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## Corrosion inhibitive properties of *Epimedium grandiflorum* on mild steel in HCl acidic media

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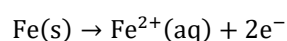
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**Abstract.** Corrosion inhibitors in controlling metal failure had been the practice for handling the menace of corrosion. Most of synthetic inhibitors is expensive and not environmental friendly, hence, the need for cheap, renewable, non-hazardous and green inhibitors to handle environmental issues. In this particular study, the inhibitory properties of *Epimedium grandiflorum* plant extract on the corrosion of mild steel in HCl acidic media was investigated. The gasometric, weight loss and the linear polarization methods were used in the study with adsorption isotherms (Langmuir, Freundlich, Frumkin and Temkin) validating the state of the reaction. The concentration of the extract was prepared in serial dilution of 10 - 50% using a stock solution of 1.75 M HCl. Mild steel coupons of known elemental compositions were immersed in test solutions of both stock solution and extract solutions. In the gasometric method, a decrease in volume of hydrogen gas evolved was observed as concentration of extract increases. Result from the weight loss shows similar trend of inhibitory behaviour for the weight loss method as the weight loss experienced by the coupons reduces as extract concentration increases. The Taffel plot for the extract indicates good inhibitive properties with inhibition efficiency increasing with extract concentration. In all the three methods studied, the maximum inhibition efficiency was observed in the 50% extract concentration. The extract fits best into the Freundlich isotherm indicating physisorption. This study showed that this particular plant extract is an effective inhibitor in suppressing the corrosion on the surface of the metal.

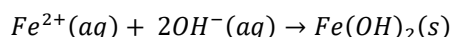
**Keywords:** Corrosion, mild steel, isotherm, Langmuir

### 1. Introduction

Corrosion can be said to occur whenever a metal or substance's surface is destroyed or degraded by being converted into a compound [1]. It can also be defined as the process by which metals or other substances degrade by forming or converting to a compound which is more chemically stable or form, such as the compound of sulphide, hydroxide or oxide [2]. Corrosion can also be said to be the slow degradation of materials through electrochemical or chemical reactions with compounds present in the environment; these include water, oxygen, carbon dioxide etc. metals that have been corroded tend to revert to the forms which their ores are found this is because these compounds are more stable. The commonly known example of corrosion is the corrosion of iron. When unprotected steel is exposed to the environment or environmental elements, the surface begins to form a reddish-brown color this indicates that steel is corroding. Rust consists of hydrated iron (iii) oxide  $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  (where n represents the number of moles of water which varies) rust begins in faults or areas of impurity. In these areas iron (ii) ions are formed in solution the reaction is given as:



This shows that iron undergoes an oxidation reaction, these areas where the oxidation takes place are known as the anodes. The ions move away from the anodic regions and react with hydroxide ions present in water and form iron (ii) hydroxide:



A corrosion inhibitor refers to chemicals compounds that are added to a gas or liquid to reduce the rate of corrosion of a material. The efficiency of an inhibitor is dependent on the composition of the fluid, the amount of moisture [3]. The usual mechanism of action is formation of a covering or coating on the metal surface, this prevents corroding materials from gaining access to the metal surface thereby preventing corrosion [4].

These inhibitors can be mixed with solutions that are in direct interaction with the metal. They prevent the anodic or cathodic reactions in the electrochemical or corrosion cell that leads to corrosion of the metal surface. They do this by forming passive or invisible films over the surface. These films can also be insoluble and form over anodic or cathodic reaction sites.

Acidic solutions have wide applications in the industry, the well-known fields of application are acid pickling, industrial acid cleaning and oil well oxidizing. Acids increase the rate of corrosion of metals as a result the drill of corrosion inhibition is usually employed in the reduction of the rate of corrosion of metals by acidic attack [4].

The selection of inhibitors to be used largely depends on the acid's concentration, temperature, velocity of flow and or organic substances and the metallic area or material exposed to the acidic solution. The commonly used inhibitors in acidic media are mostly compounds of organic origins which contain sulfur, oxygen and nitrogen.

The study of plant extracts as cheap, affordable and environmental friendly source of corrosion inhibitors has been of great interest and its presently attracting lots of attention [5]. These class of inhibitors are biodegradable and renewable. Plant extracts has been successfully applied as corrosion inhibitors for mild steel in different corrosive media. The use of Eucalyptus oil as inhibitor of the corrosion of mild steel has been carried out [6], inhibitive action of *Opuntia* extracts have also been reported [7], *Azadirachta indica* inhibitory action was successful on mild steel as reported by Eddy and Ebenso [8] and also successful on aluminium as reported by Ajanaku *et al.* [9].

*Epimedium grandiflorum* (Goat weed) is a species of flowering plant in the family of *Berberidaceae* from China. It has been used for centuries for medicinal purpose such as anti-diabetic, anti-hypertension, anti-inflammatory activities and anti-atherosclerotic effect [10, 11]. It contains bioactive compounds such as lignans, phenol glycosides, flavonoids, polysaccharide sterols and alkaloids. Though several studies have been carried out on the use of plant extract as cheap and non-toxic corrosion inhibitor but there still exist enormous opportunities to explore the use of other forms of plants. Literature review shows that *Epimedium grandiflorum* has not been studied for corrosion inhibition properties. This prompted us to carry out the evaluation of this plant for corrosion inhibition studies in 1.75 M HCl.

The aim of this present study is to determine the corrosion inhibition and adsorption behaviour *Epimedium grandiflorum* extracts on mild steel in 1.75 HCl using potentiodynamic polarization, weight loss and gasometric techniques.

## 2. Experimental

### 2.1. Material Preparation

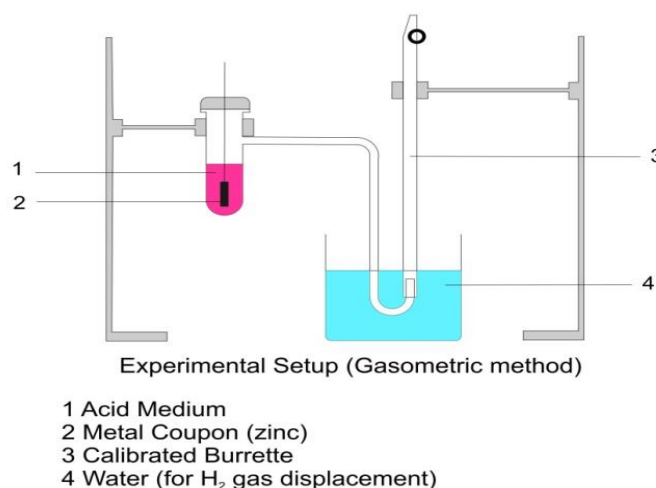
Rectangular samples of the metal (mild steel) were mechanically pressed into coupons of 15mm X 8.5 mm using manual edge metal cutter and weight of each coupon ranges between 10 – 11 g. The metal was fined using 60D, 120, 166, P 220C, P 600A, P 800A, emissary papers. Surface treatment of the metal was done by degreasing in ethanol and acetone. The composition of mild steel was analysed using optical emission spectrometer and the result obtained were (wt. %) Si 0.0018%; Fe 99.36%; Cu 0.034%; Mn 0.0189%; Pb 0.006%; Cr 0.025%; Ni 0.031%; Al 0.052%; P 0.013%; C 0.142%; S 0.012%; Co 0.045%; V 0.016%

## 2.2. Preparation of *Epimedium grandiflorum* extract

The leaves were hand-plucked and washed under running tap water to wash off the dirt in the form of sand and stones. The leaves were air-dried in the lab at room temperature for one week. The leaves were dried and grinded in a blender. 20g of grinded leaves was weighed wrapped in filter papers and put in the soxhlet extractor containing 200 mL of 1.75M HCl. Extracts concentration of 10%, 20%, 30%, 40% and 50% (v/v) was obtained via serial dilution. All reagents used were of analar grade.

## 2.3. Gasometric technique

Metal coupons were dropped into the gasometric chamber containing 30 mL of the acid solution and inhibitor solutions (10%, 20%, 30%, 40% and 50%). The acid solution consists of 1.75M HCl. The volume of hydrogen produced in the course of corrosion is recorded by a burette, this is due to the displacement of water in the burette by hydrogen gas. The difference in the amount of water present in the burette was recorded. This procedure was carried out for the five concentrations of the inhibitors (10%, 20%, 30%, 40% and 50% v/v). The experimental set up (Fig. 1) is similar in literature [12] and all reagents were of analar grade.



**Figure 1.** Schematic diagram of the Gasometric setup used in measurement.

## 2.4. Linear Polarisation Test

The electrochemical polarization analysis test was carried out using Autolab Nova 2.1.1 potentiostat-galvanometer system at normal room temperature in test solution. The Linear polarization resistant (LPR) consists of three electrodes system, which includes, the saturated calomel reference electrode (SCE), the working and the counter electrode. The working electrode is the mild steel with an exposed area of 1cm<sup>2</sup> for each metal, while platinum electrode acted as counter electrodes. Prior to the measurement, the working electrode were dipped in seawater containing different volumes of *Epimedium grandiflorum* extracts for 15mins until a stable open circuit potential (OCP) was obtained. The linear polarization resistance (LPR) OCP values started from -0.1 mV and stopped at +0.1 mV at a scan rate of 0.001 mV

## 2.5. Weight Loss Measurement

The weight loss measurement was achieved using the method already reported in literature [5, 12, 13]. The volume of the corrosive solution was maintained at 100 mL. The coupons were immersed in the corrosive and inhibitor concentrations of 10 – 50% v/v. After 24hrs interval the coupons were removed and first washed with washing agent (zinc dust and sodium hydroxide pellet) and water then dropped in acetone to stop the effect of the concentrated HCl, and was then weighed accurately with a weighing

balance to determine its new weight. The corrosion rate ( $W$ ) and the inhibition efficiency I.E (%) were calculated using equations 1 and 2 [5].

$$W = \frac{W_L}{A \times T} \quad (1)$$

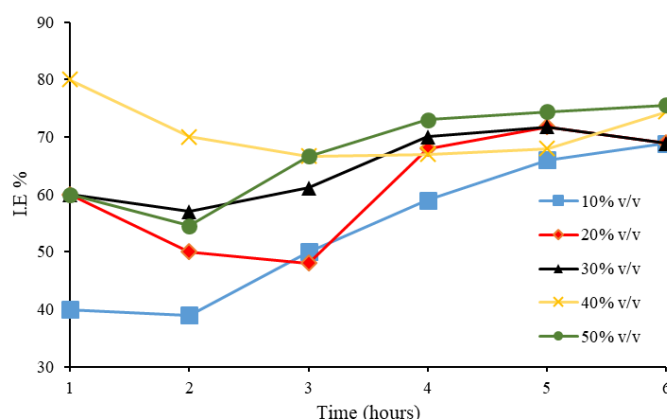
$$I.E(\%) = \frac{\Delta W_0 - \Delta W_{inh}}{\Delta W_0} \times 100 \quad (2)$$

Where  $W_L$  is the difference between the initial weight and the final weight after the coupon has been immersed in the above solutions,  $A$  is the surface area of the alloy and  $T$  is the time of immersion.  $\Delta W_0$  is the change in weight without the inhibitor and  $\Delta W_{inh}$  is the change in weight with the inhibitor.

### 3. Result and Discussion

#### 3.1. Inhibitor efficiency of *Epimedium grandiflorum*

The variation of inhibitor efficiency against time is shown in Fig.2. As shown in the Fig. 2, the inhibition efficiency increased with increase in concentration for the plant extract of *Epimedium grandiflorum*, this is an indication of the extract's effective in suppressing the corrosion on the surface of the metal. The anti-corrosion activity of *Epimedium grandiflorum* can be attributed to the presences of alkaloids, tannins, saponins and Phytic acid. Phytic and tannins have been reported as non-toxic inhibitors for metals in aggressive media [12, 14]. The inhibitory action of phytic acid can be as a result of its ability to bind into cathodic sites of the surface [15].



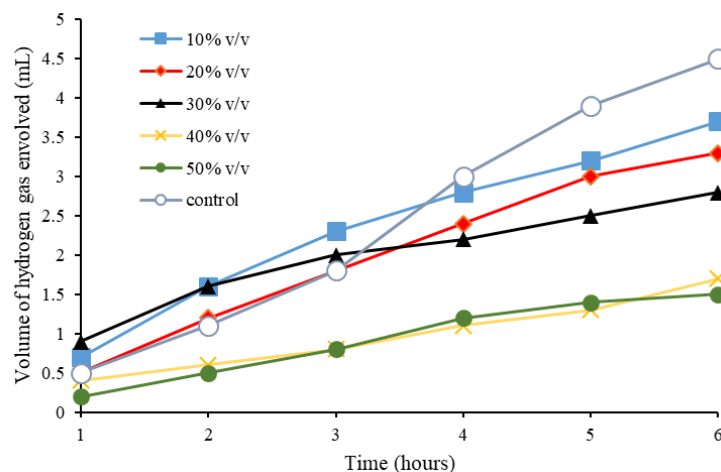
**Figure 2.** Inhibition efficiency of varying concentration of *Epimedium grandiflorum* extracts with time on mild steel.

#### 3.2. Hydrogen gas evolution and corrosion rates

The amount of hydrogen gas released (volume) during the corrosion reaction of mild steel in 1.75 M HCl in the absence and presence of the inhibitor at room temperature were measured in relation to time at room temperature in order to monitor the corrosion rate. The apparatus used (Fig. 1) is similar to that described in literature [12]. The plot (Fig. 3) shows a decrease in the rate evolution of hydrogen gas as the *Epimedium grandiflorum* extract was introduced into the corrodent. This is an indication that the plant extract inhibits the corrosion of mild steel in HCl media. A more appreciable decrease in the volume of hydrogen gas evolved was observed as the extract concentration increases from 10% -50% v/v; indicating that the inhibitive action was temperature dependent. The best inhibitor concentration can be seen to be the 50% v/v as it had the lowest amount of hydrogen gas released from the surface of the mild steel. This is in resemblance with what was observed by Umoren *et al.* [16] on *sida acuta* as an inhibitor for mild steel in  $H_2SO_4$  media. From the volume of hydrogen gas evolved inhibition efficiency was obtained using equation 3 [17].

$$\text{I.E (\%)} = \frac{V_H - V_{HI}}{V_H} \times 100 \quad (3)$$

Where  $V_H$  is the volume of hydrogen evolved in absence of the inhibitor and  $V_{HI}$  is the volume of the hydrogen gas evolved in presence of the inhibitor.

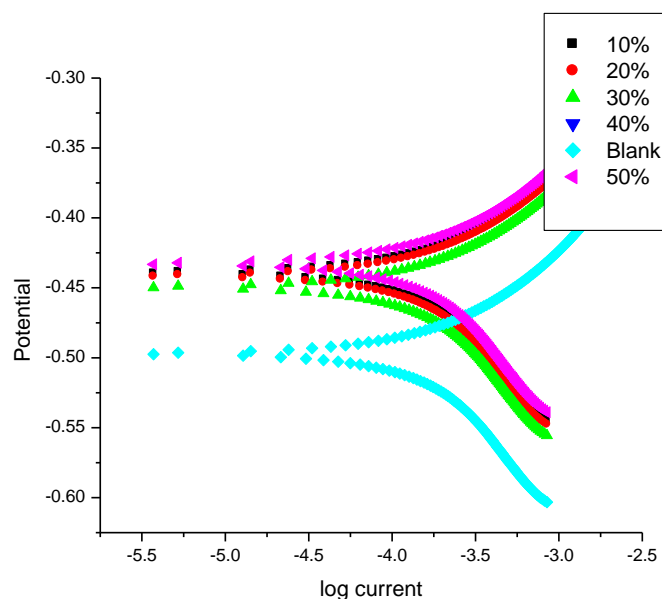


**Figure 3.** Variation of amount of hydrogen gas evolved with time of mild steel coupons for different extracts concentration of *Epimedium grandiflorum*.

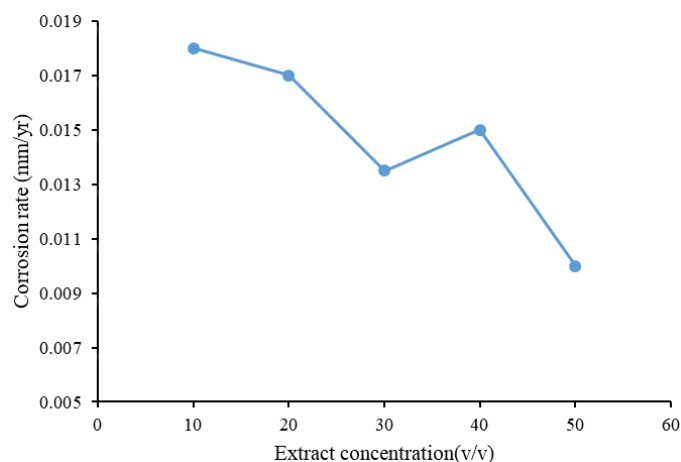
### 3.3. Linear polarization measurements

The effect of the concentration of the *Epimedium grandiflorum* extracts were also studied using the linear polarization meter. The corrosion characteristic of the mild steel coupons was studied in 1.75 M HCl and taffel plots (potential difference against log current) were generated by the polarization meter, these plots can be seen in Fig. 4. From the plot, it can be seen that the increase in concentration led to an increase in potential difference and the difference in potential difference between the inhibited and uninhibited solutions was high, this shows that there is a marked difference in aggressiveness of the medium upon addition of the inhibitor.

The plots also show that this inhibitor acts as a mixed inhibitor, because it had no marked effect on the anodic and cathodic taffel slopes upon addition of the inhibitor [18]. The Tafel slope is almost unchanged, this is an indication that the corrosion inhibition of the extract does not occur due to the interference on the reactions of metal dissolution and reduction of protons but rather through adsorptive inhibition. The inhibitor reduces the anodic dissolution and slows down the rate of hydrogen evolution by blocking the active reaction sites on the surface of the mild steel. The extract inhibitor can also shield the unexposed part of the electrode thereby protecting it from the further action of the corrosive medium [19]. Also the plot of corrosion rate against concentration of the extract (Fig.5) also indicate good inhibitory characteristic of the *Epimedium grandiflorum* with the best inhibition prowess exhibited by the 50% v/v extract concentration.



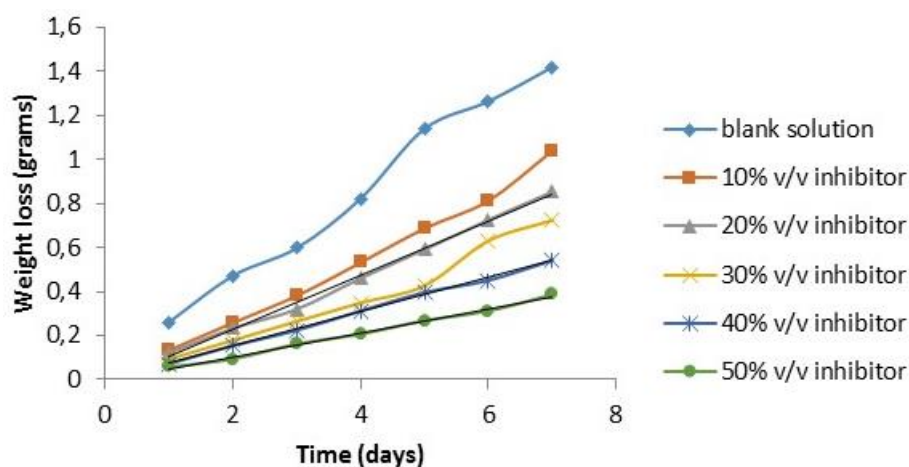
**Figure 4.** Plot of potential difference (V) against log current (A) (taffel plot) for different concentrations of *Epimedii grandiflorum* extract and blank (1.75 M HCl).



**Figure 5.** Graph of corrosion rate against concentration of *Epimedii grandiflorum* extract.

### 3.4. Weight loss studies

The trend in weight loss of the coupons immersed in the blank and extracts inhibitors is shown in Fig.6. As shown in the plot, the weight loss of the coupons in both the blank solution and solution containing various extract concentration increases with the immersion time. This is an indication that the rate of corrosion of mild steel increase with time. Also, the weight loss is observed to reduce as extract concentration increases indicating that loss in weight is concentration dependent. There is a major difference between the inhibited and the uninhibited solutions.



**Figure 6.** Graph of weight loss against time of different extract concentrations of *Epimedium grandiflorum*.

### 3.5. Adsorption Studies

Adsorption studies provide valuable information on the interaction of the adsorbed molecules among themselves and also on the metal surface. The manner of adsorption (physio or chemisorption) is determined by the electronic structure of the metal, nature of the corrodent and the chemical nature of the inhibitor [20]. Adsorption also play a major role in understanding the behaviour of non-homogenous organo-electrochemical reactions involving solid surfaces [21].

The experimental data of the studied inhibitor extract obtained from the gasometric readings could be fitted into the Freundlich adsorption isotherm ( $R^2 = 0.963$ ) (Fig. 7), which is a form of physisorption. This tells us that the adsorbed species were adsorbed physically on the surface of the metal. The surface coverage ( $\theta$ ) according to this isotherm is related to the inhibitor concentration by

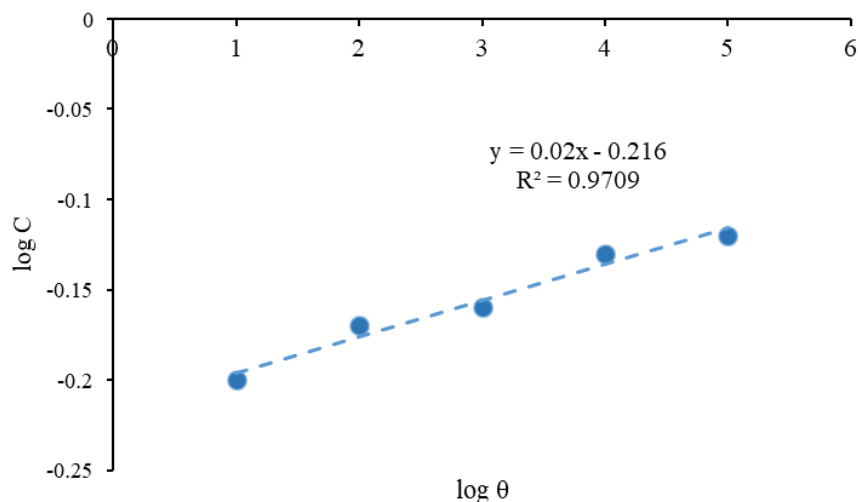
$$\theta = K_{ads}C^n$$

Re-arranging

$$\log \theta = \log K_{ads} + n \log C$$

where  $0 < n < 1$ ;  $\theta$  is surface coverage,  $K_{ads}$  is given as the adsorption-desorption constant and  $C$  is concentration of the inhibitor [16].

A plot of  $C$  against  $\theta$  gives a straight line with a slope of almost unity is an indication that the adsorption of the inhibitor on mild steel obey Freundlich's isotherm.



**Figure 7.** Freundlich adsorption isotherm of *Epimedium grandiflorum* on the surface of the metal in 1.75M HCl.

#### 4. Conclusions

The plant extract of *Epimedium grandiflorum* acts as inhibitor for mild steel corrosion in HCl media and the inhibitory ability is concentration dependent. The potential difference increases with concentration of the extracts as revealed in the Tafel plots. The inhibition was as a result of the adsorption of the extracts on the metals surface and the extract fits best into the Freundlich adsorption. The inhibition efficiency was also concentration dependent as the highest inhibition efficiency in all the methods used was the 50 % v/v extracts.

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