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INVESTIGATION OF CORROSION INHIBITION OF MILD STEEL IN 0.5 M HCL WITH *AZADIRACTHAINDICA* AND *SPONDIAMOMBIN*

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ABSTRACT

The corrosion behaviour of mild steel in 0.5 M HCl solution in the presence of Azadiracthaindica and Spondiamombin (AS) was investigated using potentiodynamic polarization and weight loss techniques. Pulverized barks of 60 g of each plant were soaked in 1500 ml, 0.5 M HCl for 48 hours, filtered and mixed in the ratio of 1:1 giving a concentration of 400 g/L (serving as 100 % concentration). The AS mixture was then diluted to 20, 40, 60 and 80% (80, 160, 240 and 320 g/L). The weight loss experiment was carried out for 192 hours at ambient temperature (25^oC) and corrodant solution without AS served as the control. Potentiodynamic polarization study was carried out using a device called AutolabPotentiostatGalvanostat (PGSTAT101) in the potential range of ±1.5v versus corrosion potential at a scan rate of 0.005 ms^{-1}. The results obtained showed that corrosion rate reduced in the presence of all the concentrations of AS extract investigated. Highest inhibition efficiency of 99.6% obtained was for the polarization measurement why the highest obtained for gravimetric study was 75.39%. Gibb's free energy of -3.859 kJ mol^{-1} was obtained, indicating physisorption and the correlation coefficient was 0.996. The study showed that AS was a very good corrosion inhibitor of mild steel in 0.5 M HCl acid.

Keywords: *Azadiractaindica, Spondiamombin, potentiodynamic, gravimetric, corrosion inhibition*

INTRODUCTION

Nowadays most important consideration in industry is reduction of overall cost by protection and maintenance of materials used. The protection of metals surface from corrosion prevents waste of resources and money in industrial application and is vital to equipment lifetime extension, limiting the dissolution into the environment of toxic metals from the components. Mild steel is extensively used in engineering constructions due to its important structural properties, good mechanical workability and low cost (Ishwara and Vijaya, 2011).

Corrosion is a natural process that reduces the binding energy in metals with the end result involving a metal being oxidized as the bulk metal looses one or more electrons (Chinkwo, *et al.,* 2014). Corrosion processes are responsible for numerous loses mainly in the industrial scope. The area of operations of mild steel often include industrial processes in which acids play important roles, for example in acid pickling, acid cleaning, and acid descaling and oil well acidification. These activities often lead to corrosion, resulting in the degradation of the integrity of the metal.

Use of inhibitors is one of the best methods of protecting metals against corrosion (Sathiyanarayanan *et al.,* 2005; Ouchrif *et al.,* 2005; Al-Otaibi *et al.,* 2012, Obot *et al.,* 2009, Yildirim *et al.,* 2008, Gentil *et al.,* 2003).

Corrosion inhibitors are compounds that are added in small quantities to an environment to prevent corrosion of metals (Sathiyanarayanan *et al.,* 2005). Efficient inhibitors are organic compounds containing heteroatoms: nitrogen, sulphur, phosphorus and/ or oxygen atoms in their molecules (Sudhish and Quraishi, 2010; Eddy and Ebenso, 2008; Sharma *et al.,* 2008).

The corrosion inhibition of metals by organic and inorganic compounds results from the adsorption of molecules at the surface of metals. The extent of adsorption of inhibitors depends on the nature of the surface charge of the metal, the mode of adsorption of the inhibitor, the inhibitor's chemical structure, and the type of corrodants. This adsorption process is enhanced by the presence of heteroatoms, triple bonds and aromatic rings in the chemical structure of the inhibitor (Deyab *et al.,* 2013).

So many attentions are being given to natural plants whose leaves, barks, seeds, fruits and roots have organic constituents with molecular structures containing nitrogen or oxygen atoms for their potentials, as they are cheap, highly available, nontoxic, and environmentally friendly (Khadraoui *et al.,* 2015; Oguzie *et al.,* 2012).

The extracts of several plants such as *Azarictaindica, Fenugreek* leaves, *Zenthoxylumarmatum, Opuntia*, *Nypafruticans, Ocimumviridis, Phyllanthusamarus, Chamomile, Halfabar*, and *Murrayakoenigii* were studied as corrosion inhibitors in sulphuric and/or hydrochloric acid media (El-Etre, 2006).

Srivatsava and Srivatsava (1981) worked on tobacco, black pepper, castor oil seeds, acacia gum and lignin and concluded that they made very good inhibitors for steel in acid medium. Inhibitive performance of acid extract of Stevia rebaudiana on mild steel in sulphuric acid was investigated by Cang *et al*., (2012). The performance was reportedly good.

Khamis and Al-Andis (2002) proved that herbs such as coriander, hibiscus, anis, black cumin and garden cress inhibited the corrosion of steel. Parikh and Joshi (2004) also studied the anticorrosion activity of onion, garlic and bitter gourd for mild steel in hydrochloric acid media.

Inhibition properties of acid extract of *Spondiasmombin* were investigated by Obi-Egbedi *et al.,* (2012) and it reportedly gave good results.
Obiukwu *et al.,* (2013) used *Vernonia amygdalina* (Bitter Leaf) and *Azadirachta indica* (Dogoyaro) immersed in hydrochloric acid solution, tetraoxosulphate (VI) acid solution, trioxonitrate (V) acid solution to inhibit corrosion on stainless steel, and reported good performance.

Azadiractha indica and *Spondiamombin* have been investigated separately for their inhibitive performance which were reported to be good (Obi-Egbedi *et al.,* 2012; Obiukwu *et al.,* 2013; Kuye *et al.,* 2018). Study is still ongoing on the inhibition effects of combining plants rich in phytochemicals.

This work investigated the inhibition effect of the combination of the bark extracts of *Azadiracthaindica* and *Spondiamombinon* the corrosion of mild steel in 0.5 HCl acid. *Azadiracthaindica* and *Spondiamombin* possess some phytochemical constituents that made them good candidates for this investigation.

MATERIALS AND METHODS

Mild steel cut into rectangular coupons of dimensions 1.25 cm x 1.5 cm was used for the experiments. The coupons were cleaned using emery paper to remove any form of dirt from the surface and suspended by string, to enable complete immersion into solutions prepared. The corrodant was 0.5 M HCl. The AS extract was prepared by soaking 60 g each of pulverized *Azadiractha indica* and *Spondiamombin* separately in 1500 ml of the corrodant for 48 hours, filtered and then added together in the ratio 1:1, giving a concentration of 400 g/L. The AS mixture was then diluted to 20, 40, 60 and 80% (80, 160, 240 and 320 g/L) while the undiluted AS represented 100% solution.

The gravimetric method (weight loss) is probably the most widely used method of corrosion inhibition assessment (Khadom *et al.,* 2009). The initial weights of the mild steel specimens were taken and recorded using analytical weighing balance. The weight loss experiment was carried out for 192 hours by suspending the mild steel specimens using string inside plastic bowls containing 100 ml solution of the corrodant and AS of different concentrations at ambient temperature (25°C) while corrodant solution without AS served as the control. The specimens were retrieved after every 48 hours, cleaned, dried and reweighed.

The weight loss (ΔW) was calculated from the difference between initial (Wi) and final (Wf) weights. The average weight loss for three identical experiments was obtained and the Corrosion Rate (CR) is expressed according to Oguzie *et al.,* (2008) in Eq. 1.

$$CR = \frac{\Delta W}{AT} \quad \text{......................................(1)}$$

where, CR = the corrosion rate
ΔW = the weight loss in mg
A = the exposed area of the coupons (cm^2)
T = the immersion time in hours

Inhibition Efficiency (IE%) was calculated according to Abd El Haleem *et al.,* (2013) and Al-moubarak *et al.*, (2015) as

$$\%IE = \left(1 - \frac{CR_{AS}}{CR_{blank}}\right) \times 100 \quad \text{.........(2)}$$

where,
CR_{AS} = Corrosion rate with AS
CR_{blank}= Corrosion rate without AS

Electrochemical measurements

The mild steel specimens were covered with aluminum foil so that only one square surface of area 1.0 cm^2 was left uncovered and copper rod was attached to enable immersion into the prepared solutions (corrodant and AS).

Polarization experiments were carried out to investigate the influence of AS on the anodic and cathodic reactions of the corrosion process using a device called AutolabPotentiostatGalvanostat (PGSTAT101) in the potential range of ±1.5 v versus corrosion potential at a scan rate of 0.005 ms^{-1}. A graphite rod was used as auxiliary electrode and silver chloride electrode (Ag/AgCl) was used as the reference electrode. The set-ups are shown in Figure 1. The steady state Open Circuit Potential (OCP) was noted. The corrosion current density (jcorr) and the corrosion potential (Ecorr) were determined from the Tafel plots of E (v) versus current density (I).

Figure 1: Polarization set-up of the potentiodynamic measurement of corrosion of mild steel in 0.5 M HCl with AS

RESULT AND DISCUSSION

Weight Loss, Corrosion Rate and Inhibition Efficiency

Figure 2 shows the result of weight loss measurements against exposure time for the corrosion of mild steel in 0.5 M HCl solution in the presence and absence of different concentrations of the extract of AS for different immersion times (48–192 hrs) at ambient temperature (25°C). Corrosion rate of the experiment is given by Figure 3 and close observation of the plot revealed that the rate of corrosion reduced in the presence of AS extracts with immersion times for all the concentrations.

The inhibitive effect of AS in retarding the dissolution of mild steel in 0.5 M HCl environment was determined by comparing the weight loss of the metal in the blank acid solution and in the presence of AS. Figure 4 shows the relationship between the inhibition efficiency and different concentrations of AS in the acidic solution. It could be observed from the plot that the inhibition efficiency of AS on mild steel in 0.5 M HCl is about the same for all the concentrations with very slight difference that tends to favour increase in AS concentrations.

The high IE% values obtained indicate a strong adsorption of the constituents of AS species on a corroding metal surface.

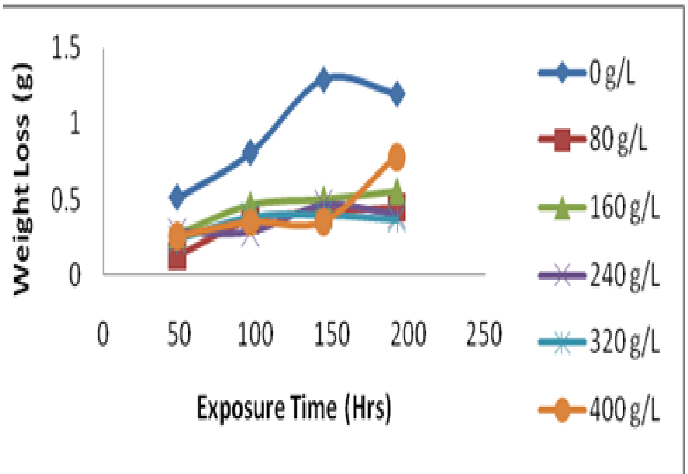

Figure 2: Variation of Weight Loss with Exposure Time for Mild Steel Samples in 0.5 M HCl for all AS Concentrations

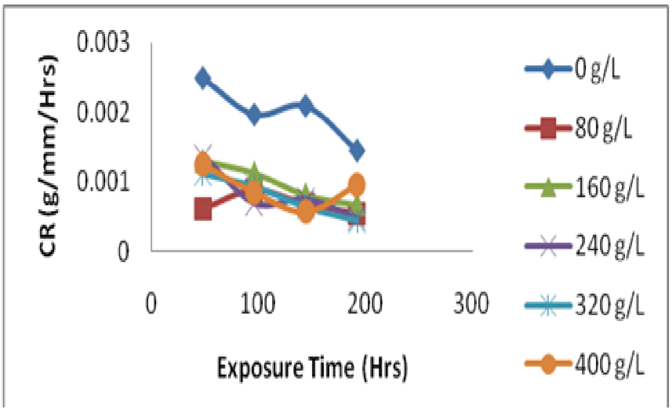

Figure 3: Corrosion Rate with Exposure Time for Mild Steel Samples in 0.5 M HCl for all AS Concentrations

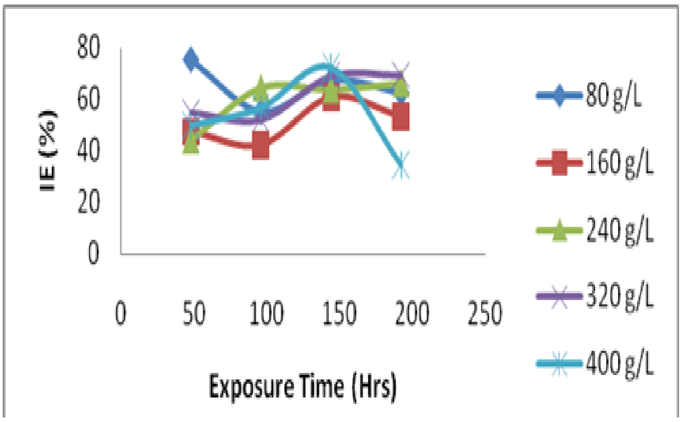

Figure 4: Inhibition Efficiency at all AS concentrations

Potentiodynamic Polarization Results

Figures 5 and 6 show the polarization curves of mild steel in 0.5 M HCl in the presence and absence of AS concentrations.

Table 1 shows the polarization data for mild steel in 0.5 M HCl in the presence and absence of AS.

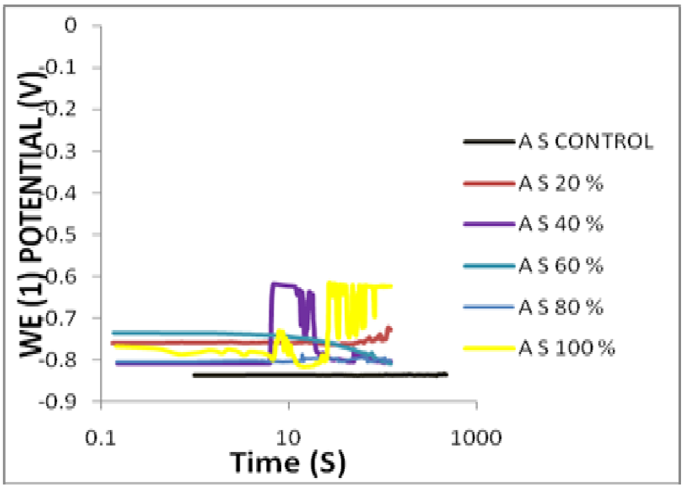

Figure 5: WE(1) Potential at Scan Rate of 0.005v/s Against Time

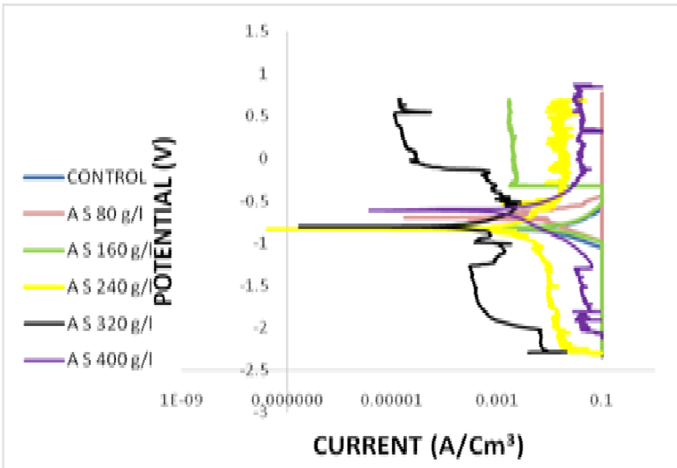

Figure 6: Plot of Linear Polarization Scan for Mild Steel in 0.5 M HCl in the Presence and Absence of AS at Ambient Temperature

Table 1: Polarization Data of the Electrochemical System

Samples	Inhibitor conc. (g/L)	ba (V)	bc (V)	E_{corr}obs	Jcorr	CR mm/yr	Polarization resistance (Ω)	Inhibition efficiency (IE %)
A	Blank	0.007225	0.0083223	-0.83123	0.00045627	5.3018	3.6812	0
B	80	0.0072962	0.0021382	-0.71573	6.3023E-07	0.0073232	1139.5	99.86
C	160	0.010074	0.0087608	-0.81867	0.00059589	0.000006923	2.4518	99.9
D	240	0.0024836	0.013877	-0.60072	1.1142E-05	0.12947	82.11	97.56
E	320	0.0056933	0.0017881	-0.80485	5.7617E-06	0.066951	102.57	98.74
F	400	0.011337	0.0052274	-0.83939	3.3732E-05	0.39196	46.004	92.60

where,
Ecorrobs = corrosion potential
Jcorr = corrosion current density
Bc = cathodicTafel constant
Ba = anodic Tafel slope
WE =generated potential voltage

Mechanism of Inhibition

In the presence of AS, corrosion is inhibited by absorption of the organic molecules on the metal surface. It is necessary for a chemical bond between the inhibitor and the metal atom (stronger than the one for water molecules) to be formed in order for an inhibitor to have a high coverage on the metal surface. The adsorption of corrosion inhibitors at the metal/solution interface is due to the formation of either electrostatic or covalent bonding between the absorbates and metal surface atoms.

Adsorption Mechanism

The experimental data of mild steel in HCl in the presence of AS fitted Langmuir isotherm model given according to Obi-Egbedi *et al.,* (2012) by Eq. 3.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \text{ ....(3)}$$

where,
θ = surface coverage (fraction, dimensionless),
C = extract concentration and
K_{ads} = adsorptive equilibrium constant

The Inhibition efficiency and surface coverage for mild steel corrosion in 0.5 M HCl in the presence of AS are shown in Table 2. The Plot of C/θ against C is given by Fig. 7, where the adsorptive equilibrium constant K_{ads} is given by the intercept of the plot. K_{ads} was obtained as 0.08556 mol^{-1}, free energy of adsorption was -3.859 kJ mol-1 and the correlation coefficient (R^2) was 0.996.

The negative values of $\Delta G^o{}_{ads}$ shows the spontaneity of the adsorption process and the stability of the adsorbed species on the low carbon steel surface (Shukla and Ebenso, 2011; Khadom *et al.,* 2009). Generally, $\Delta G^o{}_{ads}$ of -20 kJ mol^{-1} or lower are said to be consistent with the electrostatic interaction between charged organic molecules and the charged metal surface indicating physisorption (Obi-Egbedi, Obot and Umoren, 2012; Abd El Haleem *et al.,* 2013).

The $\Delta G^o{}_{ads}$ for this system is -3.859 kJ mol^{-1} which gives the system to be physisorption.

Table 2: Adsorption Parameters for the Corrosion of Mild Steel in 0.5 M HCl Acid Solution in the Presence AS Extract

Temperature	R^2	K_{ads} mol^{-1}	$\Delta G^o{}_{ads}$ kJ mol^{-1}
298 K	0.996	0.08556	-3.859

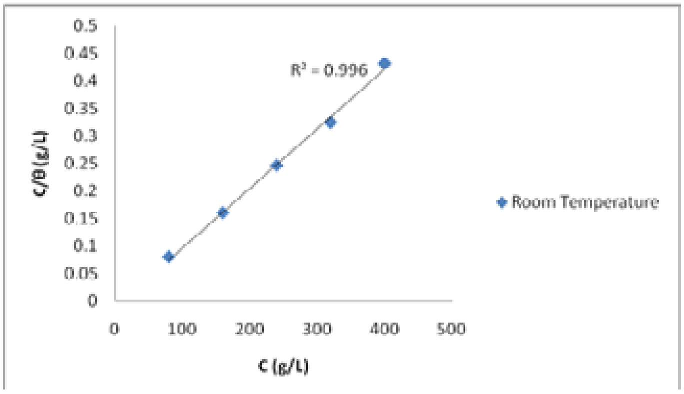

Fig. 7: Graph of C/θ against C for the Corrosion of Mild Steel in HCl Acid in the Presence of AS

CONCLUSION

Corrosion performance of mild steel in 0.5 M HCl was investigated in this work using both gravimetric and polarization method. The two methods gave good corrosion efficiency for the mild steel in 0.5 M HCl in the presence of the combination of *Azadiracta indica* and *Spondia mombin* (AS) bark extract. The highest inhibition efficiency obtained for gravimetric method was 75.39% at the concentration of 80 g/L compared with that of polarization method which was 99.9% at the concentration of 160 g/L of the extract.

The Gibb's free energy for the system was obtained as -3.859 kJ mol-1 which indicates physisorption reaction. The correlation coefficient (R2) was 0.996.

The results established that the synergistic combination of *Azadiracta indica* and *Spondia mombin* (AS) bark extracts was a very good corrosion inhibitor of mild steel in 0.5 M HCl and the inhibition was by physisorption.

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