303 K and decreases thereafter. A maximum inhibition of 95.21 % at 303 K was observed for 0.7 g/L extract with KI of the peel of *C. maxima.* As temperature increases, the rate of corrosion also increases due to the fact that the process of corrosion occurs quickly at higher temperatures due to the hot movement of inhibitor molecules that decreases the adsorption capacity on the steel surface. These results are relatable to the works done by (Anbarasi 2016; Madu *et al.,* 2019; Jovine and Joseph 2021).

It can also be seen from Table 1 that after the addition of KI into the H_2SO_4 solution with the extracts, corrosion rates decreased significantly in comparison with the blank alone. As shown in Table 1, when 0.5 g/L KI was added into the 1 M H_2SO_4 solution containing 0.7 g/L of the extracts, the weight losses were reduced. Accordingly, the percentage of inhibition efficiency increased. These results suggest that there is a synergistic effect between inhibitor molecules and halide ions. In addition, it has been found that different halide ions resulted in a different extent of inhibition efficiency. The order of synergism of halide ions was found to be in the order of KI > KCl with the percentage of inhibition efficiency given by the highest concentration of each halide ion. The iodide has the strongest synergistic effect among the two halides and thus will be focused on. This result agrees with the work done by (Eddy *et* al., 2023' 2003; Ridhwan *et al.*, 2012).

Table 1. Corrosion rate, surface coverage, and inhibition efficiency of peel Extract of *Cucurbita maxima* on stainless steel in 1 M H_2SO_4

T(K)	*C(G/L)*	*ΔW (MG)*	*CR (MM/Y)*	*%IE*	*Θ*
303K	Blank	3817	418	-	-
	0.3 g in KI	383	42	89.95	0.8995
	0.3 g in KCl	449	49	88.27	0.8827
	0.5 g in KI	227	25	94.01	0.9401
	0.5 g in KCl	286	31	92.58	0.9258
	0.7 g in KI	186	20	95.21	0.9521
	0.7 g in KCl	363	40	90.43	0.9043
333K	Blank	5896	646	-	-
	0.3 g in KI	1801	197	69.50	0.6950
	0.3 g in KCl	2925	320	50.46	0.5046
	0.5 g in KI	1425	156	75.85	0.7585
	0.5 g in KCl	1952	214	66.87	0.6687
	0.7 g in KI	1175	129	80.03	0.8003
	0.7 g in KCl	1674	183	71.67	0.7167
363K	Blank	7215	790	-	-
	0.3 g in KI	4557	499	36.84	0.3684
	0.3 g in KCl	4894	536	32.15	0.3215
	0.5 g in KI	4271	468	40.75	0.4075
	0.5 g in KCl	4443	487	38.35	0.3835
	0.7 g in KI	3861	423	46.45	0.4645
	0.7 g in KCl	4058	445	43.67	0.4367

**** C = concentration of the inhibitor, CR = corrosion rate, Δ*W* = weight loss , *%IE* = inhibition efficiency and *Θ* = degree of surface coverage**



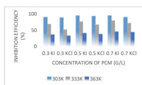


Fig.s 1 and 2: Corrosion rate and Inhibition efficiency of peel extract of *C.maxima*

It is evident that the inhibition efficiency and surface coverage increased with increasing inhibitor concentration and decreased with increasing temperature from 303-363 K.

This observation suggest the prevalent of the physical adsorption (physisorption) mechanism. Fig. 1 and 2 show that the inhibition efficiency ranges from 88% to 95% at 303 K for the peel extract with halide ion whereas at high temperature (363 K) it is much lower ranging from 32% to 46% for the peel extract with halide ion for the different concentrations of the inhibitors. This suggests physical adsorption for the inhibition process.

3.2 Potentiodynamic polarization results

The related electrochemical parameters such as *Icorr*, *Ecorr*, the cathodic Tafel slope (*βc*), and anodic Tafel slope (*βa*) obtained from the polarization curves are listed in Table 2. The fact that an inhibitor reduces corrosion current density (*Icorr*) values without significantly altering corrosion potential (*Ecorr*) implies that the compound is a mixed-type inhibitor and inhibits corrosion by being absorbed on the surface. In all concentrations, *βc* is greater than *βa* suggesting that although inhibition is under mixed control, the inhibitor's effect on the anodic polarization is less pronounced than on the cathodic polarization. As shown in Fig. 3, the Tafel plot in the presence of KI showed higher gradients on the anodic side as compared to the cathodic region. This is caused by the mass transfer phenomena, in which dissolved metal ions gather at the corroding surface. As a result, a concentration gradient will arise in the diffusion layer adjacent to the electrode as a result of these ions diffusing toward the bulk solution

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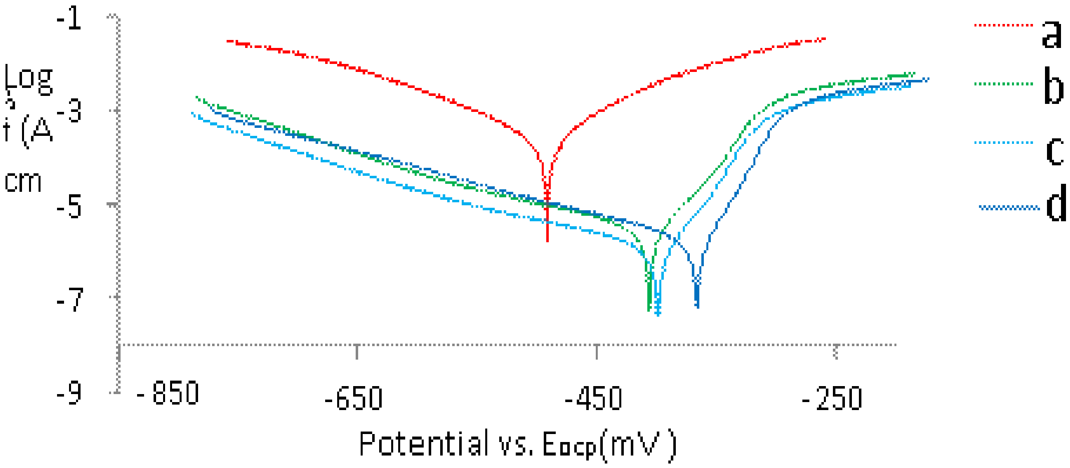

Fig. 3. Polarization curves of stainless steel in 1 M H_2SO_4 in the presence of different concentrations of the peel extract with KI: (a) blank; (b) 0.3 g/L PCM (c) 0.5 g/L PCM (d) 0.7 g/L PCM

3.3 Adsorption isotherm

The experimental data were applied to different adsorption isotherm models (Langmuir, Temkin, and Freundlich). It was found that the experimental data fitted best in the Langmuir adsorption isotherm for the peel extract. The plot of C/θ against C yields straight lines as shown in Fig. 4. This plot yields straight lines with linear regression, and R^2 values of 0.999. This supports the assumption that the adsorption of the extracts in the presence of the halide ions on the stainless steel surface in 1M H_2SO_4 solution follows the Langmuir adsorption isotherm which is represented by Equation 6 below

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (6)$$

where K is the equilibrium constant which represents the degree of interaction between the inhibitor and the metal surface during the adsorption process, and C represents the inhibitor concentration. ΔG_{ads} was calculated using the following equation:

$$\Delta G_{ads} = -RT \ln(55.5K_{ads}) \quad (7)$$

where R is the molar as constant (8.314 J/K), T is the temperature in Kelvin, and value 55.5 is the molar concentration of water in solution (Okewale and Adesina 2020).

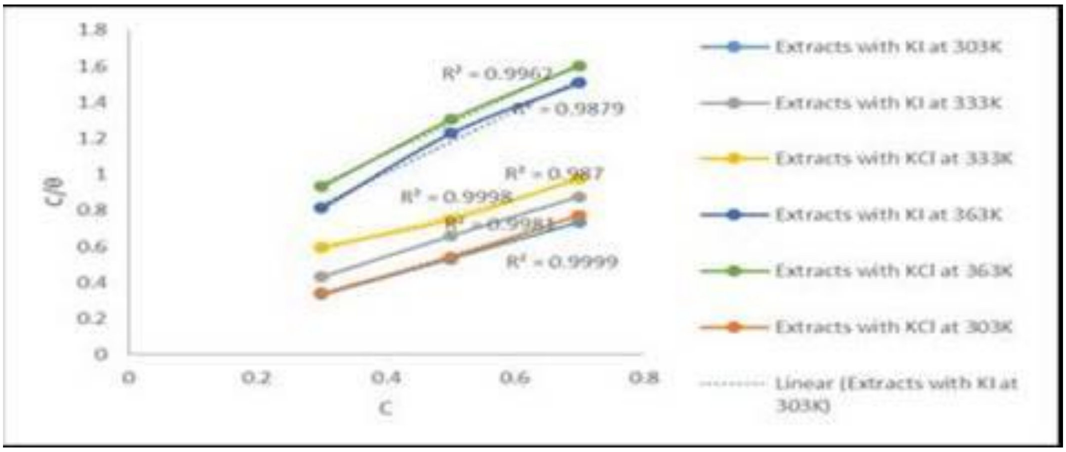

Fig. 4: Langmuir adsorption isotherm plot for peel extract of stainless steel corrosion in 1M H_2SO_4

The plot of log CR versus 1/T yields straight lines as shown in Fig. 5 which indicates the Arrhenius adsorption isotherm. The calculated values obtained for ΔG_{ads} given in Table 3 were negative indicating that the adsorption process is spontaneous.Generally, ΔG_{ads} values less than -20 kJ mol^{-1} are consistent with the physical adsorption (physisorption) of charged inhibitor molecules onto charged metal surfaces

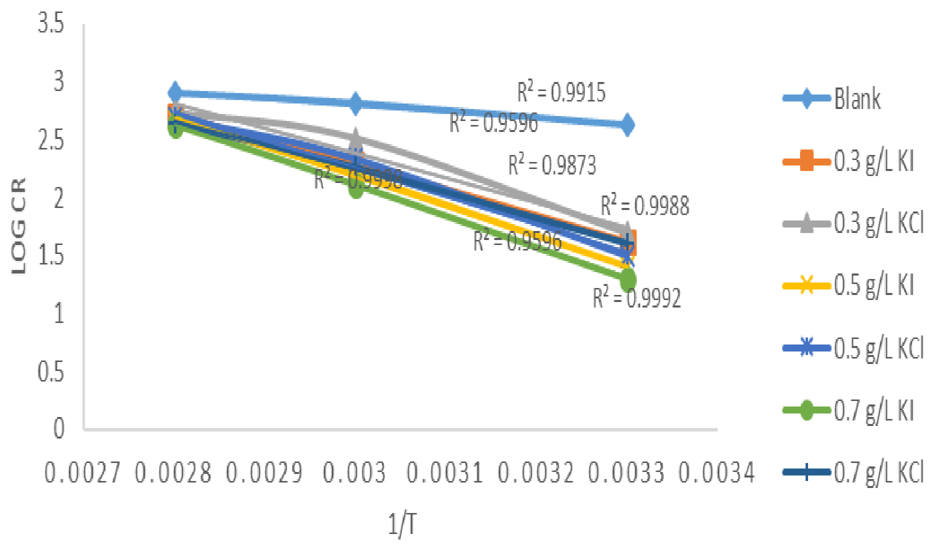

Fig. 5: Plot of log CR versus 1/T for the peel extract

whereas values more negative than -40 KJ mol^{-1} involve the sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a coordinate or covalent type of bond (chemisorption) (Abeng *et al.*, 2017). The results listed in Table 3 show that ΔG_{ads} values are less than -20 kJ mol^{-1}. This revealed that the adsorption of the inhibitor on the metal surface is spontaneous and confirms the physisorption mechanism.

Table 3: Calculated Thermodynamic parameter ΔG_{ads} at different temperatures

C (g/L)	ΔG_{ads} (kJ/mol)		
	303K (PCM)	***333K (PCM)***	***363K (PCM)***
0.3 in KI	-18.64	-16.72	-14.12
0.3 in KC l	-18.39	-14.51	-13.55
0.5 in KI	-18.90	-16.22	-13.13
0.5 in KC l	-18.14	-14.95	-12.68
0.7 in KI	-18.64	-15.95	-12.68
0.7 in KC l	-16.68	-14.67	-12.40

The transition state theory equation given by equation 8 was used to calculate the thermodynamic parameters of the corrosion process, such as enthalpy (ΔH_{ads}) and entropy (ΔS_{ads}) (Mouhedin *et al.*, 2018; Ogoke *et al.*, 2009).

$$\text{Log}\left(\frac{CR}{T}\right) = \left[\text{Log}\left(\frac{R}{Nh}\right) + \frac{\Delta S^{\circ}}{2.303R}\right] - \frac{\Delta H^{\circ}}{2.303RT} \quad (8)$$

where R is the Universal gas constant (8.314J/Kmol), N is Avogadro's number, (6.022×10^{23} mol^{-1}), h is the Planck's constant (6.626176×10^{-34}Js), and T is the temperature of the medium. The plot of log CR against 1/T is seen to be linear in Fig 5 from which (ΔH^{o}) and (ΔS^{o}) values were deduced from the slopes and intercept of the graph respectively and listed in Table 4.

The activation energy for PCM's blank (10.72 kJ/mol) is lower than in the presence of the inhibitors with KI. This increase of apparent activation energies for stainless steel dissolution with inhibitor may be interpreted as a physical adsorption mechanism. The endothermic nature of the stainless-steel dissolving process in the presence of both extracts is reflected in the positive sign of the ΔH^{o}.

Table 4: Calculated activation and thermodynamic parameters

C (g/L)	E_a (kJ/mol) *PCM*	ΔH^0 (kJ/mol) *PCM*	ΔS^0 (kJ/mol) *PCM*
Blank	10.72	4.66	37.21
0.3 in KI	41.30	17.93	72.73
0.3 in KC l	40.75	17.69	72.87
0.5 in KI	48.87	21.22	81.72
0.5 in KC l	46.45	20.17	79.21
0.7 in KI	50.81	22.06	83.66
0.7 in KC l	40.22	17.46	71.02

3.4 SEM analysis

Selected samples (blank and 0.7g/L with KI) were analyzed for surface morphology using SEM. The micrographs show severe corrosion on the surface of the blank sample plates. These images confirmed the rates at which the metal corroded in 1 M H_2SO_4 solution at 303K temperature after a 3-hour immersion time. It could be seen from the micrographs in Fig. c that the stainless steel's surface was inhibited against corrosion and a smoother surface was seen with an increment in the concentration of the inhibitor.

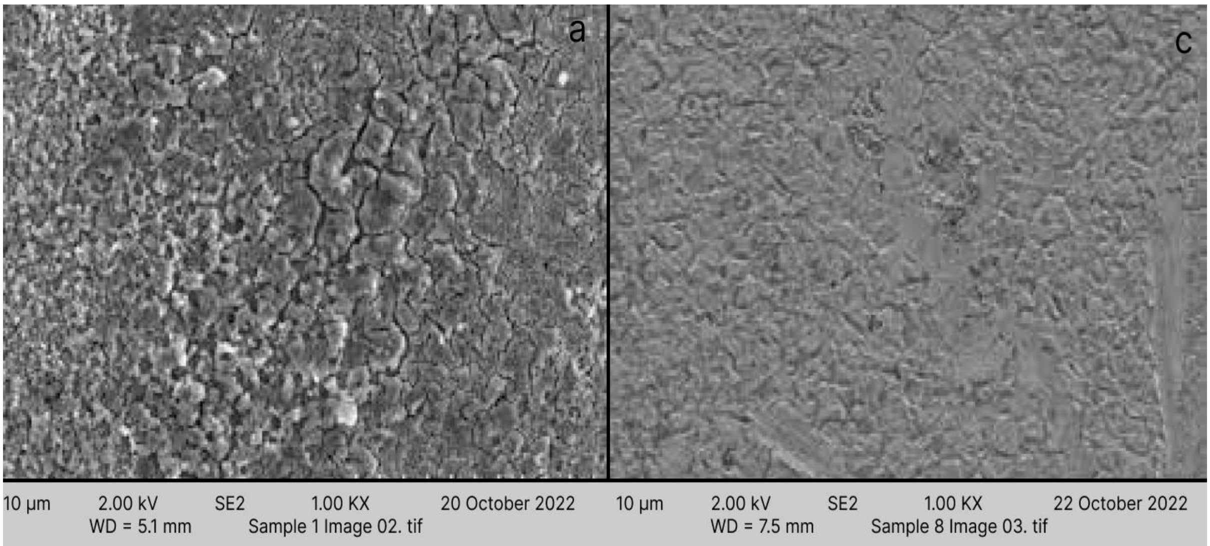

Fig. 6: SEM micrographs of stainless steels after corrosion in 1 M H_2SO_4 containing the peel extract at 303 K (a) Blank (c) 0.7 g/L PCM.

4.0 Conclusion

In a solution of 1M H_2SO_4, the peel of the Cucurbita maxima functions as a green inhibitor to inhibit the corrosion of stainless steel. The IE increases as extract concentrations are increased. The results of the weight loss measurement for different concentrations of inhibitor at higher temperature shows maximum inhibition efficiency of 95.21 % for PCM at 0.7 g/L with KI extract concentration and temperature of 303K for 3 hours' immersion time and an efficiency of 90.43% at 0.7 g/L concentration with KCl at 30 ºC. According to the potentiodynamic polarization curves, *C. maxima* functions as a mixed type of inhibitor. The inhibition action occurs due to the adsorption of the extract compounds on the stainless-steel surface. The adsorption process is physical and follows the Langmuir adsorption isotherm. The presence of PCM extract increases the activation energy of the corrosion reaction. The negative values of ΔG_{ads} reveal the

spontaneity of the adsorption process and the values range from -12 kJ/mol to -18 kJ/mol indicating the physical adsorption. The effectiveness of the plant and halide extracts as a corrosion inhibitor for stainless steel was proven by surface investigations using SEM.

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Compliance with Ethical Standards Declarations

The authors declare that they have no conflict of interest.

Data availability

All data used in this study will be readily available to the public.

Consent for publication

Not Applicable

Availability of data and materials

The publisher has the right to make the data Public.

Competing interests

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