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Full Paper

Corrosion Inhibitive Behaviour of the Natural Honey in Acidic Medium of A315 Mild and 304 Austenitic Stainless Steels

Ayodeji Ayodele Ayoola1,[*] Oyinlola Rukayat Obanla,[1] Oluwabunmi Grace Abatan,[1] Ojo Sunday Isaac Fayomi,[2,3] Itopa Godwin Akande,[4] Oluranti Agboola,[1] Omoniyi Augustine Ayeni,[1] Daniel Oyekunle,[1] Victoria Abiodun Olawepo[1] and Oyinkansade Oluwasayo Ayo-Aderele[1]

[1]*Chemical Engineering Department, Covenant University, P.M.B. 1023, Ota, Ogun State, Nigeria*
[2]*Mechanical Engineering Department, Covenant University, P.M.B. 1023, Ota, Ogun State, Nigeria*
[3]*Surface Engineering Research Centre, Tshwane University of Tech., P.M.B. X680, South Africa*
[4]*Mechanical Engineering Department, University of Ibadan, Ibadan, Oyo State, Nigeria*

*Corresponding Author, Tel.: +234 803 562 4739
E-Mail: ayodeji.ayoola@covenantuniversity.edu.ng

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Abstract- The corrosion inhibition performance of the natural honey in H_2SO_4 acidic medium containing mild steel and stainless steel, using weight loss and electrochemical techniques was investigated. The study involved the determination of the effects of the variation of the concentrations of natural honey inhibitor on the corrosion process. Potentiodynamic polarization for the electrochemical measurements was carried out by using Autolab PGSTAT 101 Metrohm potentiostat. Results obtained showed that increase in natural honey concentration (0–10 v/v%) retards the rate of metal dissolution and hence inhibits the corrosion of the metals. And the efficiency of the natural honey inhibitor increased with increased inhibitor concentration. The Tafel plots showed that the natural honey significantly decreased the corrosion potential (E_{corr}) and current density (J_{corr}); but increased the surface coverage (θ) and polarisation resistance. Adsorption and thermodynamics studies revealed that the Langmuir adsorption isotherm was obeyed and the large values of ΔG_{ads}obtained as well as its negative sign implied strong interaction and high efficiency of adsorption. SEM analysis of the metals (before and after corrosion) revealed significant reduction in corrosion rate as the concentrations of natural honey inhibitor increased.

Keywords- Corrosion, Honey, Inhibitor, Mild steel, Stainless steel

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1. INTRODUCTION

Corrosion is basically defined as the deterioration of any metallic material due to the chemical or electrochemical attack of the material by its corrosive environment. The loss suffered from the corrosion of metals is huge for individuals, organisations and even countries. These losses range from components or equipment breakdown, plant shutdown, loss of life and properties, to mention a few [1–5].

The study of the corrosion of mild steel and stainless steel has received considerable attention because both form of steels are among the most commonly used metallic materials, particularly in automobile, food processing, chemical, construction and pharmaceutical industries [6,7]. Despite the widespread use of these alloys, the disadvantage of not having perfect resistance to corrosion has not been overcome [8].

Among the techniques of combating corrosion, the application of inhibitors is quite effective. It is an economical way of controlling corrosion and its ease of introduction makes it popular. Corrosion inhibitors are compounds that are added in small doses to the corrosive medium in order to prevent or impede corrosion reaction [9,10].

For a substance to be considered an inhibitor, it has to be able to restrict or slow down the corrosion process by reducing the activity of either a reactant or catalyst on the surface of the metal. Through the effect of oxidation, the inhibitor also has to enhance the formation of a protective film of oxide that will create a barrier between the surface of the metal and the species that are selectively adsorbed, resulting in a retardation of the corrosion process [11].

Commercial inhibitors for the prevention of corrosion are usually inorganic, with the inclusion of some kinds of organic compounds. However, the use of some commercial inhibitors has been limited owing to their toxicity and inadequate inhibition efficiencies at low dosages [12,13]. In recent years, intense efforts made by researchers show that innovative, non-toxic and efficient corrosion inhibitors can be obtained from the utilization of natural products derived from plants, animals or minerals. This is due to the presence of their certain essential organic components such as tannins, polyphenols, alkaloids, carbohydrates and proteins as well as products of their acid hydrolysis. Different plant extracts of polyphenols, flavonoids and phenolic acids have been shown to have anticorrosive as well as antioxidant properties [14,15]. These natural products are more effective as anticorrosion agent, couple with the added advantage of being environmentally friendly and harmless in comparison to inorganic compounds that have been in use make them the better choice in any chemical or any industrial application [15–17].

Research as shown that organic inhibitors impede corrosion through the mechanism of adsorption and formation of films on the surface of metals. The adsorption action of organic inhibitors on the surface of a metal can affect the corrosion resistance behaviour of the metal significantly.

The adsorption of organic inhibitor, in general, can take any of the following forms: electrostatic attraction between the charged molecules of inhibitors and charged metal surface, interaction between unshared electron pairs of the molecules with the metal surface, interaction of the presence of conjugated bonds in the compound with the metal. In these cases, corrosion is being controlled by any of these the followings: retarding reactions at the anode and/or cathode, retarding the rate of diffusion of aggressive species to the surface of the metal or by reducing the surface's electrical resistance [18].

In this study, the use of natural honey as an eco-friendly green corrosion inhibitor for mild steel and stainless steel in an acidic environment will be studied. Natural honey is non-toxic, it contains phenolic compounds which makes it a good source of antioxidants that prevent oxidation reaction of corrosion process [16]. The major chemical constituents of a natural honey responsible for the inhibitive corrosion performance of the honey are shown in Figure 1.

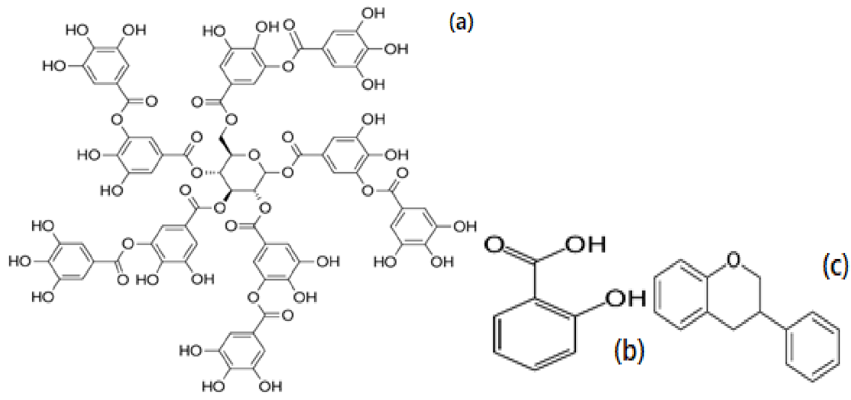

Fig. 1. Corrosion inhibition constituents in honey **(a)** polyphenol; **(b)** phenolic acid; **(c)** flavonoid (tannin)

2. EXPERIMENTAL PROCEDURES

The materials used in this research are A315 mild steel, type 304 austenitic stainless steel and natural honey which was obtained from a local market in Ota, Nigeria.

2.1. Preparation of the materials used

The mild and stainless steels were cut into 35 coupons each, with a dimension of 15×15×5 mm. The surface of all the samples were simply abraded with emery paper, of different grades and then rinsed with distilled water before being dried at room temperature. Table 1 shows the elemental composition of both the mild steel and stainless steel used. And the concentrations of honey used as inhibitor are 2.5, 5.0, 7.5 and 10 %v/v, calculated using Equation 1.

$$\%v/v = \frac{mL\ of\ honey}{200\ mL\ of\ the\ acid} * 100 \quad (1)$$

Table 1. Composition of mild steel and stainless steel

Element	**%composition**	
	mild steel	**stainless steel**
C	0.134	-
Si	0.119	-
Mn	0.237	-
Mo	0.083	-
Co	0.012	-
Al	0.050	-
Cu	0.044	-
Nb	0.108	-
Sn	0.046	-
Ni	0.019	9.32
Cr	0.094	20.11
Fe	98.80	69.32

2.2. Tests for honey compositions

The natural honey used as inhibitor in this study was tested for the presence of certain constituents that aid in its inhibitory behaviour. The following tests were carried out:

2.2.1. Test for alkaloids

50 mg of the natural honey was stirred with a few ml of dilute hydrochloric acid and filtered. To 1 ml of the filtrate, few drops of Mayer's reagent was added to the side of the test tube. The presence of a white or creamy precipitate indicated a positive result.

2.2.2. Test for flavonoids

Alkaline reagent test was used to test for the presence of flavonoids in natural honey by adding a few drops of dilute sodium chloride to a sample of the natural honey. An intense yellow colour was observed while the sample turned colourless upon the addition of a few drops of a dilute acid added indicating that flavonoids were present.

2.2.3. Test for phenols

50 mg of the natural honey was dissolved in 5 ml of distilled water. Few drops of neutral 5% Ferric chloride solution were then added. The appearance of a dark green colour confirmed the presence of phenols.

2.2.4. Test for terpenoids

2 ml of Chloroform and concentrated sulphuric acid was carefully added to 0.5 ml of the sample of natural honey. The appearance of a red-brown colour at the interface confirmed that terpenoids were present in the natural honey.

2.2.5. Test for saponins

2 ml of distilled water was added to the natural honey and shaken lengthwise in a graduated cylinder for about 15 min. The appearance of 1cm foam confirmed the presence of saponin.

2.3. Weight loss experiments

Both the mild steel and stainless steel samples were initially weighed before being totally immersed in a corrosive environment of 200 mL of 0.5 M of H_2SO_4 (containing varied concentration of honey inhibitor) for 15 days in order to allow corrosion to occur. The weight loss of each sample was determined at intervals of three days.

2.4. Electrochemical measurements

Electrochemical measurements were carried out at ambient temperature of 25 °C using Autolab PGSTAT 101 Metrohm potentiostat/galvanostat with NOVA software version 2.1.2 and electrode cell containing 200 mL of the electrolyte (H_2SO_4), with and without varied concentrations of honey inhibitor. The experimental set up was a conventional three-electrode cell assembly with working electrode (metal sample), graphite rod as the auxiliary electrode and Ag/AgCl as the reference electrode. Potentiodynamic polarization data were obtained from potential of −2.0 to +1.5 V versus open circuit potential at a scan rate of 0.005 V/s. The working electrode (mild steel and stainless steel) was completely immersed in the electrolyte solution to attain the steady-state potential. The polarization potential (E_{corr}) and current density (I_{corr}) data were evaluated from the tafel plots.

2.5. Adsorption studies

Considering the data obtained from weight loss and electrochemical experiments, the appropriate adsorption isotherm model that described the adsorption process was inferred by considering the adsorption plots obtained. The process of adsorption of the inhibitive behaviour of the honey was best explained using Langmuir adsorption isotherm model (Equation 2):

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh} \tag{2}$$

where θ=degree of surface coverage at different concentrations of the inhibitor, C_{inh} = concentration of the inhibitor, K = equilibrium constant.

2.6. SEM analysis

Scanning electron microscopy analysis was used to investigate the morphology of the surface of the uninhibited and inhibited metal samples (mild steel and stainless steel samples). The SEM analysis was carried out using (Jeol JSM–7600F UHR Analytical FEG SEM).

3. RESULTS AND DISCUSSION

3.1. Weight loss of metal samples

Figures 2(a) and (b) show the trends of the weight loss observed for both mild steel and stainless steel samples immersed in 20 mL of 0.5 M sulphuric acid (with and without varied concentrations of natural honey inhibitor).

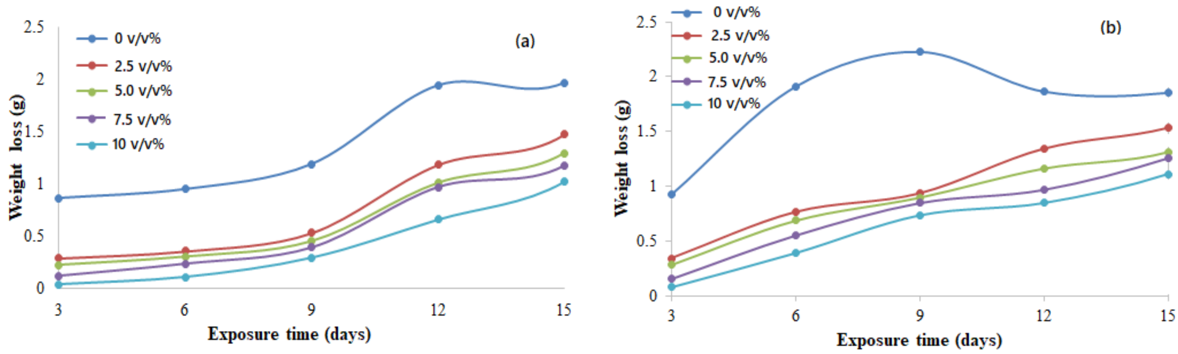

Fig. 2. Trends of the weight loss observed for **(a)** mild steel and **(b)** stainless steel samples

From Figure 2, it could be seen that the weight loss of the samples (due to corrosion) increases with the time of exposure. And the weight loss experienced by mild steel was higher than the one encountered by stainless steel, at the same corrosion conditions. The reason for the differences could be attributed to the higher resistance to corrosion that stainless steel possesses in comparison to mild steel.

Also, the Figures show that the rate of weight loss of sample was higher when no honey inhibitor was used (especially within the first nine days) for both mild steel and stainless steel. This is an indication that the introduction of honey inhibitor reduces the corrosion reaction of the process. It could also be observed that the rate of corrosion (weight loss per time) reduces as the concentration of the inhibitor applied increases, for both mild steel and stainless. This implies that the corrosion resistant property of the natural honey increases as the concentration of the inhibitor increased. That is the bond between the inhibitor molecules and metal surface increases hence providing a greater surface coverage (θ) and better inhibition efficiency [19].

3.2. Inhibitive efficiency of the natural inhibitor

Figures 3(a) and (b) reveal the inhibition efficiency against the inhibitor concentration over a period of 15 days for metal samples in the acidic and corrosive media.

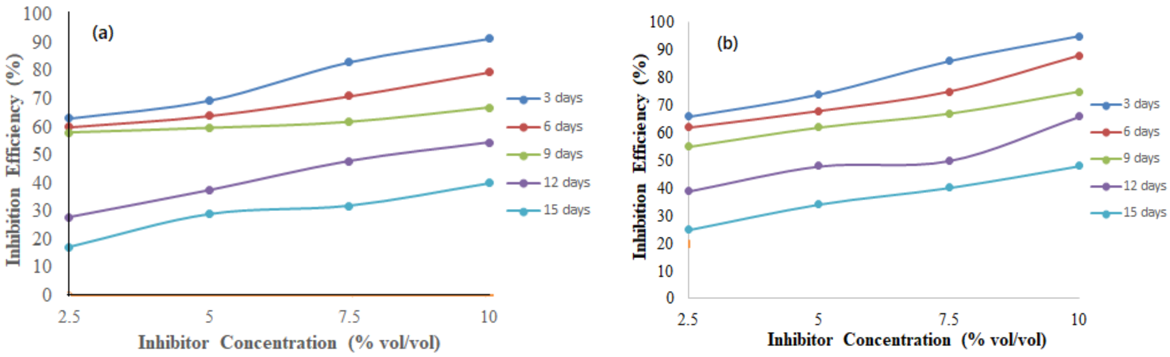

Fig. 3 Inhibition efficiency of **(a)** mild steel and **(b)** stainless steel

From Figure 3, the efficiency of the inhibitive natural honey used during the metal corrosion process increases with increase inhibitor concentration. Also, the inhibition efficiency was higher when stainless steel was used, compared to when mild steel was adopted, at same environmental condition. These findings support the results obtained under weight loss. That is, as the concentration of the natural honey increased, the adsorption behaviour of the inhibitor increased by covering more reaction sites on metal surfaces, thereby reducing corrosion reactions [20].

Chemical constituents such as tannins, saponins, flavonoids present in natural honey could act as inhibiting passive film on the metal surface. This film serves as a barrier between the sample and corrosive environment interface, thus preventing and/or stifling corrosion reactions of anodic (oxidation/dissolution) and cathodic (reduction) processes [21].

3.3. Electrochemical behaviour of mild steel and stainless steel in H_2SO_4

Tables 2 and 3 show the electrochemical parameters for both inhibited and uninhibited mild steel and stainless steel respectively. Increase in polarisation resistance, as the inhibitor concentration increased, implies reduction in corrosion rate and increased honey inhibitor efficiency.

Table 2. Electrochemical tests parameters for inhibited and uninhibited mild steel

Corrosion conc. (v/v %)	E_{corr}, (Obs) V	j_{corr} (A/cm^2)	Corrosion rate (mm/yr)	Polarization resistance
0	-0.6257	0.00075	9.0714	3.4980
2.5	-0.5338	0.00063	4.7241	6.9596
5.0	-0.5102	0.00061	3.4447	15.9390
7.5	-0.5005	0.00047	2.3433	34.1560
10.0	-0.3709	0.00028	2.2220	53.3540

Table 3. Electrochemical tests parameters for inhibited and uninhibited stainless steel

Corrosion conc. (v/v %)	E_{corr}, (Obs) V	j_{corr} (A/cm^2)	Corrosion rate (mm/yr)	Polarization resistance
0	-0.5857	0.00087	8.3687	4.0902
2.5	-0.5745	0.00045	4.0032	6.2487
5.0	-0.4988	0.00039	2.3660	41.6260
7.5	-0.3111	0.00025	2.0044	67.0160
10.0	-0.2651	0.00021	1.8458	79.9060

It could be seen that increase in concentration of the honey inhibitor in the corrosive medium reduced the current density (j_{corr}), corrosion rate and increase polarisation resistance significantly.

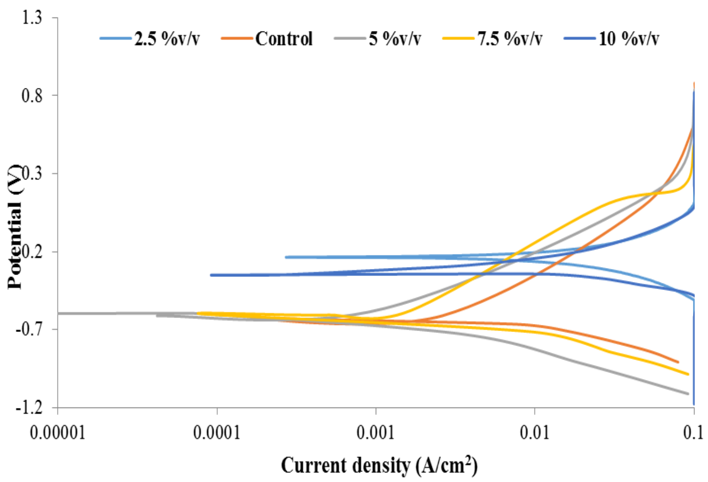

Fig. 4. Tafel plots for A315 mild steel in acidic medium with varied concentrations of natural honey inhibitor

These are in conformity with the results obtained in weight loss approach that is an increase in the concentration of the inhibitor hindered the corrosion of both the mild and stainless steels. The E_{corr} values defines the potential at which the rate of oxidation is equal to the rate of reduction and at this point, both polarities of current are present. If the values tend towards the more negative side of the E_{corr}, then the cathodic current predominates at the expense of the anodic current. The little variations in the E_{corr} values suggests a mixed type behavior in polarization of both steels, as it doesn't fully assume either the negative or the positive type [22]. This fact is further confirmed by the anodic and cathodic nature of the Tafel plots obtained for both types of the metal steels, as shown in Figures 4 and 5. That is, Figures 4 and 5 below show the Tafel plots for mild steel and stainless steel in the given potential range.

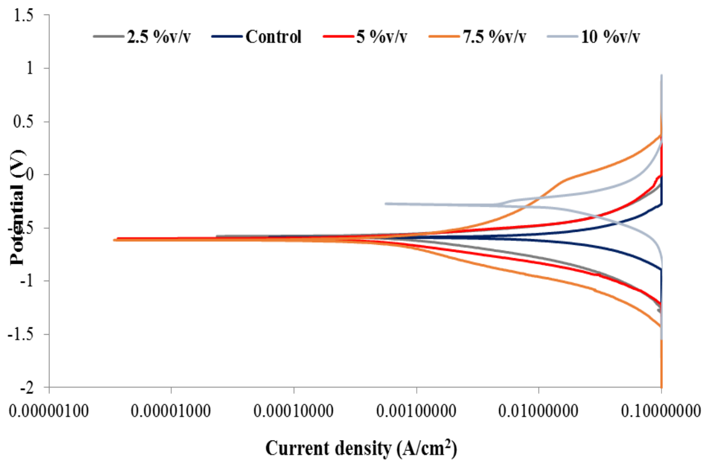

Fig. 5. Tafel plots for 304 stainless steel in acidic medium with varied concentrations of natural honey inhibitor

The corrosion rate, as seen in Figure 6, show a sharp reduction trend in corrosion rate as the concentration of honey inhibitor applied increased from 0 to 10 %v/v. The corrosion rate was highest when no natural honey inhibitor was used while the rate was the least at 10 %v/v honey inhibitor, for both mild steel and stainless steel. This trends further confirm the fact that the natural honey was an effective corrosion inhibitor. Similar results were recorded using weight loss method; hence this behaviour validates the adsorptive performance of the chemical constituents in the natural honey used. That is, the anticorrosion performance observed could be attributed to the synergistic effect of the combination of all the effective inhibitive compounds (such as flavonoids, polyphenols, phenolic acids) present in the honey [20].

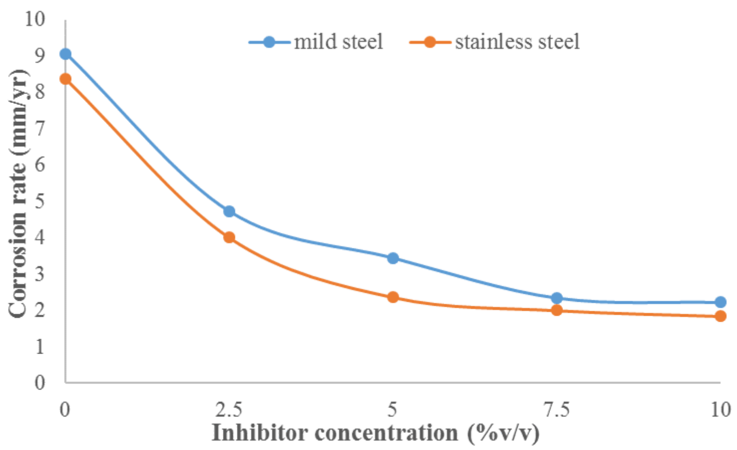

Fig. 6. Corrosion rate of A315 mild steel and 304 stainless steel samples in acidic medium with varied concentrations of natural honey inhibitor

3.4. Adsorption and thermodynamics considerations using natural honey inhibitor

Identified adsorption properties can also be used to determine the inhibitive nature of the natural honey. Based on Langmuir adsorption isotherm, the plots of C/θ versus C yield straight lines as shown in Figure 7. Table 4 shows the linear correlation coefficient of the fitted data obtained from the Langmuir adsorption model for mild and stainless steel samples at 25 °C.

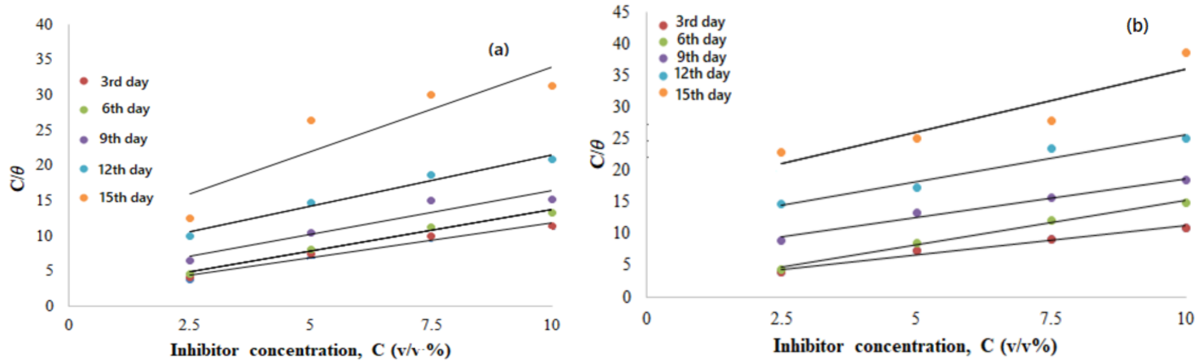

Fig. 7. Plots of ***C/θ*** versus ***C*** for mild steel and stainless steel

It can be seen that as the corrosion period increase, the linear correlation coefficients (**R^2**) decrease. That is, the inhibition efficiency of the honey reduces gradually as the corrosion progress in days. This may be due to the fact that the adsorptive layers formed during the first three days gradually suffered depletion, thereby reduce the inhibitive behaviour of the honey due to desorption process [18]. And this was also confirmed by the results obtained in Figure 2 and Table 4.

Table 4. Linear correlation coefficient of the fitted data obtained from the Langmuir adsorption model for mild steel and stainless steel at 25 °C

Day	Mild steel R^2	Stainless steel R^2
3rd	0.9901	0.9962
6th	0.9817	0.9847
9th	0.9462	0.9698
12th	0.9022	0.9007
15th	0.8712	0.8902

Table 5 shows the values of the adsorption constant (K_{ads}) and Gibbs free energy (ΔG_{ads}) obtained for the two forms of the steels used. K_{ads} and ΔG_{ads} were determined by considering the intercepts of the straight lines using the Langmuir isotherm, as well as the expression ΔG_{ads} = - 2.303RT log (55.5 K_{ads}). R is the universal gas constant (8.314 JK^{-1} mol^{-1}), T is absolute temperature (K) and 55.5 is the molar concentration of water in the solution expressed in molarity units (mol L^{-1}).

Table 5. Thermodynamics properties obtained for mild and stainless steel samples

Day	Mild steel		Stainless steel	
	K_{ads}	ΔG_{ads} (kJ/mol)	K_{ads}	ΔG_{ads} (kJ/mol)
3rd	0.3571	-7.4009	0.3174	-7.1089
6th	0.4206	-7.8065	0.3855	-7.5906
9th	0.5076	-8.2724	0.4268	-7.8427
12th	0.6109	-8.7314	0.4791	8.1292
15th	0.6703	-8.9614	0.5498	8.4703

The large values of $\Delta G_{ads}$and its negative sign are usually indicators of the strong interaction and high efficiency of adsorption. In general, the values of ΔG_{ads} around −20 kJ mol^{-1} or less negative are associated with an electrostatic interaction between charged inhibitor molecules and charged metal surface (physisorption), and the ΔG_{ads} around −40 kJ mol^{-1} or more negative involve charge sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a coordinate type bond of chemisorption [18].

From Table 5, the results show that the free energy of adsorption, ΔG_{ads} are negative and significantly less than the threshold value of –40 kJ mol^{-1} needed for chemisorption, indicating that the adsorption of natural honey on the surface of both the mild steel stainless steel is spontaneous and occurred according to the mechanism of physical adsorption [23].

3.5. SEM analysis of the sample surfaces

The images of the SEM analysis of the surfaces of the mild steel and stainless steel samples after immersion in 0.5 M sulphuric acid in the absence and presence of the natural honey inhibitor are shown in Figures 8 and 9.

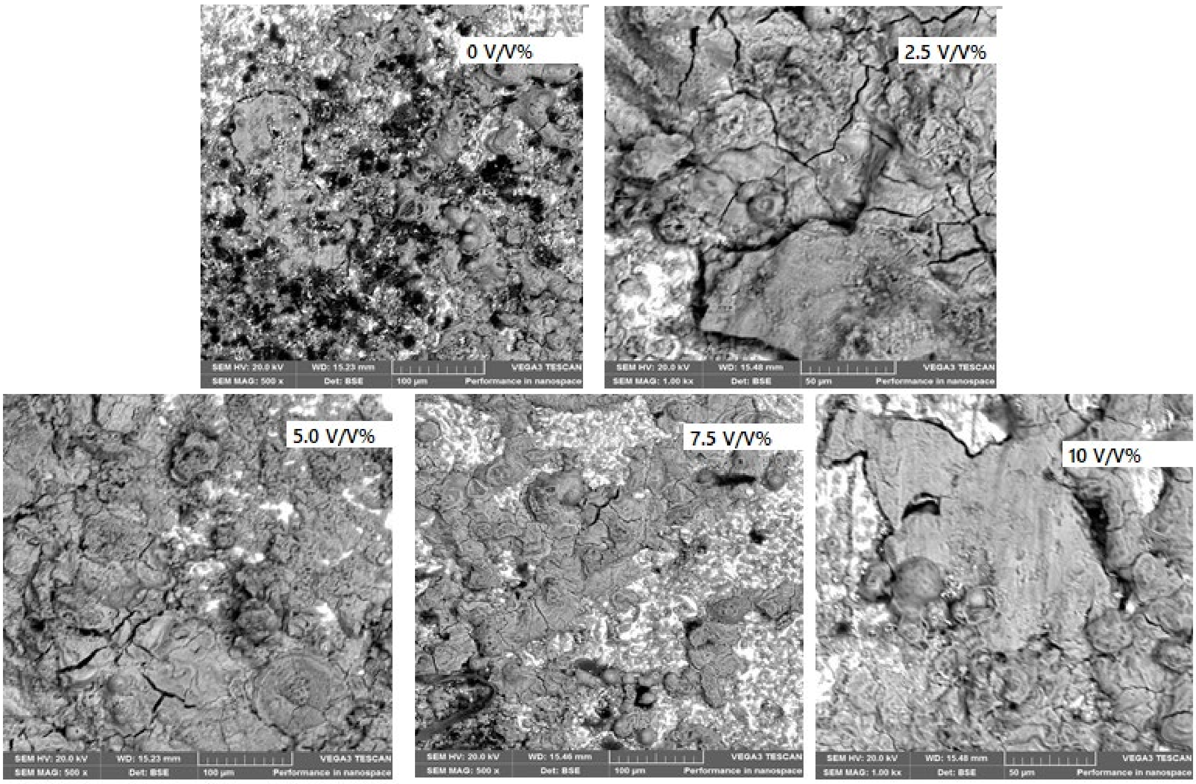

Fig. 8. SEM analysis of the surfaces of the mild steel

In Figure 8, general (uniform) form of corrosion was observed in the mild steel samples, at varied degrees. Sample without honey inhibitor (0 v/v%) suffer corrosion most, and serious pitting corrosion resulting from the significant wearing away of the sample surface was noticed. It could also be seen that as the concentration of the honey increased, corrosion extent in the form of the surface rupture reduced. This further confirms the inhibitive activity of the natural honey during the corrosion process.

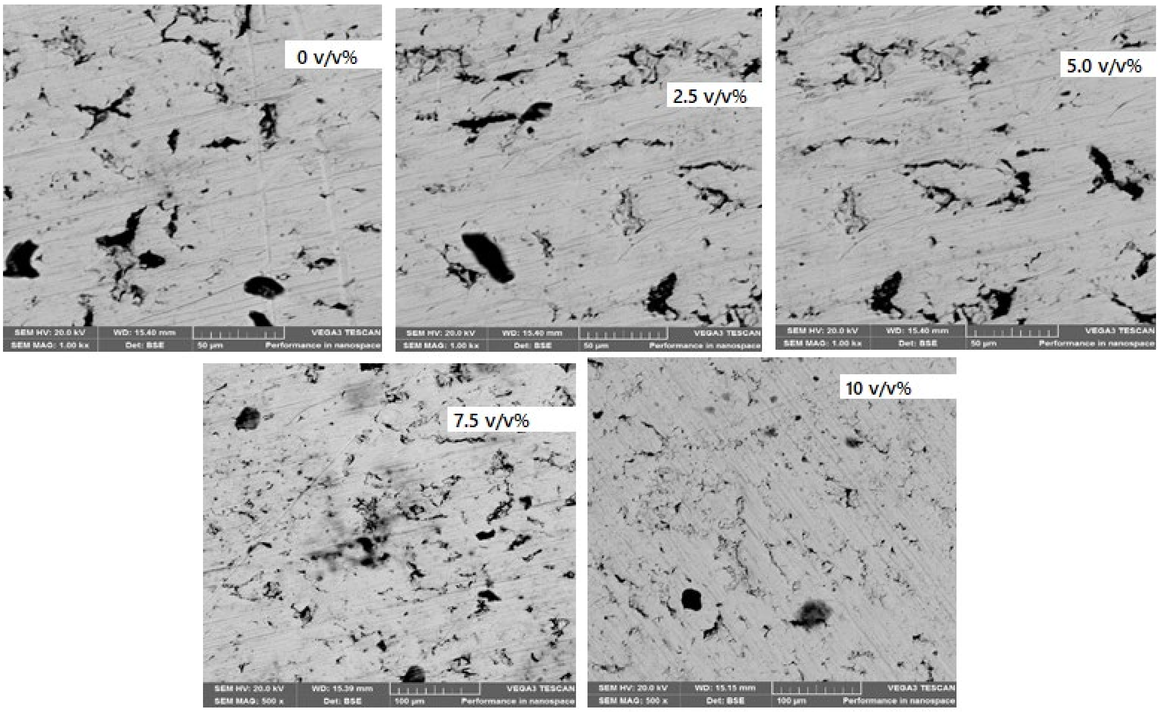

Fig. 9. SEM analysis of the surfaces of the stainless steel

In Figure 9, uniform (general) form of corrosion was not noticed. Rather, tiny (but many) and large (but few) pits were observed on the surface of the stainless steel samples. This is an indication that stainless steel has higher corrosion resistance compared to mild steel. It could also be seen that the level of corrosion damage reduced as the concentration of the inhibitor increase.

3.6. Chemical constituents of the natural honey inhibitor used

Table 6 shows the main constituents of the natural honey used as ecofriendly corrosion inhibitor and their proportions.

Table 6. Analysis of the constituents of the natural honey

Parameter	Inference
Alkaloids	**
Flavonoids	***
Saponins	**
Tannins	***
Phenols	***
Terpenoids	**

***Highly present, **moderately present

4. CONCLUSION

From this research work, it could be seen that natural honey was found to be an effective corrosion inhibitor (for both mild and stainless steels) for an increase in its concentration up to 10 vol./vol. % led to an increase in inhibition efficiency (attaining a maximum inhibition efficiency of 89% for the mild steel and 94% for stainless steel, both at an optimum concentration of 10 v/v% in H2SO4 medium). Also, Langmuir adsorption isotherm was obeyed by the inhibition of mild and stainless steel using honey in 0.5M H2SO4 with the values of the regression coefficients near unity. The negative values of ΔGads show the spontaneous adsorption of inhibitor unto the mild and stainless-steel surfaces and the electrochemical potentiodynamic polarization studies show that the honey acted as mixed-type inhibitor. And the overall results show that stainless steel has a higher corrosion resistance compared to mild steel.

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Conflict of interest

No conflict of interest in this research work.

REFERENCES

[1] A. A. Ayoola, O. S. I. Fayomi, and S. O. Ogunkanmbi, Data Brief 19 (2018) 804.
[2] S. M. Haleem, Brit. Corros. J. 14 (2013) 171.
[3] R. T. Hmimou, and T. Touhami, J. Mater. Env. Sci. 3 (2012) 543.
[4] O. S. I. Fayomi, A. P. I. Popoola, T. Oloruntoba, and A. A. Ayoola, Cog. Eng. 4 (2017) 1.
[5] J. Varney, N. Thompson, J. Payer, and M. Gould, NACE Int. 1-4 (2016) 1
[6] A. A. Ayoola, D. O. Adeniyi, S. E. Sanni, K. Osakwe, and J. Jato, Environ. Eng. Res. 23 (2018) 54.
[7] A. A. Ayoola, O. S. I. Fayomi, and A. P. I. Popoola, Defence Technol. 15 (2019) 106.
[8] D. Dwivedi, K. Lepková, and T. Becker, RSC Adv. 7 (2017) 4580.
[9] O. Ajayi, O. Omotosho, K. Ajanaku, and B. Olawore, J. Eng. Appl. Sci. 6 (2003) 10.
[10] R. T. Loto, C. A. Loto, A. P. I. Popoola, and T. I. Fedotova, South Afr. J. Chem. 68 (2005) 105.
[11] O. S. I. Fayomi, A. A. Ayoola, E. B. Omoniyi, and S. T. Okolie, Int. J. Adv. Manuf. Technol. 99 (2018) 2579.

[12] A. A. Ayoola, E. B. Igho, and O. S. I. Fayomi, Data Brief 18 (2018) 512.

[13] I. Owate, and E. Chukwuocha, Sci. Res. Essay. 3 (2007) 74.

[14] P. B. Raja, and M. G. Sethuraman, Mater. Lett. 62 (2008) 113.

[15] G. Gunasekaran, and L. Chauhan, Electrochim. Acta 49 (2004) 4387.

[16] R. Radojcic, and K. Berković, Corros. Sci. 50 (2018) 1498.

[17] S. Umoren, I. Obot, A. S. Israel, and A. Udoh, J. Ind. Eng. Chem. 20 (2014) 3612.

[18] R. Sudha, K. Kalpana, T. Rajachandrasekar, and S. Arivoli, J. Chem. 4 (2017) 238

[19] M. Adam, P. Odola, and I. Aji, Univ of Maiduguri Fac of Eng Sem Series. 7 (2016) 78.

[20] A. El-Etre, Corros. Sci. 40 (2003) 1845.

[21] N. O. Obi-Egbedi, I. B. Obot, and S. A. Umoren, Arabian J. Chem. 5 (2012) 361.

[22] W. Li, S. Zhang, C. Pei, and B. Hou, J. Appl. Electrochem. 38 (2008) 289.

[23] S. Bilgic, and M. Sahin, Mat. Chem. Phys. 70 (2012) 290.