CORROSION INHIBITION OF CARBON STEEL IN SALINE AND CARBON DIOXIDE SATURATED SALINE SOLUTIONS USING PUMPKIN POD EXTRACT AS INHIBITOR

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Abstract: The evaluation of the inhibitive efficiency of pumpkin pod extract as a green inhibitor in mitigating carbon steel corrosion using weight loss method was investigated. The environment considered were 3.5% w/v saline solution and CO_2 saturated saline solution. Five temperatures over the range of 40 – 80^{0}C and four pH media ranging from 3.15 – 8.0 were used. The parameters varied were; pH, temperature, time and concentration. The inhibition efficiency increases as concentration of pumpkin pod extract is increased. It was observed that the maximum inhibition efficiency of 94.954% was achieved at 250 ppm concentration, and 3.15 pH. It was observed that the weight loss decreases as the solution pH is increased. Thermodynamics parameters were evaluated from results of temperature studies where it was observed that the activation enthalpy of corrosion process increases from 23.124 to 66.970 kJ/mol and is endothermic in nature, while the mechanism of adsorption is chemisorption.

Keywords: Corrosion, carbon steel, weight loss, pumpkin pod extract, EDX

Introduction

Corrosion is the deterioration of metal by chemical attack or reaction with its environment. Corrosion is defined as the chemical or electrochemical reaction which proceed over the entire surface area at the same rate leading to degradation, loss and change in the morphology of the metal resulting in the lowering of mechanical strength of the component (Perez, 2016). Corrosion inhibitors minimize or stop corrosion when added in small concentrations to a corrosive medium (Riggs, 1973). There are different types or classes of corrosion inhibitors viz; passivation, volatile, cathodic, anodic, mixed, synergistic and precipitation inhibitors which are hazardous to the environment and human health due to the use of some chemicals that are generally harmful.

In practice, corrosion inhibition studies have become oriented towards human health and safety considerations. For this purpose, recently the researchers have been focused on the use of eco-friendly compounds such as plant extracts which contain many organic compounds (Bothi Raja and Mathur, 2008). Amino acids, alkaloids, pigments and tannins are used as green alternatives for the toxic and hazardous compounds. Due to biodegradability, eco friendliness, low cost and easy availability, the extracts of some common plants and plant products have been studied as corrosion inhibitors for various metals and alloys under different environment (Sharma *et al.*, 2015).

Green inhibitor has been studied to have 98% efficiency (Amitha and Bharathi, 2012. This present work studied the pumpkin pod extract as a possible green corrosion inhibitor, thermodynamics, and mechanism of its adsorption on carbon steel metal surface.

Materials and Method

Materials: The pumpkin pods waste was collected from Otor-Iyede community market in Isoko North Local Government Area of Delta State, Nigeria. Carbon steel was procured from an accredited iron sheet dealer in Warri, Delta State, Nigeria. Oven, weighing balance of model (BH – 600), beakers, pH meters (HANNA pH – 211) were made used of for the study. Analytical grades (Sigma Aldrich) ethanol, hydrochloric acid, acetone, carbon dioxide, and sodium chloride were used for the corrosion study. Distilled water was procured from the Department of Chemical Engineering Laboratory, Federal University of Petroleum Resources, Effurun Delta, State, Nigeria for sample and solutions preparation.

Methods

Sample pretreatment and its characterization

The pumpkin pods samples were washed thoroughly, thereafter sun dried and later pulverized into powdery form with the aid of a laboratory blender. It was then sieved with a sieve of 0.143 µm mesh. It was then stored in a desiccators prior to use for the corrosion study.

Fourier transform infrared (FTIR) spectroscopy

The structural organization of the substrate is investigated to identify the functional group present. The substrates were examined using Agilent Fourier Transform spectrometer Carry 630 with the range 500 – 400 cm^{-1} (wavelength). KBr (potassium bromate) is used as a background material in the analysis.

Scan electron microscopy energy dispersive X – rays analysis

The elemental composition of the carbon steel sample was inspected using a scanning electron microscope (SEM – EDX) PHENOMWORLD that was operated at 25kV. The metal surface was fixed to a metal stub 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 Scanning Electron machine.

Phytochemical analysis of the pumpkin pod extract

Thephytochemical screening of the pumpkin pod extract was carried out to identify the main active chemical constituents inherent in the pumpkin pod extract. The presence of saponins, alkaloids, terpenes, flavonoids, glycosides, reducing sugars and tannins were tested for by the simple quantitative and qualitative methods (Okwu, 2001; Herborne, 1973; Odeja *et al*., 2015; Rahilla *et al*., 1994; Sofowora, 1993).

Extraction of Pumpkin pod extract

The pumpkin pods (*Telfairia occidentalis*) were thoroughly washed with running water to remove any inherent dirt in the sample. The washed samples were then sun dried for 14 days and grinded to a particle size of 0.143 µm. 50 g of the dried Pumpkin pods (*Telfairia occidentalis*) powder was poured into a 500 mL Soxhlet extractor and 300 mL of 70% ethanol was reflux continuously for 3 hours at 78^{o}C. The set-up was placed on a heating mantle and the Pumpkin pods (*Telfairia occidentalis*) extract was extracted exhaustively by heating the solution. Rotary evaporator (model R-210) at 40^{o}C was used to recover the ethanol the residue left is now the pumpkin pod extract (Adesanmi, 2015). The extract was then stored in a tightly covered bottle prior to use.

Saturation of CO_2 in aqueous solution of NaCl

The experiment was performed with 1000 mL CO_2 saturated saline solution. The saline solution was prepared using analytical grade sodium chloride and deionized water. 1 L of NaCl solution of 3.5% w/v concentration was saturated by passing the CO_2 gas at 4 bar until a steady (saturated) pHs of 3.15, 4, 6 and 8 were obtained (Bashir, 2017).

Procedure of experimentation

The gravimetric or weight loss method was employed in the study. The carbon steel was mechanically polished with silicon carbide abrasive sand paper, degreased with ethanol, washed in distilled water and dried in acetone and later air dried before use. Each carbon steel coupon was sized 20 × 40 × 2 mm with total geometric surface area of 18.4 cm^2. Before polishing, a hole of 0.1 cm was drilled on each coupon. Pre-weighed carbon steel sample was suspended with the aid of a nylon thread in 100 mL beaker of the 3.5% w/v sodium hydroxide concentration without and with the different concentrations of Pumpkin pod extract as inhibitor which ranges from 50 to 250 ppm. The duration of the immersion was 24 h at ambient temperature (27°C). The thermodynamic parameters and inhibition mechanism of carbon steel corrosion were studied at 313, 323, 333, 343, and 353 K temperatures at contact immersion time of 5 h at various pH of 3.15, 4, 6, and 8 in saturated CO_2 saline solution. Each of the carbon steel metal coupons at the end of the specified duration time after the corrosion process was dipped in both distilled water and ethanol solutions. The sample was thereafter scrubbed to remove any remaining residual inhibitor concentration and NaCl solution. Subsequently, the carbon steel sample was then thoroughly washed with washing liquor, rinsed in de-ionized water and subsequently dried in acetone before been reweighed.

Determination of inhibition efficiency

The efficiency of pumpkin pod extract inhibitor on corrosion inhibition of carbon steel was obtained using Equation 1;

$$E(\%) = \frac{W_u - W_i}{W_u} \, x \, 100 \quad (1)$$

Where: W_u is the loss in weight in uninhibited medium (blank), and W_i is the loss in weight in inhibited medium.

Determination of rate of corrosion inhibition

The expression for measurement of rate of corrosion (C.R) in millimeters penetration per year (mm/yr) was used to measure the rate of corrosion rate for the specimens, which was expressed in equation 2 (Callister, 1997).

$$C.R. = \frac{87.6w}{at\rho} \quad (2)$$

Where: w is corrosion weight loss of carbon 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).

Determination of weight loss

The weight loss of the mild steel coupon was determined using equation 3;

$$\text{Weight loss, (g)} = W_o - W_b \quad (3)$$

Where: W_o is the initial weight of the mild steel coupon, W_b is the weight of the carbon steel coupon after corrosion study.

Results and Discussion

Characterization of carbon steel and pumpkin pod extract

Phytochemical analysis

The phytochemical constituents of the pumpkin pod extract as shown in Table 1, revealed the presence of saponin, reducing sugar, protein, steroids, tanins, flavonoids, phenol, cardiac glycoside, terpenoids with the absence of both alkanoids and anthraquinones in the extract.

The presence of these compounds has been reported to promote the corrosion inhibition of carbon steel (Mathina *et al*, 2016; Umoren *et al*., 2006; Nwigbo *et al*., 2012; Owate *et al*., 2014). Molecules containing nitrogen and acetylenic alcohols are claimed to form a film on the metal surface and can retard the metal dissolution process (an anodic reaction) as well as hydrogen evolution (a cathodic reaction) (Barmatov *et al*., 2012).

Table 1: Phytochemical constituents of pumpkin pod extract

Test Performed	Results
Colour description	Green
Saponin	+
Reducing sugar	+
Alkaloids	-
Protein (Amino Acids)	+
Steroids	+
Tannin	+
Flavonoids	+
Anthraquinones	_
Phenolic compounds	+
Carddiac glycoside	+
Terpenoids	+

(+) indicates present, (-) indicates absent

Fourier transform infrared analysis

The FT-IR spectrum of Pumpkin pod extract is as shown in Figures 1 and 2. Alcoholic –OH stretching is found to appear at 3324 cm^{-1}. The peak at 2974 cm^{-1} can be assigned to alcoholic C-H. The aromatic C=C stretching frequency is noticed at 1639 cm^{-1} while the value of 1728 cm^{-1} suggest C=O stretching frequency. Both peaks at 1508 and 1421 cm^{-1} are assigned to aromatic rings due to aromatic skeletal vibrations. The broad band at 1329 cm^{-1} is due to the bending vibrations of -OH groups while 1209 cm^{-1} is due to guaiacyl ring breathing with C-O stretching. Both Carbonyl and aromatic groups is an indication that the extract can be used as a corrosion inhibitor on carbon steel.

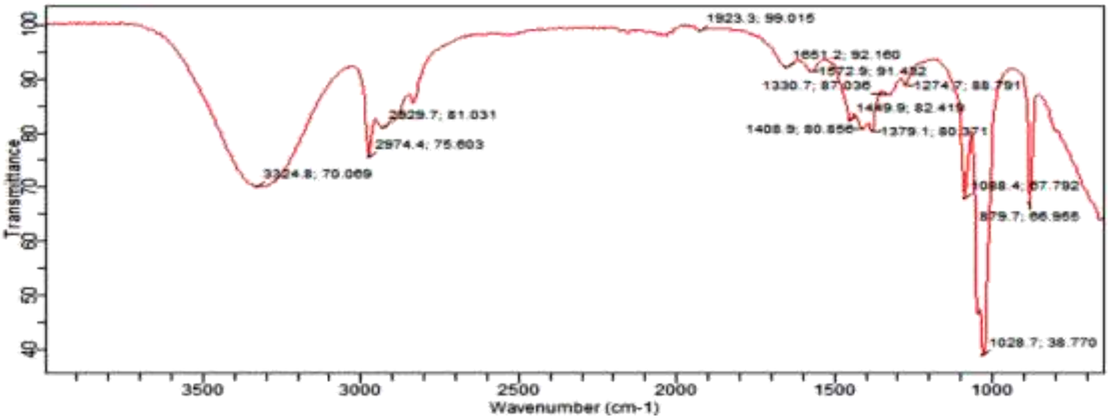

Fig. 1 FTIR spectra for pumpkin pod extract

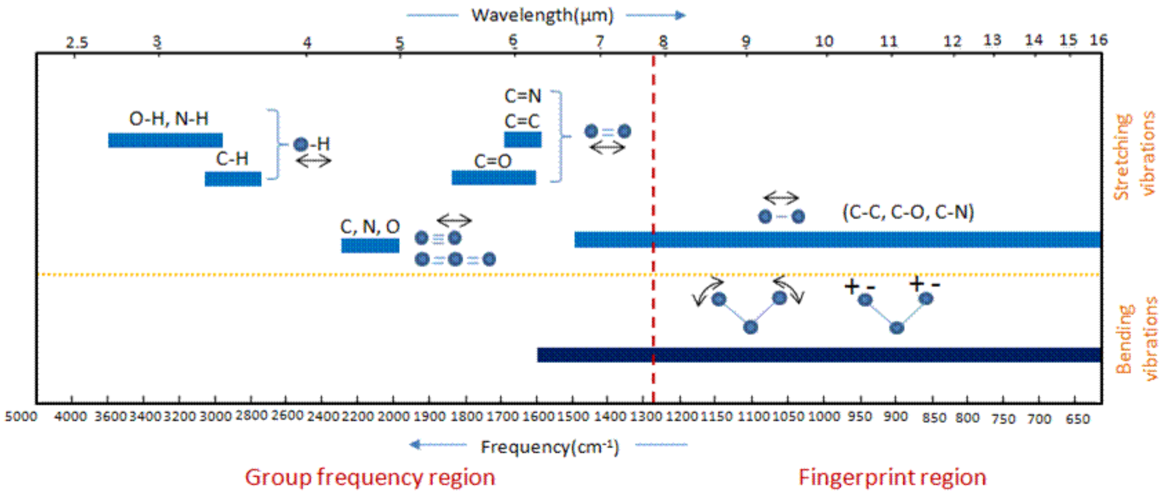

Fig. 2: Group frequency and fingerprint regions of the mid-infrared spectrum

Energy dispersive X – ray analysis

Table 2 and Fig. 3 showed the result of the EDX analysis performed on the carbon steel used. It can be seen that iron has the highest concentration.

Table 2: Result of the EDX analysis on carbon steel

Elements	Atomic Concentration (%)	Weight Concentration (%)
Iron	89.859	2.13
Silver	0.66	1.31
Yttrium	0.56	0.92
Niobium	0.54	0.91
Potassium	1.20	0.86
Calcium	1.03	0.76
Silicon	1.30	0.67
Chlorine	0.90	0.58
Sulphur	0.92	0.54
Sodium	0.84	0.35
Aluminium	0.63	0.31
Magnesium	0.37	0.17
Titanium	0.16	0.14
Phosphorus	0.23	0.13
Oxygen	0.42	0.12
Carbon	0.41	0.09

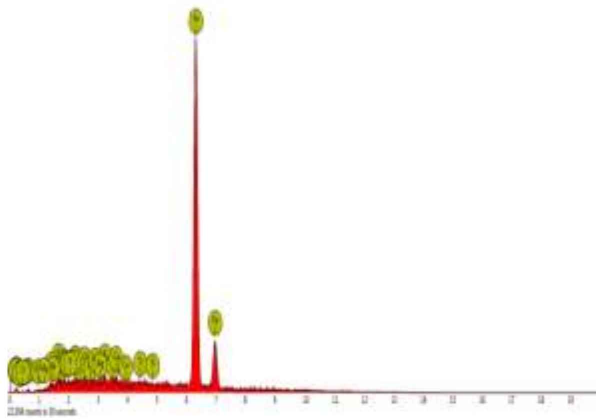

Fig. 3: EDX spectra of carbon steel

Effect of inhibition efficiency on corrosion inhibition of carbon steel

The plots of inhibition efficiency effect on immersion time were presented in Figs. 4 – 7. From the plots, it is observed that as exposure time of carbon steel increases the inhibition efficiency of the pumpkin pod extract decreases but conversely the inhibition efficiency increases as concentration of pumpkin pod extract is increased. This is due to the fact that at longer period of exposure time, there may be partial desorption of the inhibitor molecules from the metal surface which had been previously adsorbed on the surface of the metal (Ikpeseni, 2018) as well as the proportionality of the electrolyte of the pH to the corrosion of carbon steel. It was also noticed that an increase in pH favours increase in the inhibition efficiency. It is an indication that the inhibitor molecules of the protective film tends to be more favourable to the formation of reagent towards an alkaline environment. This is likely because the concentration of hydrogen ions in water decreases with the increasing pH, and thus, the depolarization of hydrogen ions in the process of metal corrosion is inhibited at high pH. Therefore, the tendency to form a protection film on the surface of carbon steel increases, as well as the corrosion inhibition rate (Liu *et al*., 2018).

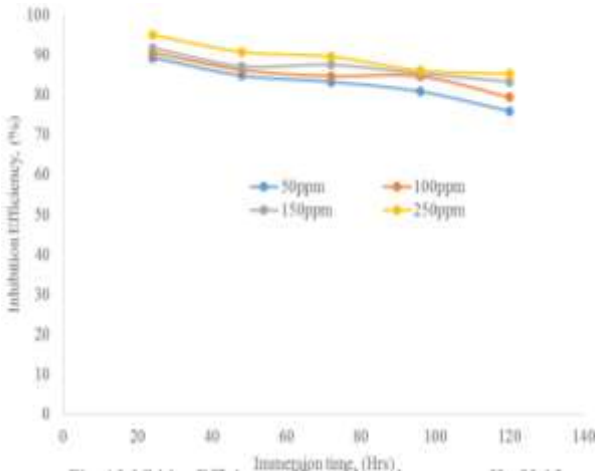

Fig. 4: Inhibition efficiency of pumpkin pod extract at pH of 3.15

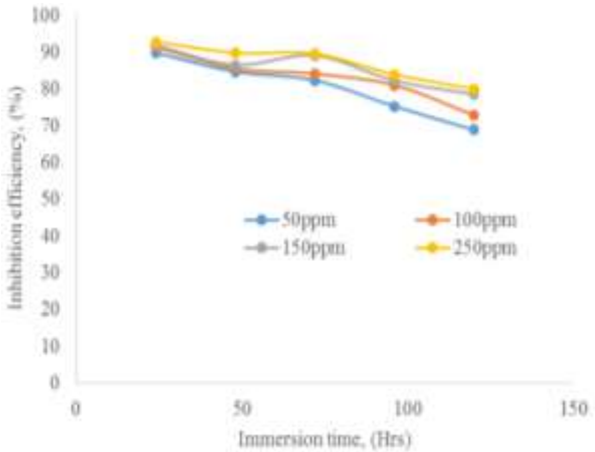

Fig. 5: Inhibition efficiency of pumpkin pod extract at pH of 4

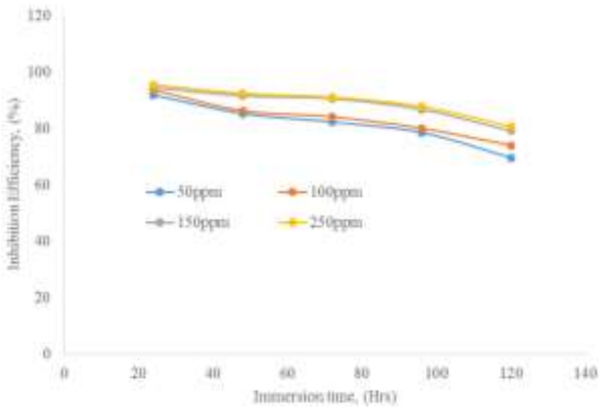

Fig. 6: Inhibition efficiency of pumpkin pod extract at pH of 6

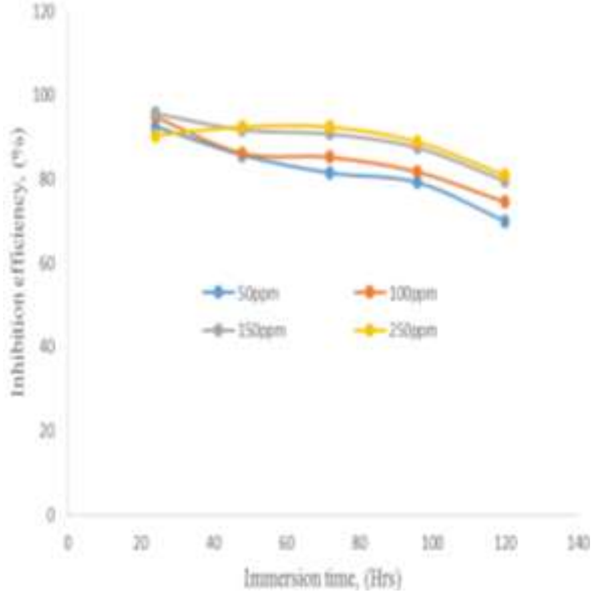

Fig. 7: Inhibition efficiency of pumpkin pod extract at pH of 8

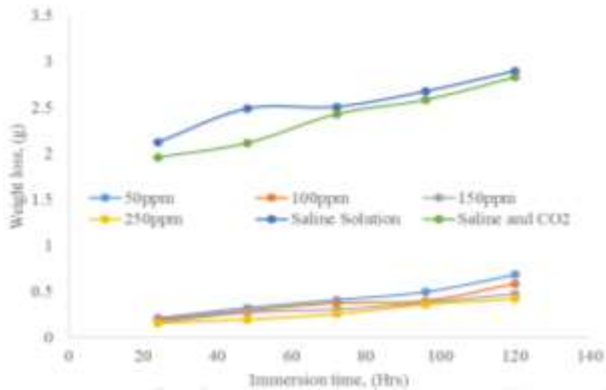

Fig. 8: Effect of weight loss on carbon steel corrosion inhibition at pH of 3.15

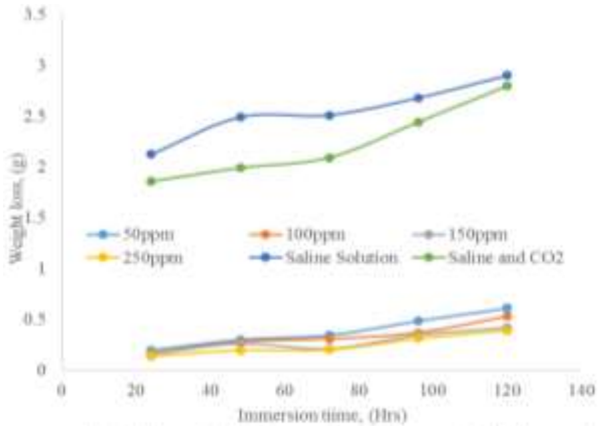

Fig. 9: Effect of weight loss on carbon steel corrosion inhibition at pH of 4

Effect of carbon steel weight loss on corrosion inhibition

The weightloss of carbon steel with varied concentrations of pumpkin pod extract inhibitor from 50 – 250 ppm, pH 3.15 – 8.0, and time of immersion from 24 – 120 h were shown in Figs. 8 – 11. It was observed that the weight loss of carbon steel decreases as the solution pH is increased. This is because at pH of 3.15 the cathodic reaction becomes hydrogen evolution which is chemically controlled instead of oxygen reduction. However, between pH 4 – 8 the cathodic reaction of the corrosion cell is reduction of oxygen because in this range of pH the weight loss of the carbon steel depends on the rate of oxygen diffusion to the cathodic sites of the corrosion cells to the surface of carbon steel and at this stage not the pH of the solution.

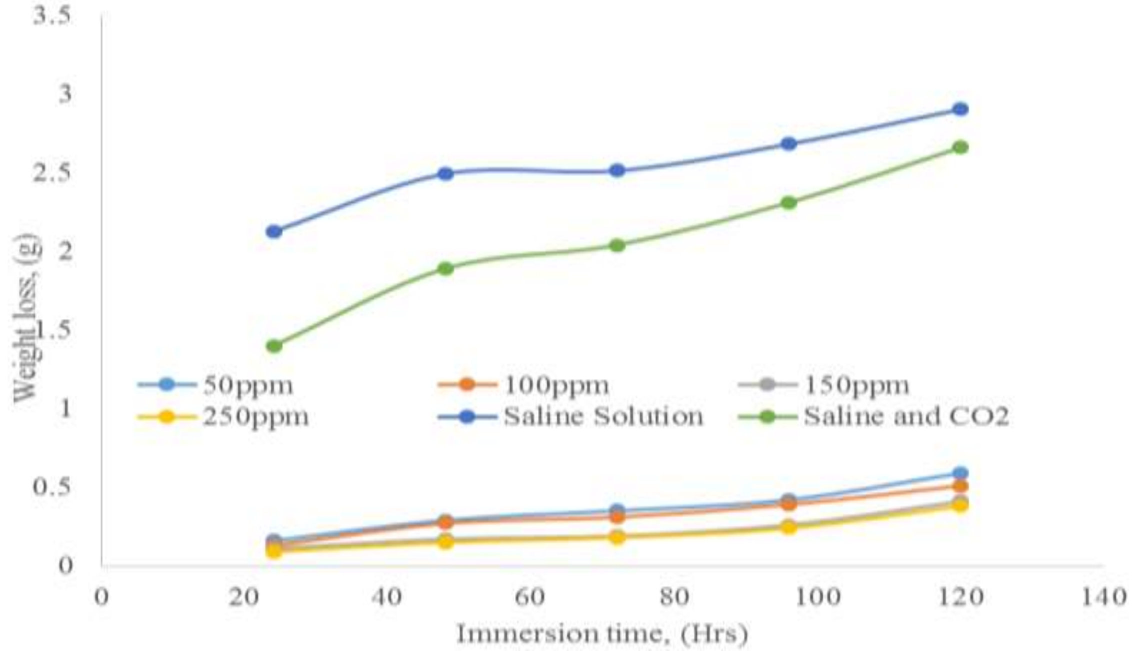

Fig. 10: Effect of weight loss on carbon steel corrosion inhibition at pH of 6

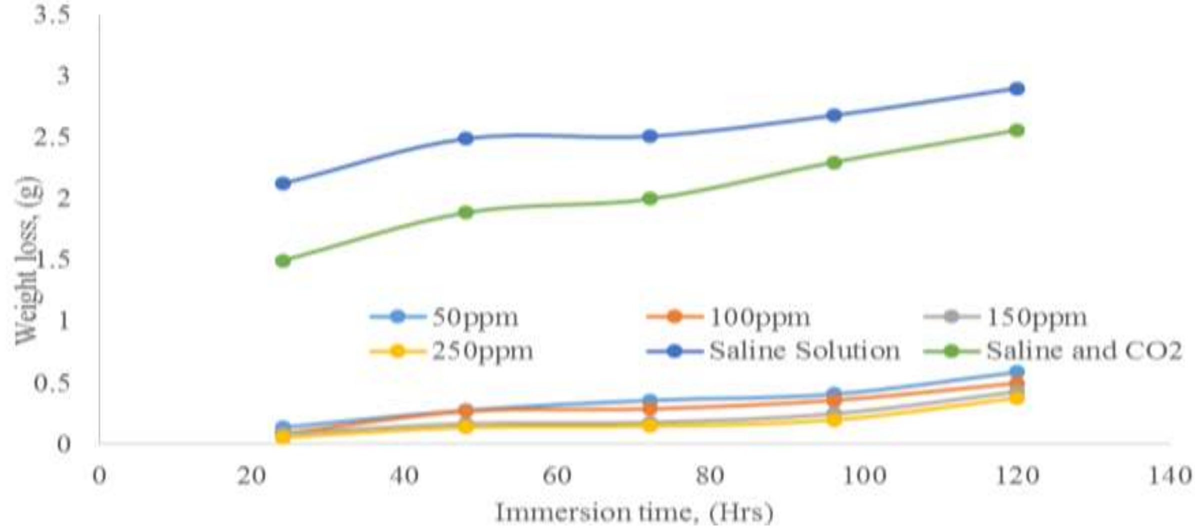

Fig. 11: Effect of weight loss on carbon steel corrosion inhibition at pH of 8

Effect of temperature

Figures 12 – 15 shows inhibition efficiency of the inhibitor against temperature at a fixed time of 5 h. The results show that the percentage inhibition efficiency of the inhibitor (at different concentration) decreases with increase in temperature. However, the inhibition efficiency increases as pH of solution is increased. This trend supports physical adsorption mechanism which enable us to ascertain that the protective films of the inhibitor was formed on the surface of the carbon steel metal that are less stable at higher temperature. This may be due to the desorption of some adsorbed molecules from the metal surface of the carbon steel at higher temperature which later makes most of the metal surface area of the carbon steel to be exposed to attack from the CO_2 saturated saline solution.

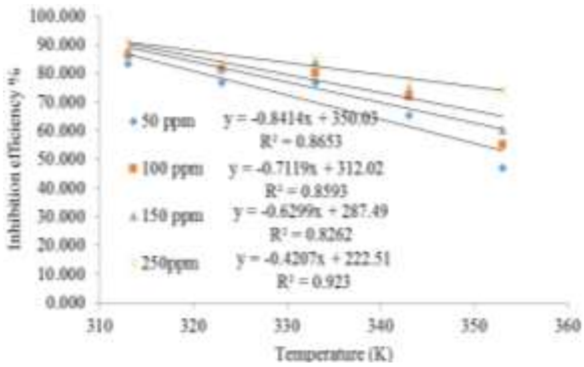

Fig. 12: Temperature effect on inhibition efficiency of pumpkin pod extract at pH of 3.15

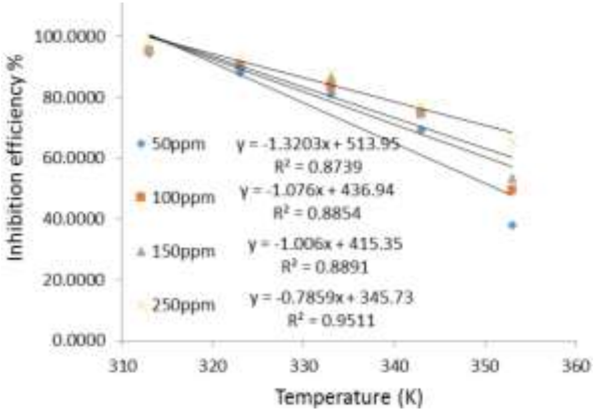

Fig. 13: Temperature effect on inhibition efficiency of pumpkin pod extract at pH of 4

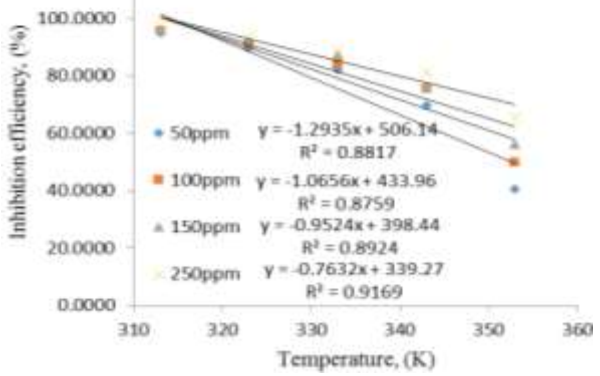

Fig. 14: Temperature effect on inhibition efficiency of pumpkin pod extract at pH of 6

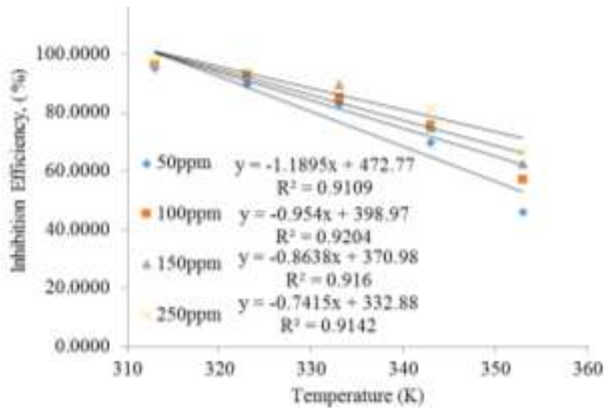

Fig. 15: Temperature effect on inhibition efficiency of pumpkin pod extract at pH of 8

Parameters of thermodynamic activation for the corrosion inhibition study

Thermodynamic properties such as Enthalpy (ΔH°) and Entropy of Activation (ΔS°) were undertaken so as to know the mode of adsorption mechanism involved in the corrosion inhibition process. The transition state theory equation given by equation 4 was used to calculate the adsorption thermodynamic activation parameters at varying pH of 3.15 – 8 (Mouheddin *et al*., 2018; Ogoke *et al*., 2009).

$$\log\left(\frac{C_R}{T}\right) = \left[\log\left(\frac{R}{Nh}\right) + \frac{\Delta S^o}{2.303R}\right] - \frac{\Delta H^o}{2.303RT} \quad (4)$$

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 (8.314 J/Kmol) and T is the temperature of the medium. The plot of log (C_R/T) against 1/T were seen to be linear in Figs. 16 - 19 from which (ΔH°) and (ΔS°) values were obtained from the slopes and intercept of the graph, respectively and listed in Tables 3 – 6. The large positive values of ΔH_{ads} revealed that the adsorption of Pumpkin pods extract inhibitor on the surface of carbon steel is endothermic in dissolution of carbon steel metal. It is observed that the enthalpy value of adsorption decreases with increase in inhibitor concentration which is an indication that the carbon steel dissolution becomes fast in the presence of the pumpkin pod extract inhibitor. Typically, an endothermic adsorption process that has a positive value of ΔHads is attributed unequivocally to chemisorption, while an exothermic adsorption process with ΔHads of negative value may involve either physisorption or chemisorption, or a combination of both the processes (Bentiss *et al*., 2005). The positive value of ΔHads obtained in this work shows a chemisorption mechanism corroborating the work of (Chien *et al*., 2020). Large and more negative values of entropies ΔS_{ads} show that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place when going from reactants to the activated complex of the corrosion process as well as a result of the replacement process of water molecules during adsorption of pumpkin pod extract inhibitor molecules onto carbon steel (Dahmani *et al*., 2010; Bouklah *et al*., 2006).

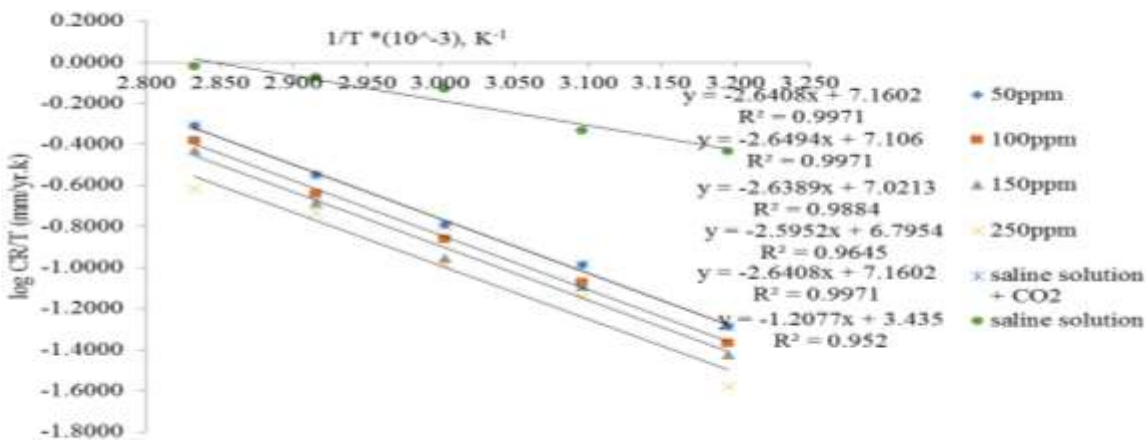

Fig. 16: Plot of log CR/T against the inverse of absolute temperature at pH of 3.15

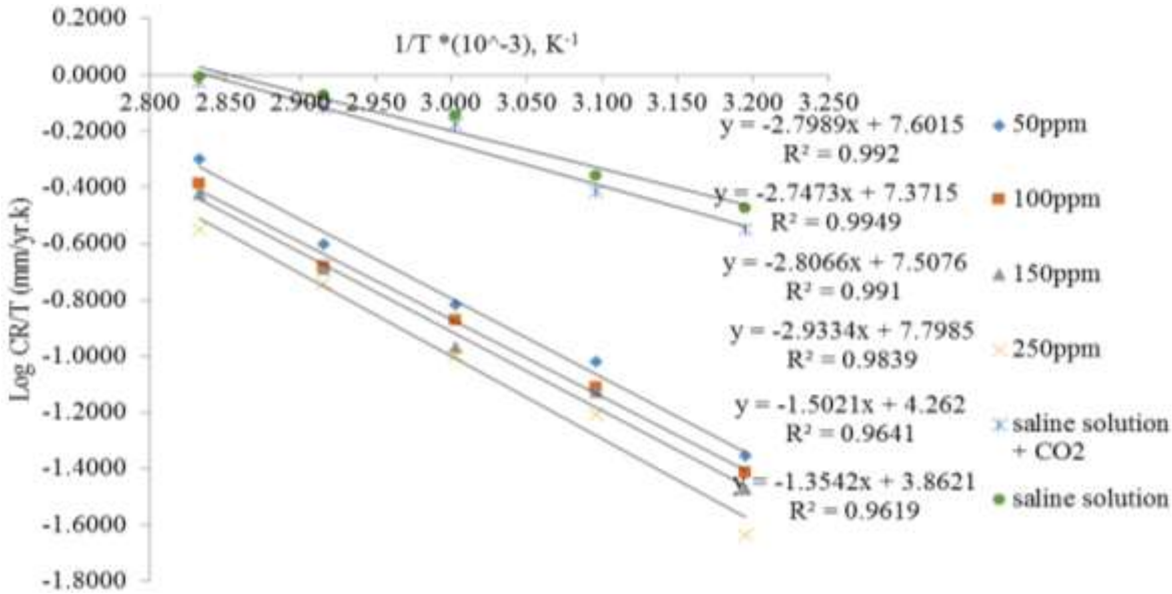

Fig. 17: Plot of log CR/T against the inverse of absolute temperature at pH of 4

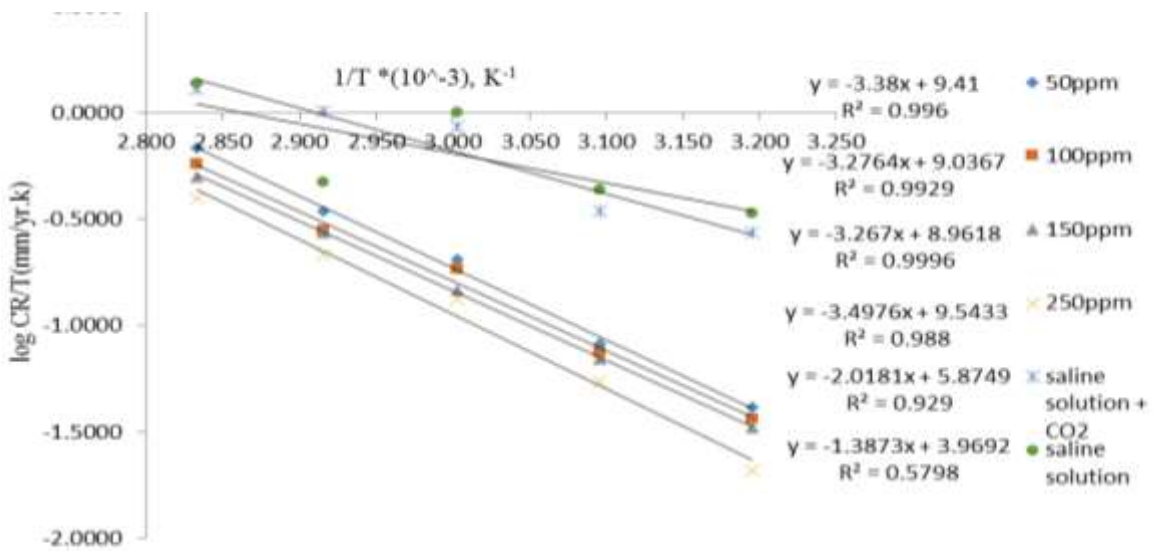

Fig. 18: Plot of log CR/T against the inverse of absolute temperature at pH of 6

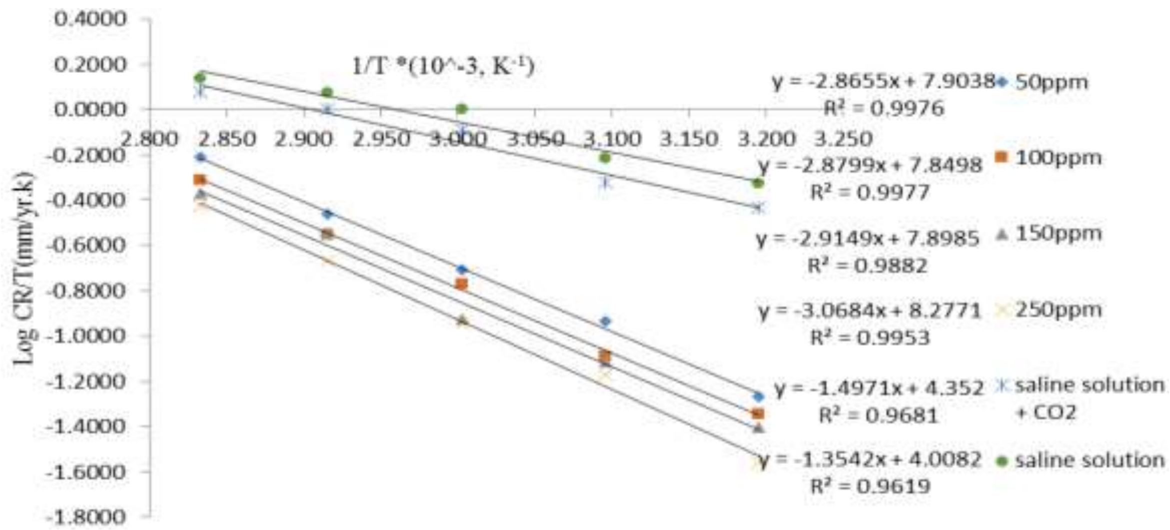

Fig. 19: Plot of log CR/T against the inverse of absolute temperature at pH of 8

It can be seen in Tables 3- 6 that ΔS_{ads} decreased in value in the presence of pumpkin pod extract in comparison to saline and CO_2 saturated saline solutions. This is because the transition state of the rate determining recombination step represents a more orderly manner of arrangement in relative to the initial state which makes the entropy of activation value obtained to be high. However, in the presence of the pumpkin pod extract inhibitor, the rate determining step is the discharge of hydrogen ions to form adsorbed hydrogen atoms because the surface is covered with the pumpkin pod extract molecules.This will eventually retard the discharge hydrogen ions at the metal surface causing the system to pass from a random arrangement, and hence entropy of activation is decreased (Nwosu and Muzakir, 2016). It was also noticed that the enthalpy of the dissolution increases as the pH of solution is increased until it get to the pH of 8 where it decreased.

Table 3: Enthalpy and entropy of corrosion inhibition at pH of 3.15

Inhibitor's Concentration (ppm)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol K)
50	50.728	-55.412
100	50.564	-60.478
150	50.564	-60.478
250	50.527	-63.138
Saline solution	23.124	-130.656
Saline solution + CO_2	49.697	-67.463

Table 4: Enthalpy and entropy of corrosion inhibition at pH of 4

Inhibitor's Concentration (ppm)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol K)
50	56.166	-48.257
100	53.738	-53.826
150	53.591	-52.029
250	52.603	-56.4322
Saline solution	25.929	-123.627
Saline solution + CO_2	28.761	-115.97

Table 5: Enthalpy and entropy of corrosion inhibition at pH of 6

Inhibitor's Concentration (ppm)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol K)
50	66.970	-14.849
100	64.717	-17.401
150	62.734	-24.549
250	62.554	-25.983
Saline solution	26.563	-121.577
Saline solution + CO_2	38.641	-85.092

Table 6: Enthalpy and entropy of corrosion inhibition at pH of 8

Inhibitor's Concentration (ppm)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol K)
50	58.751	-39.093
100	55.812	-46.342
150	55.142	-47.274
250	54.866	-46.240
Saline solution	25.929	-120.830
Saline solution + CO_2	28.665	-114.247

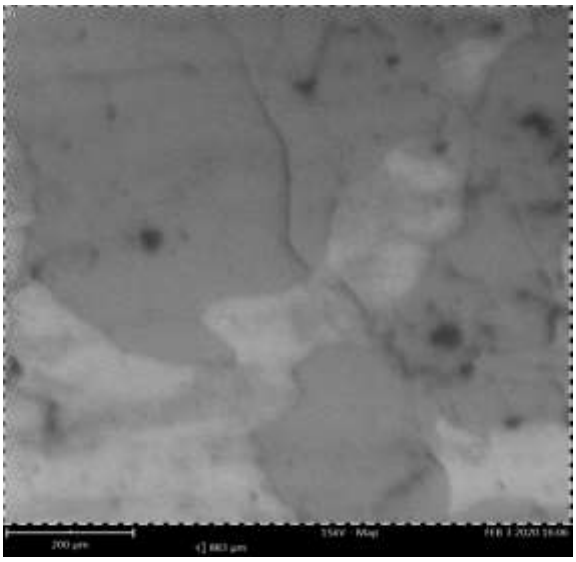

Fig. 20a: SEM of carbon steel

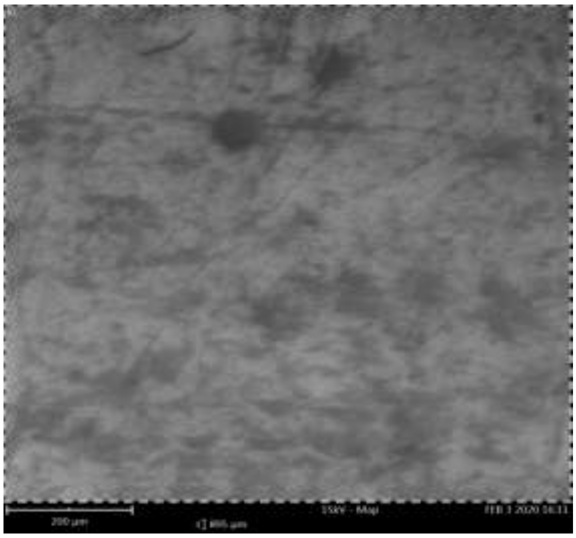

Fig. 20b: SEM of carbon steel 200 ppm at pH of 3.15

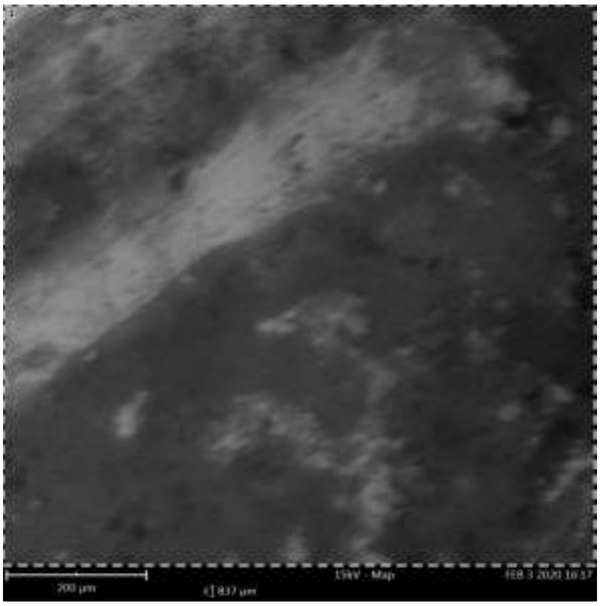

Fig. 20c: SEM of carbon steel 200 ppm at pH of 8

Surface morphology analysis of carbon steel metal

Scanning Electron Microscope (SEM) images were taken in order to study the surface morphology of carbon steel in absence and presence of Pumpkin pods (*Telfairia occidentalis* extract. SEM image (Fig. 20a) shows the plain carbon steel metal after polishing while Figure 20b reveals that with 200 ppm concentration of pumpkin pod extract at pH of 3.15 in saline solution. Fig. 20c is the carbon steel metal in 200 ppm of Pumpkin pod (*Telfairia occidentalis)* extract at pH of 8. It showed a surface with fibre –like protective layer as a result of the Pumpkin pods (*Telfairia occidentalis)* extract deposition on the carbon steel metal surface due to the formation of an adsorbed film of pumpkin pod (*Telfairia occidentalis)* molecules (protective layer) on the carbon steel surface. Comparing Fig. 20b with Fig. 20c at the same magnifications (1000X), it can be seen that the pits evidence in figure 20b has disappeared and carbon steel surface is almost free from corrosion in saline solution due to the carbon steel surface coverage by the pumpkin pod inhibitor.

Conclusion

In this present investigation, Pumpkin pod extract (*Telfairia occidentalis)* was extracted and characterized using the followings; phytochemical screening, FTIR spectroscopy, and SEM – EDX, analyses which was subsequently used as a corrosion inhibitor on carbon steel. The effects of corrosion inhibition of Pumpkin pods (*Telfairia occidentalis)* extract on carbon steel in saline and CO_2 saturated saline solutions was assessed using gravimetric method. Thermodynamics studies were carried out to estimate the mechanism of adsorption for the Pumpkin pod extract molecules on the surface of carbon steel. The inhibition efficiency increases with increase in the Pumpkin pod extract concentrations, but decreases with rise in temperature while the weight loss decreased as inhibitor concentration is increased. The corrosion inhibition performance of Pumpkin pods (*Telfairia occidentalis)* extract was found to be temperature dependent. The inhibition by Pumpkin Pod extract occurred through chemisorption as evidenced in increased value of entropy as concentration of pumpkin pod extract is increased. The activation enthalpy of corrosion process increases from 23.124 to 66.970 kJ/mol. The corrosion inhibition adsorption process on carbon steel is endothermic due to the positive value of enthalpy. The activation entropy (ΔS^o) values in the absence and presence of pumpkin pod extract were all negatives which implied that the activated complex in the rate determining step represents an association rather than a dissociation step. This indicates that during the adsorption process, an increase in the degree of disorderliness occur and the dissolution of carbon steel becomes faster in the presence of pumpkin pod extract inhibitor compared to the saline solutions.

Conflict of Interest

Authors declare that there is no conflict of interest related to this work.

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