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Full Length Research Paper

Corrosion inhibition for mild steel in 0.5 M H_2SO_4 solution using *Achyranthes aspera* L. leaf extract

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The leaf extract of *Achyranthes aspera* L. was investigated for corrosion inhibition of mild steel in 0.5 M H_2SO_4 medium at room temperature. Gravimetric technique was used to study the corrosion behavior in the absence and presence of different concentrations of the leaf extract. The result obtained showed that the *A. aspera* L. is a good inhibitor for mild steel in 0.5 M H_2SO_4 solution. The corrosion rate and inhibition efficiency were calculated. The inhibition efficiency calculated showed a great percentage result with optimum value of 92.3%. *A. aspera* L. extract was adsorbed on the mild steel surface in accordance with Langmuir, Frumkim, and Floru-Huggins adsorption isotherm models. The negative adsorption energy ΔG_{ads} obtained inferred that the adsorption rates were spontaneous and the interaction between the inhibitive molecules was found to be repulsive.

Key words: *Achyranthes aspera* L., corrosion rate, inhibition efficiency, adsorption isotherm.

INTRODUCTION

Nowadays most important considerations in industry are reduction of overall costs by protection and maintenance of materials used. The protection of corroding metal surface prevents the waste of resources and money during the industrial applications and is vital to extend the equipment's lifetime; limiting the dissolution into the environment of toxic metals from the components (Ishwara and Vijaya, 2011). Mild steel is extensively used in different industries in the merit of its good structural properties, good mechanical workability and low cost. Corrosion can be minimized using suitable preventive measures, and several techniques have been developed (Yagan et al., 2006; Aramaki, 2001; Battocchi et al., 2006; Hu et al., 2005; AL-Juhni and Newby, 2006) to control corrosion. Corrosion inhibition of mild steel in acid solutions has become one of the most urgent and severe challenges in acid pickling process (Shukla and Qurarishi, 2010; Aljourani et al., 2009; Fouda et al., 2005). Mild steel is exposed to the action of acid in industrial processes in which acids have important functions, for example in oil well acidification, acid pickling, acid cleaning, and acid descaling. Use of inhibitors is one of the best methods of protecting metals against corrosion (Sathiyanarayanan et al., 2005; Ouchrif et al., 2005). Corrosion inhibitors are compounds that are added in small quantities to an environment to prevent corrosion of metals (Sathiyanarayanan et al., 2006). Most of the efficient acid inhibitors are organic compounds containing nitrogen, sulphur and/or oxygen atoms in their molecule (Sudhish and Quraishi, 2010; Eddy and Ebenso, 2008; Sharma et al., 2008).

Thus recent interests for corrosion inhibition focus on non-toxic and environmental-friendly inhibitors due to more stringent environment quality requirements (Eddy and Ebenso, 2008). Obot and Obi-Egbedi (2010) reported that some researchers have worked on some naturally occurring materials such as *Gum Arabic, Raphia, hookeri, Ipomoea Invaculcerata, Vigna unguiculata, Pachylobus edulis, Ginseng root, Dacroydes edulis, Zenthoxylum alatum, Hisiscus sabdairffa, Datura stramonium, Limonene, prosopis*, to mention but a few; and they were found to be good corrosion inhibitors.

Aa is commonly called devil's horsewhip. It is a vascular plant widely found in temperate region. It belongs to the family of Amaranthacae and has medicinal properties used on tetanus, snake bits, treatment.

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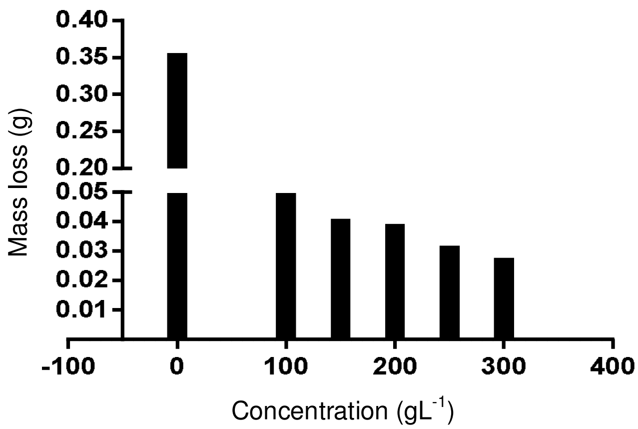

Figure 1. Mass loss for mild steel in the different concentration of *Aa* at room temperation exposure for 5 days.

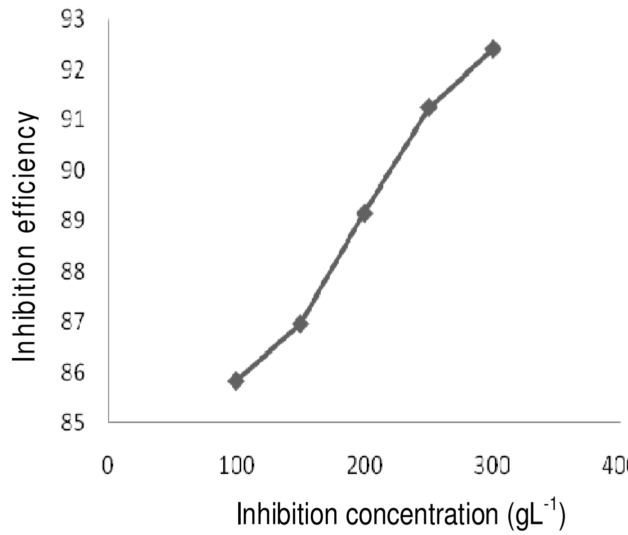

Figure 2. Inhibition efficiency of *Aa* for mild steel in 0.5 M H_2SO_4 solution.

The purpose of the study is to investigate the inhibiting influence of *Achyranthes aspera* L. (*Aa*) as a green inhibitor on mild steel corrosion in 0.5 M sulphuric acid solution. Gravimetric technique was used in the study.

MATERIALS AND METHODS

Preparation of *A. aspera* L. (devil's horsewhip) extract

The extract was prepared according to Okafor et al. (2008). *Aa* leaves were collected from Federal University of Technology Owerri (FUTO) in Imo State, Nigeria. They were washed with plenty water, dried and ground to powder form. The extraction was done in a reflux setup for 3 h at a constant temperature of 75°C using 10 g of air dried devils horsewhip in 300 ml of 0.5 M H_2SO_4 solution. The solution was cooled. The filtrate measured. Different concentrations of the inhibitor were prepared from the filtrate and the corrosive environment in the range 100, 150, 200, 250 and 300 g/L.

Mild steel preparation

The mild steel used in the studies was analyzed using optical emission spectrometry and consists (in % weight): C(0.0285), Si(0.0096), P(0.0096), Mn(0.1965), Ni(0.0153), Cr(0.0124), Mo(0.0027), Cu(0.0137), Sn(0.043), W(0.0052), Zn(0.031), As(0.0037), Ru(0.0028), and Fe(99.657%). The metal sheet was cut into coupon with the following dimensions of 30 x 30 x 1 mm and used for corrosion studies.

Gravimetric technique

Gravimetric technique used was according to the description by (ASTM G1-72, 1990). All reagents used were BDH grade. Prior to measurement, each coupon was degreased in ethanol, the surface smoothened using sic emery paper (of grades 400, 600, 800 and 1000) and then double washed with distilled water and air dried after dipping in acetone. The coupons were weighed using FA2104A analytical electronic digital weighing balance (sensitivity of 0.0001). The specimen were immersed in 250 ml beaker containing 240 ml of 0.5 M H_2SO_4 solution of different concentrations (0, 100, 150, 200, 250 and 300 g/L) of the prepared inhibitor at room temperature (303°K). The set up were exposed for a period of five days after which the specimen were taken out, washed, dried and weighed accurately. Triplicate experiments were performed in each case and the mean value reported.

RESULTS AND DISCUSSION

The mass losses of mild steel coupon in 0.5 M H_2SO_4 solution, with or without different concentrations of the investigated inhibitor, were recorded after 5 days of immersion at room temperature. The corrosion rate of mild steel was calculated using the Equation 1.

$$CR = \frac{\Delta W}{At\rho} \tag{1}$$

Where ΔW is the mass lost (in grams), A is the surface area of the coupon (in cm^2), ρ is the density (in g/cm^3), t is the period of exposure (in hours)

Figure 1 shows the variation in mass loss for mild steel in the absence and presence of inhibitor. It is evident that the mass loss of mild steel for blank solution is much higher than that obtained for solution containing various concentrations of *Aa* extract. Mass loss decreases with increase concentration of inhibitor. This implies that the presence of the inhibitor showed significant impact on the corrosion rate of mild steel in 0.5 M H_2SO_4.

The inhibition efficiency and surface coverage were calculated from the mass loss data according to the Equations 2 and 3, respectively. Figure 2 shows the inhibition efficiency in different concentration of the leaf extract and it could be seen that the %IE increases linearly with the inhibitor concentration.

$$\%IE = \left(1 - \frac{\rho_{inh}}{\rho_{blank}}\right) \times 100 \quad (2)$$

$$\theta = \left(1 - \frac{\rho_{inh}}{\rho_{blank}}\right) \quad (3)$$

Where ρ_{inh} and ρ_{blank} are the corrosion rates in the absence and presence of inhibitor, respectively. It can be observed that the inhibition efficiency increased and the corrosion rate decreased as the inhibitor concentration increased. The maximum value of inhibition efficiency was 92.3%. It could be considered that *A. aspera* L. as inhibitor of mild steel to 0.5 M H_2SO_4 solution given the high level of the inhibition efficiency.

Adsorption mechanism

The inhibition of metal corrosion by organic compounds is attributed to either the adsorption of inhibitor molecule or the formation of a layer of insoluble complex of the metal on the surface which acts as a barrier between the metal surface and the corrosive medium (Okafor et al., 2008). Since no insoluble material was observed on the metal surface, the inhibitive action of the extract may be due to its adsorption on the metal surface. Previous investigations of the leaves of *Aa* revealed the presence of the essential chemical compounds: sapogenins, alchorneine, alchorneinone, alkaloids, anthranilic acid, gentisinic acid yohimbine, flavonoids, glycosides (Maury et al., 2012). This makes it difficult to assign the observed inhibiting effect to a particular constituent. The net adsorption of these organic matters on the corroding mild steel surface creates a barrier that isolates the metal from the corrodent. Thus inhibition efficiency increases with an increase in the metal fraction occupied by the organic matter. Obot and Obi-Egbedi (2010) reported that leaf extract from *Chlomolaena odorata* L. (LECO) contained similar constituents and the leaf extract showed a good inhibitive action against the corrosion of Al in 2 M HCl.

The relationship between inhibition efficiency and the bulk concentration of the inhibitor at constant temperature, which is known as isotherm (Tsuru et al., 1978), gives an insight into the adsorption process. Several adsorption isotherms were attempted to fit surface coverage values to classical isotherms of Langmuir, Temkin, Frumkin, Flory-Huggins (Christov and Popova, 2004). The value of the correlation (R^2) was used to determine the best fit isotherm which was obtained for Langmuir, Frumkin isotherms and Flory-Huggins.

The Langmuir isotherm, which is presented in Equation 4 is most often used to calculate the equilibrium constant k (Bilgic and Caliskan, 2001; Shockry et al., 1998), which is the relationship between surface coverage and the inhibitor concentration.

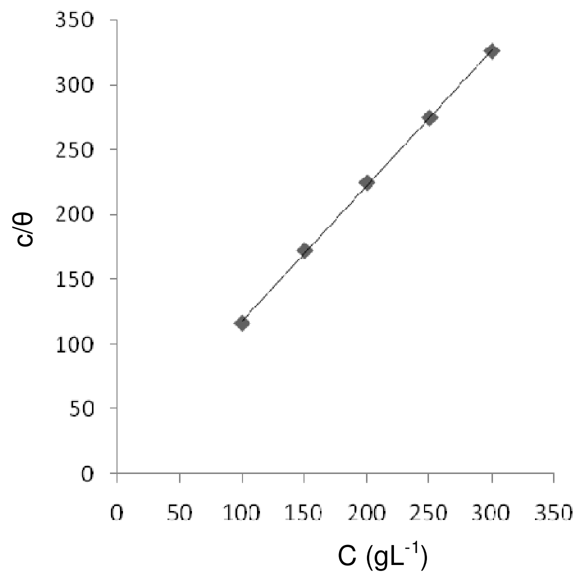

Figure 3. Langmuir adsorption isotherm for Aa on mild steel in 0.5 M H_2SO_4.

$$\left(\frac{c}{\theta}\right) = \frac{1}{k} + c \quad (4)$$

Where C is the inhibitor concentration, Θ is the surface coverage. Figure 3 shows that a plot of C/Θ versus C yields a straight line with R^2 = 0.999 and slope 1.043. The plot obeys Langmuir adsorption isotherm as the plot has linearity and good correlation coefficient. The R^2 values are very close to unity, indicating strong adherence to Langmuir adsorption isotherm (Acharya and Upadhyah, 2004). The adsorption Gibb's free energy was calculated using Equation 5 (Rajendran et al., 2000; Oguzie, 2005; Ashassi-Sorkhabi et al., 2006; Arab and Turkustuni, 2006).

$$\Delta G_{ads} = -RTIn(55.5k) \quad (5)$$

Where R is the gas constant (8.314 kJ/mol); and T is the absolute temperature (K). The constant value of 55.5 is the concentration of water in solution in mol/L. The value of ΔG_{ads} for the inhibitor on the surface of mild steel is given -15.12 kJ/mol since ΔG_{ads} is below 40 kJ/mol, it corroborates that the adsorption process is physisorption. The negative value of ΔG_{ads} indicated spontaneous adsorption of the inhibitor on the mild steel surface.

Considering the Frumkin isotherm commonly used to quantify the interactions occurring between corrosion inhibitor and a metal surface (Khamis et al., 1995;

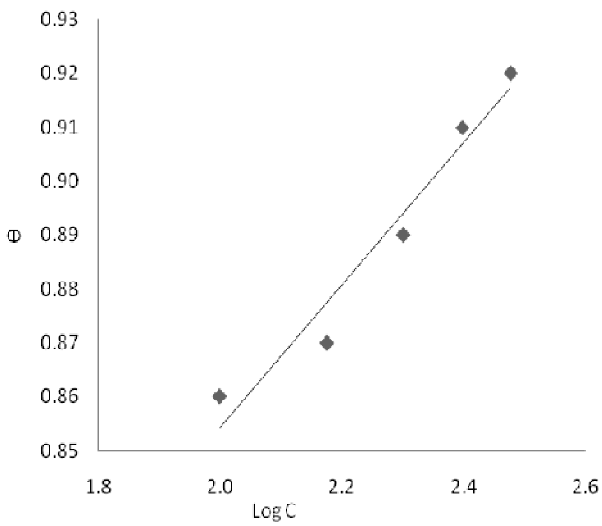

Figure 4. Frumkim adsorption isotherm Aa on mild steel in 0.5 M H_2SO_4.

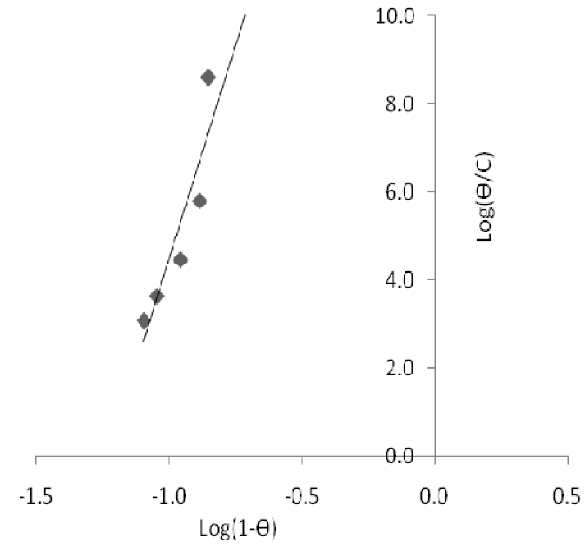

Figure 5. Flory-Huggins isotherm for adsorption of Aaon the mild steel surface.

Aljiorani et al., 2009, Li et al., 2008; Gallant et al., 2007), and it is expressed by the relationship (Li et al., 2008):

$$\exp(-f\theta) = c\left[\frac{1}{55.5}\exp\left(\frac{-\Delta G^0_{ads}}{RT}\right)\right] \quad (6)$$

Where Θ is the degree of surface coverage, *f* is the interaction term parameter (if *f* > 0, there is a lateral attraction, if *f* < 0, there is a lateral repulsion between the adsorbing molecules), c (in mg/L) is the inhibitor concentration, ΔG^0_{ads} is the standard free energy of adsorption (kJ/mol). The Frumkin adsorption isotherm is a general expression since the limiting case for which *f* = 0 is representative of an interaction free behavior between adsorbed species and defines the Langmuir isotherm (Khamis et al., 1995; Li et al., 2008). Equation 6 can be rearranged to give Equation 7 (Li et al., 2008).

$$LogC = \log\left(\frac{\theta}{1-\theta}\right) + A\theta + B \quad (7)$$

Where A = *-f/2.3* and B = (ΔG^0_{ads}/2.3RT) + log 55.5 and has the meaning of equilibrium constant of the adsorption process. Equation 7 was used to plot the Frumkin isotherm (Θ against Log C) shown in Figure 4. The existence of adsorption interactions between adsorbed *Aa* extract and the metal surface is thus confirmed since most of the experimental data fit nicely into the Frumkin isotherm plot, the slight *S*-shape. The adsorption parameters *B, f* and ΔG^0_{ads} obtained were 3.07 M^{-1}, -3.43 and -27.89 kJ/mol, respectively using two values of C (100 – 300 g/L) and the corresponding Θ. The negative value of *f* indicates that the adsorption of the tested compound is accompanied by mutual repulsion of the inhibitor molecules (Christov and Popova, 2004).

Flory-Huggins Isotherm: The assumptions of the Flory-Huggins adsorption isotherm can be expressed according to Equation 8 as reported by Eddy and Mamza (2009).

$$Log\left(\frac{\theta}{c}\right) = Logk + xLog(1-\theta) \quad (8)$$

Where x is the size parameter and is a measure of the number of adsorbed water molecules substituted by a given inhibitor molecule. As shown in Figure 5 the plot of log (Θ/C) against log (1 - Θ) gave a linear relationship (slope 19.41) with R^2 = 0.829, showing that Flory-Huggins isotherm was obeyed. The value of the size parameter (x) is 1.8. This indicates that the adsorbed specie of the inhibitor is bulky since it could displace more than one water molecule from the metal steel surface (Abd-ElNabey et al., 1996). The calculated ΔG_{ads} is -16.32 kJ/mol.

Generally, the magnitude of ΔG_{ads} about -20 kJ/mol or less indicates electrostatic interactions between inhibitor and the charged metal surface is physisorption. Those about -40 kJ/mol or more are indicative of charge sharing or transferring from organic species to the metal to form a coordinate type of metal bond is chemisorptions (Keles et al., 2008). In the present study, the calculated values ΔG_{ads} at 303 K for mild steel indicated that adsorption of the inhibitor on the surface of the mild steel is physisorption adsorption which implies that the films of the inhibitor was spontaneous on the surface of the metal.

Conclusions

Aa is found to inhibit the corrosion of mild steel in 0.5 M H_2SO_4 solution at room temperature. The inhibition efficiency increases with increasing inhibitor concentration. The value of Gibbs free energy of adsorption indicates that *Aa* leaf extract is physically adsorbed on the surface of the metal following the Langmuir, Frumkin and Flory-Huggins adsorption isotherm models. The interactions of the adsorbed molecules of the inhibitor are repulsive, and they are bulky on the metal surface. *Aa* leaf extract could be used as corrosion inhibition for mild steel in 0.5 M H_2SO_4 solution.

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