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The Activation Energy Parameters of Pumpkin Pod Extract as Corrosion Inhibitor for Stainless Steel in HCl Medium

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ABSTRACT

The inhibition effect of pumpkin pod extract (PPE) on the corrosion of stainless steel in 2M HCl has been studied by weight loss technique. The process of inhibition and temperature effects on inhibition efficiency, rate of corrosion, and weight loss were determined with a temperature range of 313K – 353K at 7 hours of dipping. An increase in temperature led to a decrease in both the inhibition efficiency of PPE extract and the rate of corrosion of stainless-steel metal surfaces. Parameters of thermodynamics activation such as; activation energy, enthalpy, and entropy values range from 73.739 - 110.056kJ/mol, 70.936 – 107.252kJ/mol, and 2.7610 – 100.373J/molK respectively. The higher value of activation energy obtained in comparison to the enthalpy of adsorption suggests a physical adsorption mechanism on stainless steel.

1. Introduction

Corrosion is a process in which loss of essential properties of material occurs as a result of its interaction with surroundings. Corrosion processes are responsible for numerous losses mainly in the industrial scope. It is almost impossible to prevent corrosion, however it is possible to control it (Groysman, 2017; Roberge, 2008). Most stainless steels are resistant to stress-corrosion cracking and have good corrosion resistance to mineral acids, cold dilute organic acids cold oxidizing and alkaline salt solutions, atmospheric corrosion, high-temperature oxidation, and hot water.

The unique corrosion resistance of stainless steel is attributed to the existence of a thin, adherent, inactive passive film that covers the surface. This film can conveniently be thought of as chromium oxide, but it also contains a small amount of other elements in the alloy. If the stainless-steel surface is free from contamination, the film forms instantaneously on exposure to air, because of the protective film, steels do not corrode as carbon or low alloy steels or cast iron constantly changing anodes and cathodes on the surface, (Svintradze & Pidaparti, 2010). However, except in solutions such as Hydrochloric acid, this general corrosion or uniform attack practically never occurs on stainless steels. While factors such as chemical environment, pH, and temperature, contamination, and maintenance procedures can affect the corrosion of stainless steels, they usually cause only some form of

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localized corrosion (Abdallah et al., 2017). A corrosion inhibitor is a chemical substance that is effective in very small amounts when added to a corrosive environment to decrease the corrosive rate of the exposed metallic material (Shehata Omnia, and Korshed Lobna., 2018). There are many industrial systems and commercial applications that inhibitors are applicable, such as cooling systems, refinery units, pipelines, chemicals, oil and gas production units, boilers and water processing, paints, pigments, lubricants, etc (Chaubey *et al*., 2021).

The development of inhibitors for stainless steel corrosion in aqueous solution, particularly in alkaline media has attracted interest of many researchers (Svintradze & Pidaparti, 2010). However, the influence of inhibitors has been the subject of numerous investigators; the corrosion mechanisms as well as the role of inhibitors are not completely explained. Although many organic, (Li et al., 2021), inorganic (Arenos, et al., 2001) and synthesized polymeric (Taghavikish *et al*., 2016) compounds were applied as inhibitors for reducing steel corrosion in alkaline media, little attention has been focused for applying natural polymers as inhibitors. (Abdallah et al., 2017), studied the corrosion of stainless steel in Hydrochloric acid, Obiukwu et al, (2013), also examined the corrosion inhibition of stainless steel using plant extracts from Vernonania Amygdalina and Azadirachta Indica. (Okewale & Adebayo, 2020), used Pumpkin Pod as corrosion inhibitor on carbon steel. In this work the potency of pumpkin pod extract in preventing the corro sion of stainless steel was examined by exploring the underlining thermodynamics and adsorption isotherm principles.

2. MATERIALS AND METHOD

2.1 Materials

Pumpkin pod was obtained from Agbarho Market, Ughelli North Local Government Area, of Delta State, Nigeria. Gallenkamph 2 hotbox oven, water bath (Grant JB series) model, analytical weighing balance (PGW 753i), rotavapour (R – 210/215), pH meter (HANNA pH – 221), beakers, analytical grades (Sigma Aldrich) hydrochloric acid, acetone, and ethanol were used to undertake the corrosion study while distilled water was procured from the Department of Chemical Engineering Laboratory, Federal University of Petroleum Resources, Effurun, Delta Sate, Nigeria.

2.2 Methods

2.2.1 Sample Collection and Pretreatment

Pumpkin pods were obtained from Agbarho Market, Ughelli North Local Government Area, Delta State, Nigeria. The waste pumpkin pods were sun dried for 14 days, and thereafter pulverized using a mechanical grinder to obtain a powdery form. It was then sieved with a sieve of 0.143µm mesh. The sample was subsequently stored in a desiccator before use.

2.2.2 Scan electron microscopy energy dispersive X – rays analysis

The elemental composition of the stainless steel was inspected using a scanning electron microscope (SEM – EDX) PHENOMWORLD operating at 25kV. The metal surface was fixed to a metal stubs with adhesive on either side, and glazed with gold in a vacuum using a coater that is IB – 3ion and allowed to pass through the dispersive X – rays of the SEM machine.

2.2.3 Extraction of Pumpkin pods (Telfairia occidentalis) extract using Soxhlet Extractor

The Pumpkin pods (*Telfairia occidentalis*) were washed thoroughly with running water to remove debris. The washed samples were sun dried for 14 days and grinded to a particle seize of 0.143µm. 100g of dried pumpkin pods (*Telfairia occidentalis*) powder was transferred into a 500mL Soxhlet extractor and 500mL of 90% ethanol is reflux continuously for 3 hours at 78°C temperature. The set-up was placed on a heating mantle and the pumpkin pod (*Telfairia occidentalis*) extract was extracted exhaustively by heating the solution. However, the extract was obtained after ethanol recovery in a Rotary evaporator (model R-210) at 40°C.

2.2.4 Procedure of the experiment

The weight loss method was used. The stainless steel was refined with an abrasive paper, degreased with ethanol, washed with distilled water and subsequently dried in acetone. Each stainless-steel coupon was sized 20mm × 40mm × 5mm. A hole of 1mm was bored on each metal coupon.

The metal coupon was suspended into the 100ml beaker containing 100ml of 2M hydrochloric acid at different inhibitor concentrations with the aid of thread. The various time intervals of 120, 240, 360, 480, 600 and 720 hours were used for the corrosion study at 30 ^{0}C. The mechanism of inhibition and thermodynamic parameters were considered at 313, 323, 333, 343, and 353K temperature at contact time of 7hours. The stainless-steel metal coupon was then immersed in distilled water and ethanol solutions. This was carried out so as to clean and eliminate any residual hydrochloric acid and pumpkin pod extract from the metal surface respectively. The stainless-steel metal was rinsed intensively with distilled water and then in acetone before it was reweighed.

2.3 Rate of Corrosion

The expression for measurement of rate of corrosion (C.R) in millimeters penetration per year (mm/yr) was used to quantify the rate of corrosion for the specimens, which was stated in equation 1 (Callister, 1997).

$$\text{C.R.} = \frac{87.6w}{at\rho} \qquad (1)$$

Where, w is corrosion weight loss of stainless steel (mg), a is the total surface area of the specimen in (cm^2), t is the exposure time in hours (hr), and ρ is the density of the specimen (g/cm^3**).**

2.5 Measurement of loss in weight

The loss in weight of stainless-steel coupon was estimated using equation 2;

$$\text{Weight loss, (g)} = W - W_i \qquad (2)$$

Where, W is the initial weight of the stainless-steel metal, W_i is the weight of the stainless-steel metal after corrosion study.

2.6 Determination of Pumpkin Pod Extract Inhibition Efficiency

The corrosion inhibition efficiency was accomplished using equation (3);

$$E(\%) = \frac{W_b - W_c}{W_b} \times 100 \qquad (3)$$

Where, W_b is the loss in weight in unconstrained environment (blank), and W_c is the loss in weight in constrained environment.

3. RESULTS AND DISCUSSION

3.1 Stainless steel characterization

Table 1 shows result of the stainless-steel ED-X analysis showing the elemental composition. Iron has the highest concentration.

3.2 Influence of Temperature on Corrosion Inhibition

Table 2 typified the influence of temperature on inhibition efficiency, and rate of corrosion at 7hour of dipping. The results revealed that the inhibition efficiency of the inhibitor at different inhibitor concentrations decreased by a rise in temperature of the acid medium studied,

Table 1: Result of the ED-X Analysis on stainless steel

Elements	Weight Percentage (%)
Magnesium	0.47
Silicon	1.56
Bromine	2.24
Carbon	2.04
Oxygen	1.89
Molybdenum	1.38
Palladium	4.26
Iron	83.95
Nitrogen	0.2
Yttrium	1.12
Boron	0.88

a trend that connotes physical adsorption mechanism. This could be due to the fact that the protecting film of inhibitor is formed on the surface of the stainless steel which is considered less steady at higher temperature. It can also be linked to the desorption of adsorbed molecules of inhibitor from the metal surface at higher temperature thereby resulting to larger part of the stainless steel been open to attack from the acidic environment. Maximum inhibition efficiency of 91.6% was obtained at 313K. The results accomplished in this study is in good agreement with the that of (Abdallah et al., 2017). It can also be observed from Table 2 that corrosion rate increases with rise in temperature but decreases with increase in inhibitor concentration.

Table 2: Corrosion rate, Inhibition efficiency at various concentration of PPE

PPE (ppm)	313K		323K		333K		343K		353K	
	IE (%)	CR (mm/yr)	IE (%)	CR (mm/yr)	IE (%)	CR (mm/yr)	IE (%)	CR (mm/yr)	IE (%)	CR (mm/yr)
50	64.71	3.968	84.64	5.1959	55.71	38.827	56.71	65.562	19.10	233.719
100	84.03	1.795	86.03	4.7235	79.96	17.571	64.44	53.848	26.10	213.503
150	85.71	1.606	86.87	4.4401	90.41	8.408	70.18	45.157	36.72	182.800
200	89.92	1.134	87.99	4.0622	86.31	11.998	78.04	33.254	44.60	160.033
250	91.60	0.945	85.75	4.8180	87.61	10.864	81.78	27.585	59.68	116.482
Blank	0.000	11.242	0.000	33.8204	0.000	87.668	0.000	151.436	0.000	288.890

3.3 Thermodynamic activation factors for the corrosion inhibition

Equation 4 depict the Arrhenius equation used to calculate the activation energy E_a in the presence and absence of PPE inhibitor (Kairi and Kassim, 2013)

$$\log C_R = \log A - \frac{E_a}{2.303RT} \quad (4)$$

where C_R is the corrosion rate of stainless steel, Ea is the apparent activation energy, R is the universal gas constant (J/mol), T is the absolute temperature (K), and A is the frequency factor. The Arrhenius plot of log C_R against reciprocal of absolute temperature (1/T) is shown in figure 1 which indicated a straight-line graph with the gradient equal to -Ea/2.303R and the intercept equal to logarithm of pre-exponential factor (A).

The thermodynamic parameters for both heat of adsorption and entropy for the inhibition process on the stainless steel (ΔH_{ads}) and (ΔS_{ads}) in the presence and absence of inhibitor were computed using the transition state equation described by equation (5) (Li et al., 2021).

$$\log\left(\frac{CR}{T}\right) = \log\left(\frac{R}{N_h}\right) + \frac{\Delta S_{ads}}{2.303R} - \frac{\Delta H_{ads}}{2.303RT} \quad (5)$$

where h is the Planck's constant (6.626176×10^{-34}Js), N is the Avogadro's number,
(6.022×10^{23} mol^{-1}), R is the Universal gas constant (J/Kmol) and T is the temperature of the sssolution (K). The plot of log (C_R/T) against 1/T is seen to be linear in figure 2 from which (ΔH^o) and (ΔS^o) values were deduced from the gradient and intercept of the graph accordingly. Therefore, the activation energy (Ea), the pre-exponential factors (A), enthalpy (ΔH_{ads}), and entropy (ΔS_{ads}) were calculated and tabulated in table 3. These values of activation energy were found to range from 73.739 kJ/mol - 110.056 kJ/mol. The value obtained for PPE extract used was higher in comparison to that of the uninhibited medium which is an indication that the rust of stainless steel is stunted by the presence of PPE extract in acidic condition. It can also be noted that the activation energy value obtained in inhibited medium is higher in comparison to the ceiling limit value of 80 kJ/mol (Okewale, A.O. & Adesina, 2020), that is essential for chemisorption adsorption mechanism in inhibited solution.

The adsorption mechanism of PPE extract on stainless steel metal surface was chemisorption in nature in inhibited solution while that of uninhibited solution showed physisorption. Increase in Ea values is an indication of an exceptionally resilient inhibitive action of PPE inhibitor thus leading to an increase in energy barrier associated with the corrosion process which illustrates that the mechanism of the PPE extract adsorption on the stainless surface emanate from electrostatic interface between the inhibitor (Bu et al., 2015). With Higher values of Ea greater than 80kJ/mol in the presence of inhibitor that was obtained it is a good suggestion that the PPE extract increases the energy barrier for the corrosion process which also confirms chemisorption in the inhibited medium.

Cathodic reaction that occurs in the cell of corrosion that resulted into hydrogen evolution in acidic environment studied emanate from an increase in the activation energy which is attributed to significant decrease in the adsorption of inhibitor on stainless steel surface as rise in temperature occurs. This process can also occur because the PPE extract forms an inexpressive film on the stainless-steel metal surface, so making the iron (Fe) solubility in acidic medium to shrink. Similar results were reported in findings of (Asadu *et al*., 2021).

Table 3: Activation energy, enthalpy, and entropy for the corrosion inhibition process

Concentration of PPE	Ea (kJ/mol)	ΔH^0 (kJ/mol)	Ea - ΔH^0	ΔS^0 (J/mol K)
50	97.964	95.299	2.665	68.092
100	109.916	107.112	2.804	100.373
150	107.737	104.932	2.805	91.757
200	110.056	107.252	2.804	97.865
250	104.511	101.708	2.803	80.154
Blank (Uninhibited)	73.739	70.936	2.803	2.7610

The large positive values of ΔH_{ads} and ΔS_{ads} signal that the adsorption of PPE extract on the surface of stainless steel is endothermic and occur spontaneously respectively (Dahmani, et al., 2010). Higher values of enthalpy showed that there is a high inhibition efficiency of PPE extract on the stainless-steel surface. The positive value of the entropy also implied that there is an increase in degree of disorderliness of the PPE extract on the stainless-steel surface. The energy of activation (Ea) values attained were higher in comparison to the corresponding enthalpy of activation (ΔH_{ads}) values which signify that the oxidation process might have occurred pointing to a reaction that is gaseous in nature, like the progression of hydrogen reaction which is connected with decreasing the whole reaction volume. The results obtained indicate PPE extract acted evenly on activation energy (E_{ads}), and adsorption enthalpy (ΔH_{ads}). The result of this work is in agreement with the findings of (Nwabanne & Okafor, 2012; Okewale, A.O, Adesina, 2020). Positive values of entropy showed that the complex of activation in the rate determining step characterize a dissociation step rather than an association step. It connotes that there is an increase in the way disordering takes place when moving from reactants to the activated complex of the corrosion process studied.

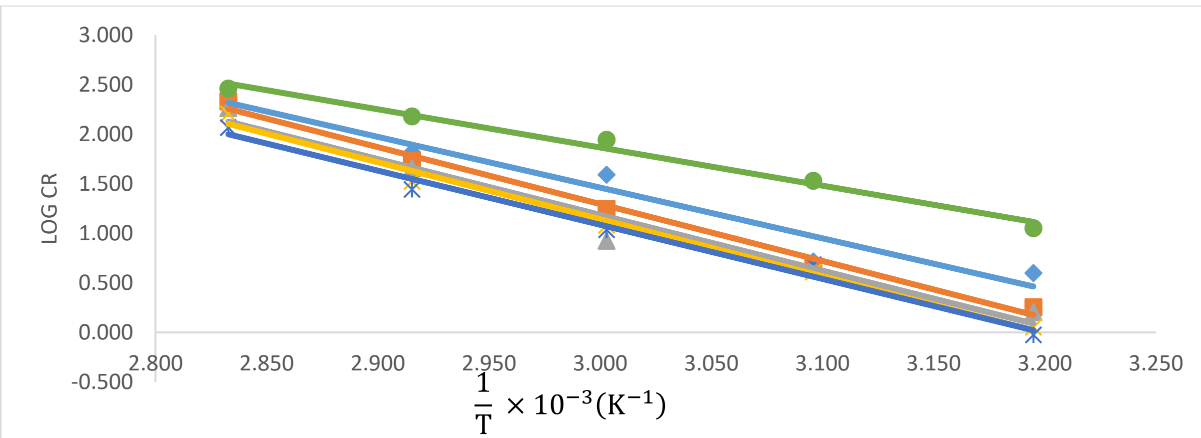

Figure 1: Plot of Arrhenius for the corrosion inhibition of stainless steel.

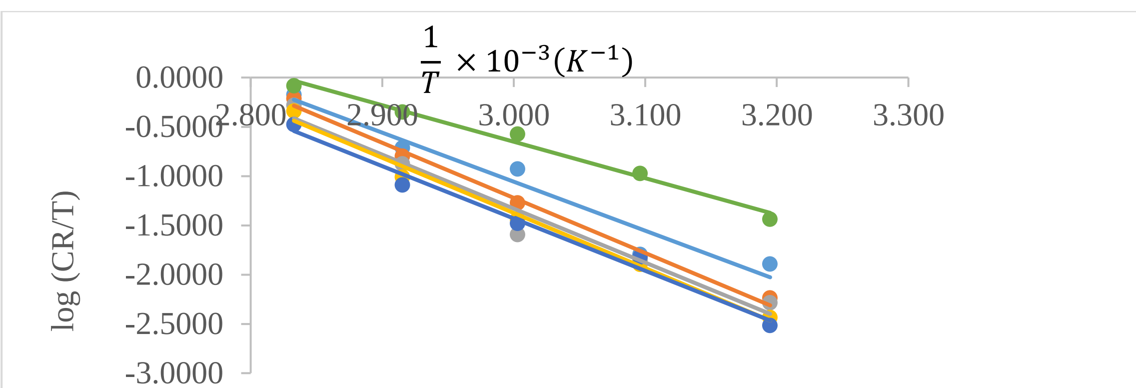

Figure 2: The transition state plot for the corrosion inhibition of stainless steel

4. CONCLUSION

An inhibitor was successfully obtained from pumpkin pod extract and used as corrosion inhibitor on stainless steel surface in 2M HCl solution. Elemental compositions of the stainless steel were carried out using SEM – EDX analysis. Adsorption process of the PPE extract molecule onto the surface of stainless steel was investigated using thermodynamic study for the corrosion process. Increase in activation energy (Ea) values compared to enthalpy of adsorption (ΔH_{ads}) is an indication of an exceptionally resilient inhibitive action of PPE inhibitor on the stainless steel thus leading to an increase in energy barrier associated with the corrosion process. Increase in temperature reduces the inhibition efficiency of the PPE extract but decreased as concentration of PPE extract is increased, this signify physisorption adsorption mechanism. The inhibition process occurs as a result of the formation of films on the metal surface thereby displacing water molecules from the metal surface. The positive values of enthalpy of activation and entropy of activation indicate an endothermic reaction and spontaneity of the adsorption process respectively. An increase in concentration resulting to higher activation energy value suggests physisorption mechanism in acid media.

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