Journal of Material Sciences & Engineering

Research Article Open Access

Corrosion Mechanism of Mild Steel in Acidic Solution and Adsorption Thermodynamics in the Presence of Water Hyacinth Extract

Babatunde O[1], Ogunrinde SO[2]*, Aribike DS[3] and Adeyemi AA[1]

[1]Department of Chemical Sciences, Ajayi Crowther University, Oyo State, Nigeria
[2]Department of Mechanical Engineering, Ajayi Crowther University, Oyo State, Nigeria
[3]Department of Chemical and Petroleum Engineering, University of Lagos, Akoka, Lagos State, Nigeria

Abstract

Inhibitory effect of water hyacinth extract on mild steel corrosion in acidified seawater was investigated by weight loss and gasometric techniques. Values of inhibition efficiency calculated from weight loss and gasometric techniques are in good agreement Inhibition efficiency was found to increase with increasing concentration of the extract. The effect of temperature, immersion time, and acid concentration on the corrosion behaviour of mild steel in the presence of extract were also studied. Temperature studies revealed an increase in activation energies and decrease in inhibition efficiency with rise in temperature. The adsorption of the inhibitor molecules on metal surface was in accordance with Langmuir adsorption isotherm. Kinetic treatment of the data obtained with or without plant extract indicates first-order electrochemical reactions. FT-IR analysis was carried out on the protective film formed on the surface of the metal to establish the formation of metal-ligand bond. The results obtained showed that water hyacinth extract could serve as an effective inhibitor of the corrosion of mild steel in acidified water.

Keywords: Water hyacinth; Weight loss; Gasometric; Adsorption; Corrosion; Inhibition

Introduction

Metal pipes offer the strength to transport fluids at high pressures but they are vulnerable to corrosion driving by electrochemical processes. The rate of corrosion is enhanced in acidic medium and salt water. Pipes are exposed to acid solution during oil well acidizing, descaling and pickling processes. Corrosion has been a major source of concern to the industry because of the huge amount of money that is involved in preventing it.

Corrosion can be minimized by cutting off the interaction between metal surface and electron acceptor/oxygen or hydrogen ion [1-6]. This can be achieved by forming a compact barrier film over the metal surface. Plant extracts have been reported to complex with Fe^{2+} release during corrosion thereby forming protective film over the surface of the metal. The heteroatoms and π electrons compounds present in plant extract facilitate the transfer of electrons between the extract and d-orbitals of Fe^{2+} [7-12].

Adsorption of heavy metals from the aqueous metal solution by water hyacinth extract has been reported. The leaf extract of this plant contains flavonoids, alkaloids, tannins, phenols, which have multifunctional properties such as to contribute as reductant (as antidote to free radical) and metal chelators [13-16]. In forming complex ion, the ligands in organic compounds donate lone pair(s) of electrons to metal ion. The organic components can serve as a metal chelating agent because of the presence of electron rich centre on them.

The aim of the present work is to test ethyl acetate extract of water hyacinth as inhibitor for the acidic corrosion of steel in sea water by gravimetric and gasometric techniques.

Experimental Section

Materials preparation

Galvanized iron rod used was obtained from local supplier and cut into 1 cm in length, 0.8 cm in diameter and 0.02 cm in thickness. The specimens were cleaned by absolute ethanol, rinsed with double distilled water, dried in acetone and kept in desiccator until used. All the chemicals used were analytical grade. Appropriate concentrations of acids were prepared by using sea water.

Water hyacinth was dried and ground to powder form. Dried (125 g) powder was macerated with ethyl acetate for 48 hrs. The extract was filtered and concentrated to dryness. The residue was dissolved in appropriate quantity of 2 M H_2SO_4 to obtain 0.025, 0.05, 0.1, 0.2 and 0.4 g/L concentrations.

Gravimetric method

Weight loss measurements were performed in triplicate on the cut specimens of the pipe in 2 M H_2SO_4 solution with and without addition of different concentrations of extract [17-19]. Each specimen was weighed and then placed in the acid solution (100 mL). The set up was left for 24 hours at room temperature. The specimens were retrieved after 24 hrs from corrodent solutions and these were repeated for six days.

Each retrieved metal specimen was immersed in cleaning reagent (50 g of NaOH, 200 g of Zn dust in 1000 mL H_2O) at 90°C for 40 minutes. After treatment corrosion product was removed by scrubbing the metal several times under running water, dried with acetone and then reweighed. The weight loss was calculated in grams as the difference between the initial weight prior to immersion, and weight after removal of the corrosion product.

***Corresponding author:** Ogunrinde SO, Department of Mechanical Engineering, Ajayi Crowther University, Oyo State, Nigeria, Tel: +234-8155861638; E-mail: o.samuel@hotmail.co.uk

Received August 22, 2019; **Accepted** September 06, 2019; **Published** September 12, 2019

Citation: Babatunde O, Ogunrinde SO, Aribike DS, Adeyemi AA (2019) Corrosion Mechanism of Mild Steel in Acidic Solution and Adsorption Thermodynamics in the Presence of Water Hyacinth Extract. J Material Sci Eng 8: 537.

Gasometric method

It had been reported that the acidic corrosion of mild steel could be characterised by hydrogen evolution, and the rate of corrosion was proportional to the quantity of hydrogen evolved [20,21]. Thus, Gasometric was also used as it involves the characterisation of steel corrosion via hydrogen evolution. This experimental design followed the method reported by Onuchukwu, et al. [20] whereby the volume of hydrogen gas evolved when metal reacted with acid was measured. Six galvanized iron of dimension 0.5 cm long, 0.8 cm diameter and 0.02 cm thick were used in the experiments for test solutions containing 5 M H_2SO_4 with the five different concentrations of ethyl acetate extract of water hyacinth. This experiment was carried out at room temperature and at 60°C. The blank experiment was performed under the same conditions. A 100 ml of test concentration solution was transferred into the reaction vessel connected to a burette that contained paraffin oil. The initial level of paraffin oil in the burette was noted. Thereafter, one metal specimen was dropped into the corrodent and the reaction vessel quickly closed. Drop in the level of paraffin oil was recorded every 1 min. The volume of paraffin oil displaced correspond to volume of hydrogen gas generated in the set-up. This experiment was repeated at five different concentrations (0.025, 0.05, 0.1, 0.2 and 0.4 g/l) of the plant extracts and a blank.

Surface analysis

The iron specimen 1 cm in length, 0.8 cm in diameter and 0.02 cm in thickness was immersed for 24 hrs in 100 mL of 2 M H_2SO_4 solution containing 0.4 g/L. Thereafter, specimen was retrieved and left to dry. The dried specimens were scratched with a knife and the resultant powder was taken for FT-IR analysis. In case of FT-IR studies of plant extract, 5 mL of 2 M a H_2SO_4 solution containing 0.4 g/L acid having 1.14 g/L of the extract was left to dry. The dried material was scratched with a glass rode and the resultant powder was taken for analysis.

Results and Discussion

Gravimetric analysis

Effect of acid concentration: Gravimetric analysis, also known as Weight-loss measurement, was performed on the mild steel specimen in different concentration of H_2SO_4 as shown in Figure 1. From the weight loss data, the corrosion rates (CR) were calculated using eqn. (1) as reported by Okafor, et al. [22].

$$CR = \frac{ML}{A.t} \tag{1}$$

Where CR is the corrosion rate in mg.cm^2 hr^{-1}, ML is the mass loss in mg, A is the specimen exposed surface area in cm^2 and t is the immersion time in hr.

Figure 1 shows that mild steel corrodes in different concentrations of H_2SO_4 solutions, since there was a decrease in the original weight of the mild steel. Both figures, i.e. Figures 1 and 2, indicated that both the weight losses and the corrosion rate increases with an increase in the concentration of the H_2SO_4, and the concentration is linearly proportional to both the weight loss and corrosion rate. The corrosion is attributed to the presence of water, air and H$^+$, which accelerate the corrosion process. In addition, Figure 2 also shows that reaction followed a first order reaction kinetics.

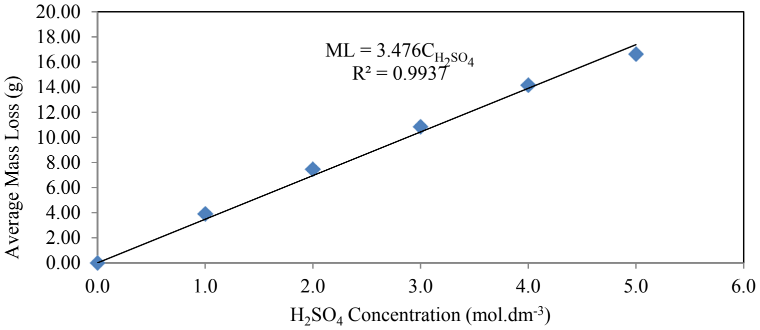

Figure 1: Galvanise steel mass loss due to H_2SO_4 corrosion.

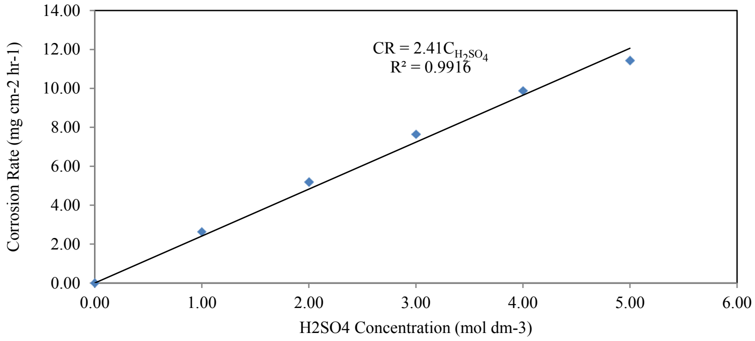

Figure 2: H_2SO_4 Corrosion rate of mild steel.

Inhibition efficiency: Figures 3 and 4 show that weight losses increase with the increase in the immersion time but decrease with the increase in concentration of the Water Hyacinth extracts.

The general decrease in the weight loss due to the presence of the Water Hyacinth extract confirms that indeed Water Hyacinth extract inhibits acid corrosion of mild steel. The results also reveal that the inhibitory effect increases with an increase in concentration of the extract. Similar trends were reported by James et al. [23] for their work on the use of Pyridoxol Hydrochloride as an inhibitor, Okafor et al. [22] for their work on the use of Carica Papaya extract as an inhibitor, and Abiola, et al. [24] for their work on the use of Aloe vera extract as an inhibitor.

From the weight loss data, the percentage inhibition efficiency (% *I*) were determined using eqn. (2) as reported by Abiola et al. [24].

$$I\% = \left(\frac{W_u - W_i}{W_u}\right) \times 100 \qquad (2)$$

Where *I* is the inhibition efficiency of Water Hyacinth in %, W_u and W_i are the uninhibited and inhibited weight losses respectively.

Figure 5 shows that percentage inhibition efficiency increases with increasing extract concentration but decreases with time. This result suggests that increase in extract concentration increases the number of inhibitor molecules adsorbed onto steel surface, which in turn reduces the available surface area for the direct acid, and as the time increases, the available vacant sites decreases due to the adsorption of the inhibitor molecules.

Adsorption isotherm: The inhibition effect of water hyacinth is due to the adsorption of water hyacinth molecules on the surface of the mild steel, which in turn, prevented the adsorption of the ion from the acidic solution. Water hyacinth contains organic compounds such as flavonoids, alkaloids, tannins, phenols, and these compounds have been reported to inhibit corrosion due to the higher adsorption affinity to metal surfaces. In other words, the adsorption of these organic compounds reduces the available surface area available for the corrosion attack.

From the inhibition efficiency (I%) data, degree of surface coverage (θ) was calculated using eqn. (3) [22-25].

$$\theta = \frac{I\%}{100} \qquad (3)$$

Values of the degree of surface coverage (θ) were tested graphically to fit different isotherms and as shown in Figure 6, a straight line was obtained when C/θ was plotted against C and the linear correlation coefficients of the fitted data is close to 1.

This indicates that the adsorption behaviour follows the Langmuir Adsorption Isotherm, which is expressed as:

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (4)$$

Where C is the inhibitor concentration and K the equilibrium constant for the adsorption/desorption process of the inhibitor molecules on the metal surface.

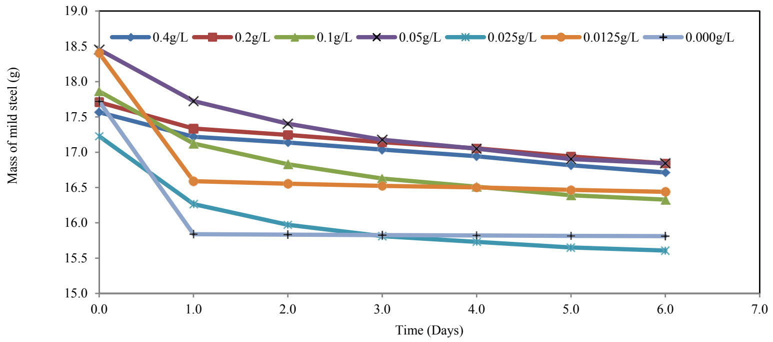

Figure 3: The plot of mild steel coupon weight versus the immersion period at different water hyacinth extract concentration in 2 M H_2SO_4 at 30°C.

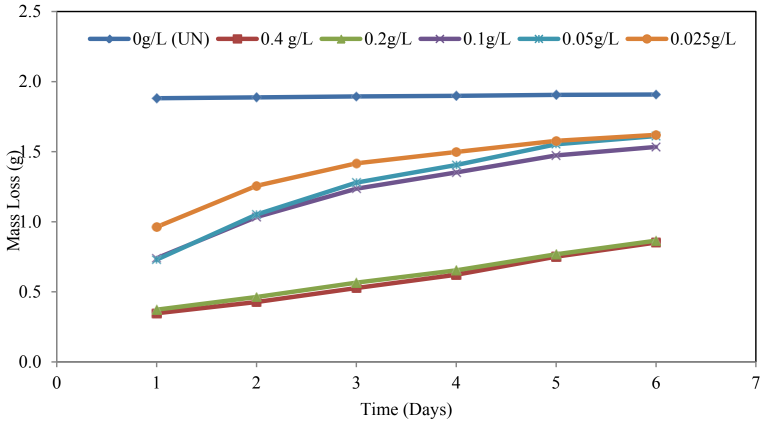

Figure 4: The plot of weight loss of mild steel coupon versus the immersion period at different water hyacinth extract concentration in 2 M H_2SO_4 at 30°C.

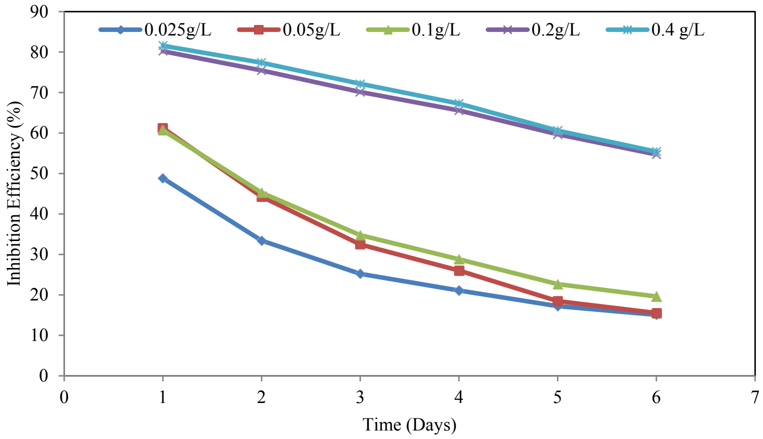

Figure 5: Water hyacinth inhibitor efficiency.

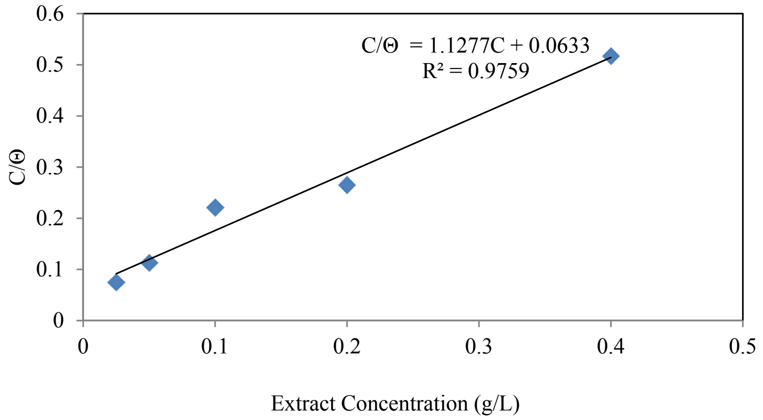

Figure 6: Langmuir adsorption model on the steel surface of water hyacinth extract in 2 M H_2SO_4 solution for 6 days immersion period at 30°C.

Reaction kinetics: The equilibrium constant K, shown in Table 1 was deduced as the inverse of the intercept of Figure 6.

The standard free Gibbs energy of adsorption was obtained from the equilibrium constant (K), using the expression reported by Abiola et al. and Qiu et al. as shown in eqn. (5).

$$K = \frac{1}{55.5} exp\left(-\frac{\Delta G^{o}_{ads}}{RT}\right) \quad (5)$$

The negative value of the Gibbs free energy of adsorption (ΔG^{o}_{ads}) confirmed the spontaneity of the adsorption process and the exothermic nature of the corrosion process.

Gasometric analysis

Effect of inhibitor concentration: As shown in Figures 7 and 8, the higher the concentration of the water hyacinth extract, the lower the corrosion rate as the time taken to evolve 50 mL of hydrogen gas increases with increasing extract concentration.

From the volume of hydrogen gas discharged data, the percentage inhibition efficiency (% I) was determined using eqn. (6) [24,26].

$$I'\% = \left(\frac{V_u - V_i}{V_u}\right) \times 100 \quad (6)$$

Where I' is the inhibition efficiency of Water Hyacinth in %, V_u and V_i are Volume of H_2 gas evolved in the absence and presence of extracts respectively.

Reaction Kinetics	Value
Equilibrium Constant (k_{ads})	15.80
Gibbs Free Energy of adsorption (ΔG^{O}_{ads})	-17.08 kJ/mol

Table 1: Reaction kinetics parameters for the adsorption.

Figure 9 suggests that increase in extract concentration increases the number of inhibitor molecules adsorbed onto steel surface, which in turn reduces the available surface area for the acidic molecule; hence the increase in the inhibition efficiency with increasing extract concentration.

Adsorption isotherm: The inhibition efficiency (I') was used to calculate the degree of surface coverage (θ') using eqn. (3) and the degree of surface coverage was tested graphically to fit different isotherms. As shown in Figure 10, a straight line with a linear correlation coefficients that was close to 1 was also obtained when C/θ' was plotted against C. This also indicates the Langmuir Adsorption Isotherm behaviour.

Reaction kinetics: The equilibrium constant K', shown in Table 2 was deduced as the inverse of the intercept of the plot in Figure 10. The standard free Gibbs energy of adsorption was calculated from the equilibrium constant (K), as earlier shown for the Gravimetric Analysis.

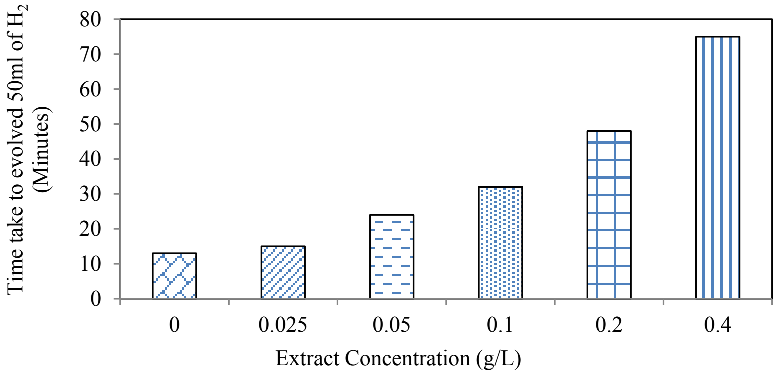

Figure 7: Time taken to evolved 50ml of Hydrogen.

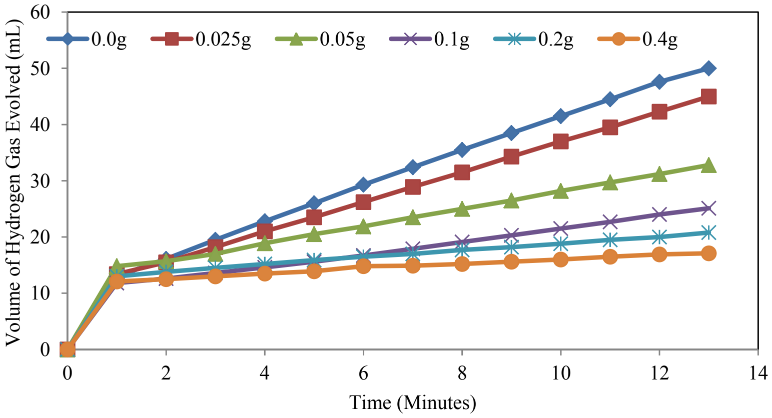

Figure 8: Plot of volume of hydrogen gas evolved with time (min) for the corrosion of mild steel in 2M H_2SO_4 solution in the presence of different concentrations of water hyacinth extracts.

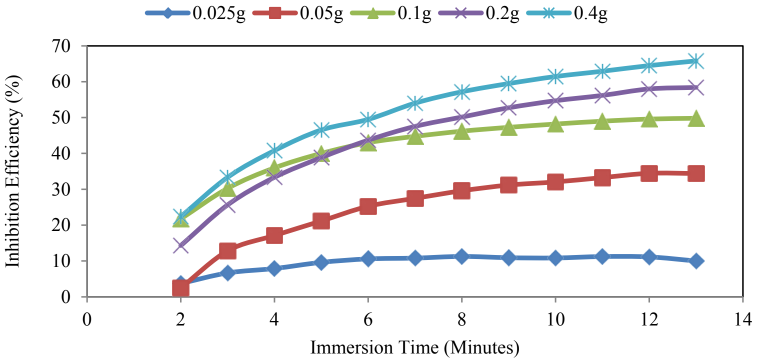

Figure 9: Water Hyacinth Inhibitor Efficiency.

The equilibrium constant and Gibbs free energy of adsorption (ΔG^o_{ads}) values obtained are similar to those obtained using the Gravimetric Analysis. Similar values were also reported by Abiola et al. [18].

Effects of temperature: As shown in Figure 11, the time taken to evolve 50 ml of H_2 at 60°C (for all inhibitor concentration) is much less than that at 30°C. This implies that the adsorption of the molecules of the acidic solution on the adsorption site of the metals surface increases as temperature increases. This is because the higher the temperature, the higher the kinetic energy of the molecules and the greater the rate at which the molecules would get to the vacant adsorption sites of the mild steel and the higher the quantity of molecules, i.e. concentration of the acidic molecules at the adsorption site, which will result in greater rate of corrosion of the mild steel.

Surface analysis of plant extract

Figure 12 and Table 3 confirmed the formation of the metal-ligand bond which acts a protective film on the surface of the steel, preventing

Reaction Kinetics	**Value**
Equilibrium Constant (k_{ads})	13.53
Gibbs Free Energy of Adsorption (ΔG^{O}_{ads})	-16.69 kJ/mol

Table 2: Reaction kinetics parameters for the adsorption (gasometric analysis).

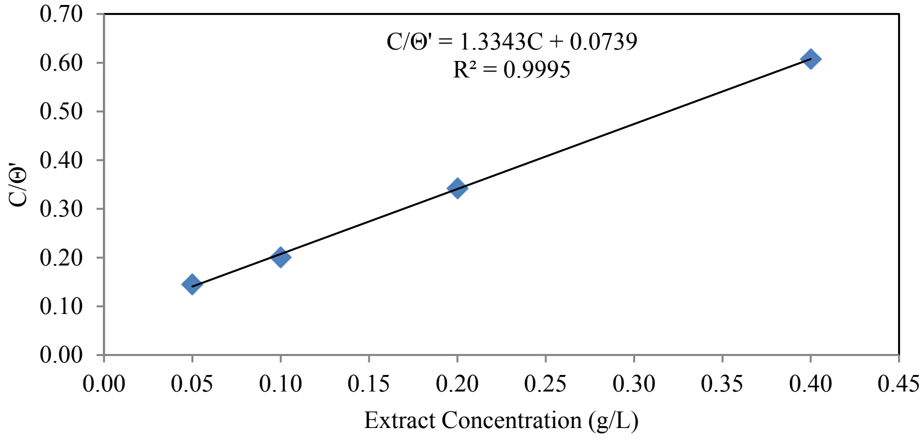

Figure 10: Langmuir adsorption model on the steel surface of water hyacinth extract in 2 M H_2SO_4 solution for 13 Minutes immersion period at 30°C.

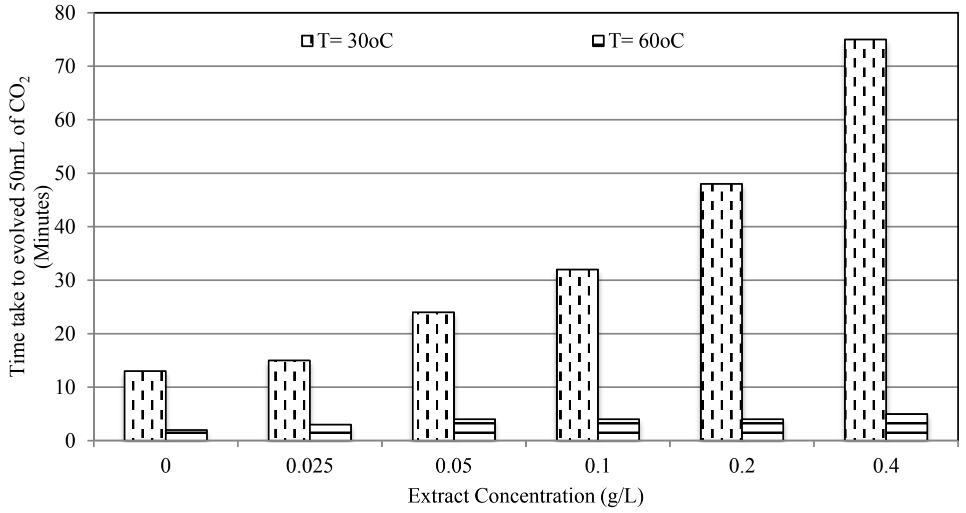

Figure 11: Effects of Temperature on Corrosion of mild steel using water hyacinth extract as inhibitor.

Peak from plant extract (Figure 12 A)	**Peak from metal-ligand complex (Figure 12 B)**	**Possible compounds**
3444 (sharp)	3451 (broad)	O-H
2925	---	=C-H
1649	1636	C=C (alkene)
1010	1082	C-O
---	651	Fe^{2+}-L

Table 3: Peaks from FT-IR spectra of samples shown in Figure 12: (A) plant extract, (B) mild steel immersed in 2 M H_2SO_4 solution containing plant extract, and their identification.

the steel from being attacked by the corrosive species. Similar peaks were reported by Chauhan et al. [27] when investigating the inhibiting actions of some plant extracts on steel.

Conclusion

1. The corrosion of mild steel in sea water follows a first order reaction kinetics and exothermic reaction.

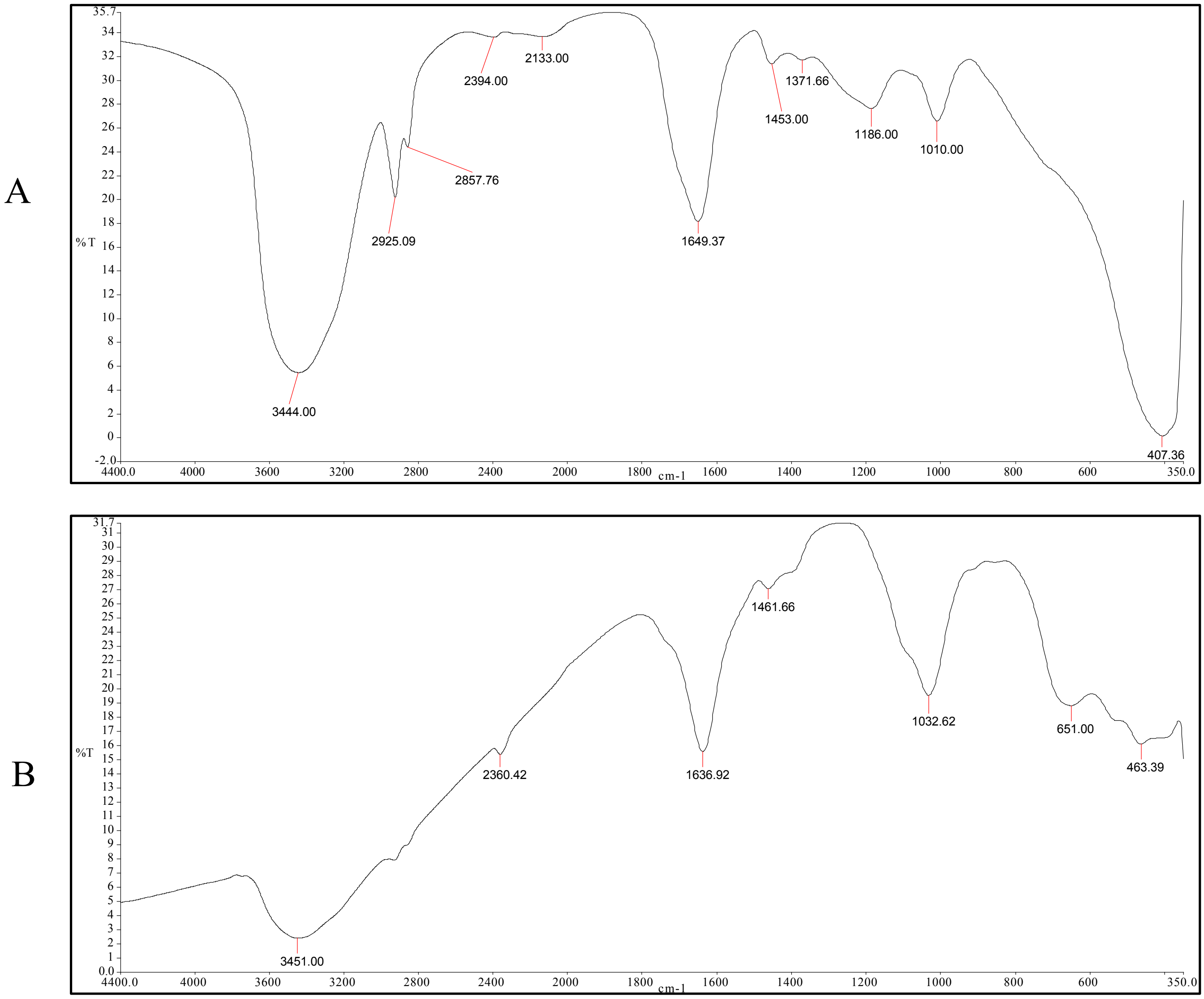

Figure 12: FT-IR spectra of samples: (A) plant extract and (B) mild steel immersed in 2 M H_2SO_4 solution containing plant extract.

2. Water hyacinth extract is a good inhibitor for mild steel in 2 M H_2SO_4 solutions. Inhibition efficiency increases with increasing water hyacinth extract concentration and the values obtained from both gravimetric and gasometric methods are in reasonable agreement and similar to those reported in the literature for corrosion inhibition using plant extracts.
3. The adsorption of water hyacinth extract on mild steel surface obeyed Langmuir adsorption isotherm with Gibbs free energy of adsorption (ΔG^o_{ads}) -17.08 kJ/mol (from the gravimetric analysis) and -6.69 kJ/mol (from gasometric analysis). The negative values of the Gibbs free energy of adsorption (ΔG^o_{ads}) confirmed the spontaneity of the adsorption process.
4. The rate of corrosion increases with an increase in temperature.
5. FT-IR analysis shows the formation of metal-ligand bond, thus confirming the formation of protective film layer on the surface of the metal.

References

1. Evans U, Arnold E (1979) The Corrosion and Oxidation of Metals. London.
2. Uhlig H (1963) Corrosion and Corrosion Control. New York: Wiley.
3. Speller F (1935) Corrosion Causes and Prevention. New York: McGraw-Hill.
4. Benard J (1962) L 'Oxidation des Mdtaux. Paris: Gauthier-Villars.
5. Wranglen G (1972) An Introduction to Corrosion and Protection of Metals. Stockholm: Institute for Metallskydd.
6. Pourbaix M (1966) Atlas of Electrochemical Equilibrium in Aqueous Solution. London: Pergamon.
7. Muralidharan S, Phani KLN, Pitchumani S, Ravichandran S, Iyer SVK (1995) Polyamino-benzoquinone polymers: a new class of corrosion inhibitors for mild steel. Journal of the Electrochemical Society 142: 1478-1483.
8. Raja PB, Sethuraman MG (2008) Natural products as corrosion inhibitor for metals in corrosive media—a review. Materials letters 62: 113-116.
9. Bothi Raja P, Sethuraman MG (2009) Strychnos nux-vomica an eco-friendly corrosion inhibitor for mild steel in 1 M sulfuric acid medium. Materials and Corrosion 60: 22-28.

10. Abdel-Gaber AM, Khamis E, Abo-ElDahab H, Adeel S (2008) Inhibition of aluminium corrosion in alkaline solutions using natural compound. Materials Chemistry and Physics 109: 297-305.
11. Ostovari A, Hoseinieh SM, Peikari M, Shadizadeh SR, Hashemi SJ (2009) Corrosion inhibition of mild steel in 1 M HCl solution by henna extract: A comparative study of the inhibition by henna and its constituents (Lawsone, Gallic acid, α-d-Glucose and Tannic acid). Corrosion Science 51: 1935-1949.
12. Abdel-Gaber AM, Abd-El-Nabey BA, Saadawy M (2009) The role of acid anion on the inhibition of the acidic corrosion of steel by lupine extract. Corrosion science 51: 1038-1042.
13. Ali H, Patel M, Ganesh N, Ahi J (2009) The world's worst aquatic plant as a safe cancer medicine-Antitumor activity on melanoma induced mouse by Eichhornia crassipes: in vivo studies. J Pharm. Res 2: 1365-1366.
14. Shanab SM, Shalaby EA, Lightfoot DA, El-Shemy HA (2010) Allelopathic effects of water hyacinth [Eichhornia crassipes]. PloS one 5: e13200.
15. Thamaraiselvi P, Lalitha P, Jayanthi P (2012) Preliminary studies on phytochemicals and antimicrobial activity of solvent extracts of Eichhornia crassipes (Mart.) Solms. Plant Science Research, pp: 115-122.
16. Aravind RK, Rajan D, Blesson J, Chandran S, Thampatty AR, et al. (2013) Detailed analysis on phytochemicals, antioxidants, antimicrobial activity of Eichhornia crassipes. Inter J Sci Res 2: 17-9.
17. Abiola OK, Otaigbe JOE (2008) Effect of common water contaminants on the corrosion of aluminium alloys in ethylene glycol–water solution. Corrosion Science 50: 242-247.
18. Abiola OK (2007) Studies on the inhibition of aluminium alloy (3SR) corrosion by (4-amino-2-methyl-5-pyrimidinyl methylthio) acetic acid and its precursor in hydrochloric acid (HCl) solution. Corrosion and Materials 32: 10-15.
19. Abiola OK (2006) Adsorption of 3-(4-amino-2-methyl-5-pyrimidyl methyl)-4-methyl thiazolium chloride on mild steel. Corrosion Science 48: 3078-3090.
20. Onuchukwu AI, Adamu AAI (1990) The kinetics and mechanism of hydrogen evolution on corroding aluminum in alkaline medium. Materials chemistry and physics 25: 227-235.
21. Okafor PC, Ikpi ME, Uwah IE, Ebenso EE, Ekpe UJ, et al. (2008) Inhibitory action of Phyllanthus amarus extracts on the corrosion of mild steel in acidic media. Corrosion Science 50: 2310-2317.
22. Okafor PC, Ebenso EE (2007) Inhibitive action of Carica papaya extracts on the corrosion of mild steel in acidic media and their adsorption characteristics. Pigment & Resin Technology 36: 134-140.
23. James AO, Oforka NC, Abiola OK, Ita BI (2007) A study on the inhibition of mild steel corrosion in hydrochloric acid by pyridoxol hydrochloride. Eclética Química 32: 31-37.
24. Abiola OK, James AO (2010) The effects of Aloe vera extract on corrosion and kinetics of corrosion process of zinc in HCl solution. Corrosion Science 52: 661-664.
25. Singh A, Ahamad I, Singh VK, Quraishi MA (2011) Inhibition effect of environmentally benign Karanj (Pongamia pinnata) seed extract on corrosion of mild steel in hydrochloric acid solution. Journal of Solid State Electrochemistry 15: 1087-1097.
26. Abiola OK, Oforka NC, Ebenso EE, Nwinuka NM (2007) Eco-friendly corrosion inhibitors: The inhibitive action of Delonix Regia extract for the corrosion of aluminium in acidic media. Anti-Corrosion Methods and Materials 54: 219-224.
27. Chauhan LR, Gunasekaran G (2007) Corrosion inhibition of mild steel by plant extract in dilute HCl medium. Corrosion science 49: 1143-1161.