

## Green Inhibitors for Prevention of Metal and Alloys Corrosion: An Overview

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### Abstract

Corrosion control of metal is of technical, economical, environmental and aesthetical importance. The use of inhibitor is the best way to prevent metal and alloys from corrosion. There is an intensive effort underway to develop new plant origin corrosion inhibitors for metal subjected to various environmental conditions. These efforts are motivated by the desire to replace toxic organic corrosion inhibitors used for mitigation of corrosion of various metals and alloys in solutions. Plants represent a class of interesting source of compounds currently being explored for use in metal corrosion protection in most systems, as possible replacement of toxic synthetic inhibitors. The green corrosion inhibitors are bio degradable, non-toxic, environmentally benign, and low cost, are obtained from renewable resources with minimal health and safety concerns. Investigations of corrosion inhibiting abilities of tannins, alkaloids, organic amino acids and organic dyes of plant origin are of interest. Development of computational modeling backed by wet results would help in understanding the mechanism of inhibition action, their adsorption patterns, inhibitor-metal surface interface and help in the development of designer inhibitor with an understanding of the time required for the release of self-healing inhibitors. The present paper restricts itself mainly to the plant materials as "Green Corrosion Inhibitor".

**Keywords:** Green Corrosion Inhibitor, Corrosion Inhibition, Plant Extracts.

### Introduction

Corrosion is nature's method whereby metals and alloys return to their unrefined naturally occurring forms as minerals and ores. Corrosion is the deterioration of metals by chemical attack or interaction with its environment. It is a constant and continuous problem, often can not be eliminated completely. Prevention is more practical and achievable than complete elimination. Corrosion is a fast process and accompanied by number of reactions that change the composition and properties of both metal surface and local environment, for example formation of oxides, diffusion of metal cations into the coating matrix, local pH changes and electrode potential. The study of corrosion of mild steel and iron is of tremendous importance as they have wide usage domestically and industrially. Acid solutions are used in the industrial processes, acid cleaning, acid descaling, acid pickling and oil well acidizing, require corrosion inhibitor to prevent the corrosion of metal.

### Corrosion Inhibitors

A corrosion inhibitor is a substance which when added in small concentration to an environment, effectively reduces the corrosion rate of a metal exposed to it. Large numbers of organic compounds have been studied and are still being studied to assess their corrosion inhibition potential. However, most of these substances are not only expensive but also possess health and environmental hazards [P. B. Raja and Sethuraman, 2008] [1] prompting the search for their replacement. Plants have been recognized as sources of naturally occurring compounds that are generally referred to as 'green' compounds, some with rather complex molecular structures and having a variety of physical, chemical and biological properties. A number of these compounds are enjoying use in traditional

applications such as pharmaceuticals and bio-fuels. Furthermore, there has been a growing trend in the use of natural products as corrosion inhibitors for metals in various corrosive media (Orubite and Oforka 2004) [2].

The term “green inhibitor” or “eco-friendly inhibitor” refers to the substances that are biocompatibility in nature, environmentally acceptable, readily available and renewable source. Due to bio-degradability, ecofriendliness, low cost and easy availability, the extracts of some common plants based chemicals and their by-products have been tried as inhibitors for metals under different environments (Abdel-Gaber *et al.* 2006, Ebenso and Ekpe 1996, Ebenso *et al.* 2004, Ekpe *et al.* 1994, Kliskic *et al.* 2000) [3-7]. Green corrosion inhibitors can be grouped into two categories, namely organic green inhibitor and inorganic green inhibitors. Molecular structure of inhibitor is the main factor determining its characteristics. Presence of hetero atom (S, N, O) with free electron pairs, aromatic rings with delocalized  $\pi$ -electrons, high molecular weight alkyl chains, substituent group in general improves inhibition efficiency. It is noticed that organic compounds show higher inhibition efficiency as compared to inorganic.

### Organic Green Inhibitor

The organic green inhibitors are the alkaloids and flavonoids and other natural products obtained from natural sources like plant. It also includes synthetic compounds with negligible toxicity. Noteworthy contributions of some researchers on organic green corrosion inhibitor are discussed here.

Some research groups have reported the successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment. *Brugmansia suaveolens* (BS) and *Cassia roxburghii* (CR) inhibited the corrosion of mild steel in 1.0 M HCl solution [8]. (Table-1) (Figure-1 and Figure-2).

Ambrish Singh, Eno E. Ebenso and M.A. Quraishi had reported *Andrographis paniculata*, *Strychnous nuxvomica*, and *Moringa oleifera* plant extracts showed inhibition efficiency above 98%. The weight loss method, Electrochemical Impedance Spectroscopy (EIS), Linear Polarization Resistance (LPR) studies were used to determine the inhibition efficiency of the inhibitors. The extracts of *Andrographis paniculata*, *Strychnous nuxvomica*, and *Moringa oleifera* were found to be the mixed type of inhibitors [9]. (Table-2).

The inhibitive effect of kalmegh (*Andrographis paniculata*) leaves extracts was reported for the corrosion of mild steel in HCl Solution. The Weight Loss Method, Electrochemical Impedance Spectroscopy, Linear Polarization and Potentiodynamic Polarization Technique were used to determine the inhibition efficiency of inhibitor. The FTIR study showed that the inhibition of mild steel was due the formation of film on the metal/acid solution interface through the adsorption of *Andrographis paniculata* leave extract molecules [10].

The inhibitive action of water extract of naturally occurring *Elettaria cardamomum* plant against the corrosion of zinc in 1.0M HCl solution was investigated by using weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy. *E. cardamomum* extract showed high inhibitory effect on the corrosion of zinc in 1.0MHCl and the inhibition efficiency increased with increasing its concentration. The inhibitory effect of *E. cardamomum* extract resulted due to its adsorption on the metallic surface through its electron rich functional groups. The adsorption of the investigated water extract on a zinc surface follows Langmuir’s adsorption isotherm [11].

In an interesting study K. Rajam et al investigated the inhibition efficiency (IE) of an aqueous extract of garlic in controlling corrosion of carbon steel in well water in the absence and presence of  $Zn^{2+}$  by wet loss method. The formulation of 2 ml of garlic extract and 25 ppm  $Zn^{2+}$  offered 70% inhibition efficiency (IE) to carbon steel immersed in well water and polarization study revealed that this formulation controls the anodic reaction. FTIR study revealed the formation of protective film of  $Fe^{2+}$ -allicin complex and  $Zn(OH)_2$  [12]. (Table-3) (Figure-3 and Figure-4).

R. Saratha and V. G. Vasudha studied the efficiency of acid extract of dry *Nyctanthes arbortristis* leaves as corrosion inhibitor for mild steel in 1.0 N  $H_2SO_4$  Solution. The leave extract showed good corrosion inhibition efficiency as high as 90% at 1% inhibitor concentration. Polarisation studies indicate that inhibitor to be of a mixed type inhibiting both cathodic as well as anodic reactions. Impedance study showed that the inhibition is due to the adsorption of the plant constituents on the mild steel surface [13].

The inhibition efficiency (IE) of *phyllanthus amarus* extract (PAE)- $Zn^{2+}$  system, in controlling corrosion of carbon steel in an aqueous solution containing 60 ppm of  $Cl^-$  was evaluated by weight loss method. Weight loss study revealed that the formulation consisting of 2 ml of PAE and 25 ppm of  $Zn^{2+}$  has 98% inhibition efficiency in controlling corrosion of carbon steel immersed in an aqueous solution containing 60 ppm of  $Cl^-$ . Polarization study revealed that this system functions as mixed type of inhibitor controlling the cathodic reaction and anodic reaction to

an equal extent. AC impedance spectra revealed that a protective film was formed on the metal surface while FTIR spectra showed that the protective film consists of  $\text{Fe}^{2+}$ -phyllanthus complex [14,15].

The inhibition effect of exudate gum from *Acacia trees* (*Gum Acacia*, GA) on the corrosion of mild steel in acidic media was studied by weight loss, hydrogen evolution, and electrochemical polarization methods. Surface Morphology was analyzed by fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and X-ray photoelectron spectroscopy (XPS) techniques. The results of weight loss, hydrogen evolution, and electrochemical polarization methods indicated that inhibitor efficiency (I%) increased with increasing inhibitor concentration. Results of weight loss method were highly consistent with those obtained by hydrogen evolution method, and both indicated that inhibitor efficiency increases with increasing inhibitor concentration and the presence of external magnetic field. Electrochemical polarization studies showed that *Gum Acacia* acts as mixed type inhibitors. The results reveal that *Gum Acacia* provided a very good protection to mild steel against corrosion in acidic media. FTIR, SEM and XPS confirmed the existence of an adsorbed protective film on the mild steel surface [16].

The inhibition effect of the *Aloes* extract on mild steel in hydrochloric acid was examined by weight loss methods, potentiodynamic polarization and electrochemical impedance spectroscopy techniques. Inhibition efficiency value increased with the increase of the extract concentration, while the efficiency decreased with increase of temperature. Polarization curves indicated that the extract acts as mixed type inhibitor in 1.0 M HCl solutions. EIS measurement results indicated that the resistance of the mild steel electrode increased greatly and its capacitance decreased by increasing the inhibitor concentration [17].

Corrosion inhibition efficiency of dry *Polyalthia longifolia* (Asoka tree) leaves in 1N HCl medium was investigated by weight loss and temperature studies. Effect of temperature (35-75°C) on the corrosion behavior of mild steel in the presence of plant extract was studied. Inhibition was found to increase with increase in concentration of the extract. Adsorption of extract molecules on mild steel surface obeyed the Langmuir, Temkin, Freundlich adsorption isotherms. The results obtained prove that the leaves of *Polyalthia Longifolia* act as a good corrosion inhibitor having efficiency of 87% at 1.5% inhibitor concentration [18]. (Table-4) (Figure-5).

### **Inorganic Green Inhibitor**

A number of inorganic elements (minerals) are essential for the growth of living things. Mineral elements in wide variety are present in trace amounts in almost all foodstuffs. The higher concentrations of many metals cause toxicity to all forms of lives. Chromates are among the most common substances used as inhibitors or incorporated in anticorrosive pretreatments of aluminium alloys. However, these compounds are highly toxic and their use produces serious environmental hazards [19]. Due to the serve environmental hazard and high toxicity use of chromates is prohibited in industries and lanthanide salts are used as alternative to chromates. It was studied by many researchers that Lanthanide salts exhibit excellent anti corrosive property. Hence Lanthanide salts can be used as green corrosion inhibitor [20-22].

The inhibitor behavior of  $\text{CeCl}_3$  was studied for AA5083 alloy and galvanized steel in aerated NaCl solutions. The Inhibition of corrosion of AA5083 was done by the addition of  $\text{CeCl}_3$  which get precipitates on  $\text{Al}_6$  (Mn, Fe, Cr) intermetallics which act as permanent cathode. The corrosion of galvanized steel was inhibited by the formation of cerium-rich film. The film contains  $\text{Ce}^{4+}$  which was formed by the cerium oxides and hydroxide [23]. Arena et al. also studied the inhibition of localized corrosion process in 3.56 wt.% NaCl for the tin (Sn) after the addition of cerium solution. The optimum concentration among those which were studied was 1000 ppm  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  with 96% efficiency of protection [24]. A Study of Growth Mechanism of cerium layers on galvanized steel confirmed by M. A.Arena, J. J. Damborenea also confirmed the corrosion inhibition behavior of cerium [25] (Table-5).

### **Selection Process of Green Corrosion Inhibitors**

In addition to corrosion inhibition, an important aspect to be considered in the selection process is the effects on the use and discharge of chemicals to health, safety and the environment. Literature study shows that green corrosion inhibitor with minimum or no health and environmental hazards which is applicable to wide range of metals and various environmental conditions is to be discovered or invented.

## Conclusion

Research work in the field of corrosion inhibition of metals by natural products has increased the awareness about the corrosion inhibiting ability of tannis, alkaloids, organic amino acids and organic dyes has resulted in sustained interest on the corrosion inhibiting property of natural products of plant origin. Natural products are eco-friendly, ecologically acceptable, inexpensive, easily available and renewable source of material. Although a number of insightful publications have been devoted to corrosion inhibition by plant extracts but detailed study about the adsorption mechanism are limited and the drawback of most of the publications on plant extracts as corrosion inhibitor is that active constituent has not been identified. Extensive research efforts are required to employ “Green Corrosion Inhibitors” to commercial level.

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**Table-1:**

Inhibition Efficiency (IE) and surface coverage (h) for various concentrations of inhibitors for the corrosion of mild steel in 0.1 N HCl

Inhibitor Concentration (in ppm)	<i>Brugmansia suaveolens</i>		<i>Cassia roxburghii</i>	
	%IE	h	%IE	h
0 (Blank)	-	-	-	-
100	74.89	0.7489	85.72	0.8572
200	85.79	0.8579	88.16	0.8816
300	91.56	0.9156	90.87	0.9087
400	93.67	0.9367	92.86	0.9286

**Table-2:**

Electrochemical Impedance, Tafel and Linear Polarization Resistance data 308 K.

Name of Inhibitor	Inhibitor Concentration	R <sub>ct</sub> (Ω cm <sup>2</sup> )	C <sub>dl</sub> (μF cm <sup>-2</sup> )	% IE	E <sub>corr</sub> (mV versus Secondary Calmol Electrode)	I <sub>corr</sub> (mA/cm <sup>2</sup> )	%IE
1 M HCl	-	8.5	68.9	-	446	1540	-
<i>Andrographis paniculata</i>	300	99	56.9	91.4	489	82	94.6
	600	108	52.4	92.1	462	59	96.1
	1200	491	40.4	98.2	486	30.6	98
<i>Strychnous nuxvomica</i>	250	130.3	52	93.5	461	132	91.4
	300	159.9	47.1	94.7	463	97	93.7
	350	263.9	43.3	96.7	494	27.5	98.2
<i>Moringa oleifera</i>	200	215	43	96	503	59	96.1
	250	324.5	41.4	97.3	472	38	97.5
	300	644.9	32.4	98.6	493	28	98.1

**Table-3:**

Corrosion Rate of carbon steel immersed in well water in the absence and presence of inhibitor and inhibition efficiency (IE) obtained by weight loss method: Immersion period-3 days, Inhibitor- Garlic Extract+Zn<sup>2+</sup>

Garlic Extract (in ml)	Zn <sup>2+</sup>			
	0 ppm		25 ppm	
	Corrosion Rate	%IE	Corrosion Rate	%IE
0	22.42	-	17.94	20
2	11.21	50	6.73	70
4	7.17	68	4.48	80
6	2.24	90	1.79	92
8	1.35	94	0.90	96

**Table-4:**

% Inhibition Efficiency of *Polyalthia longifolia* in HCl at different concentration and different temperatures

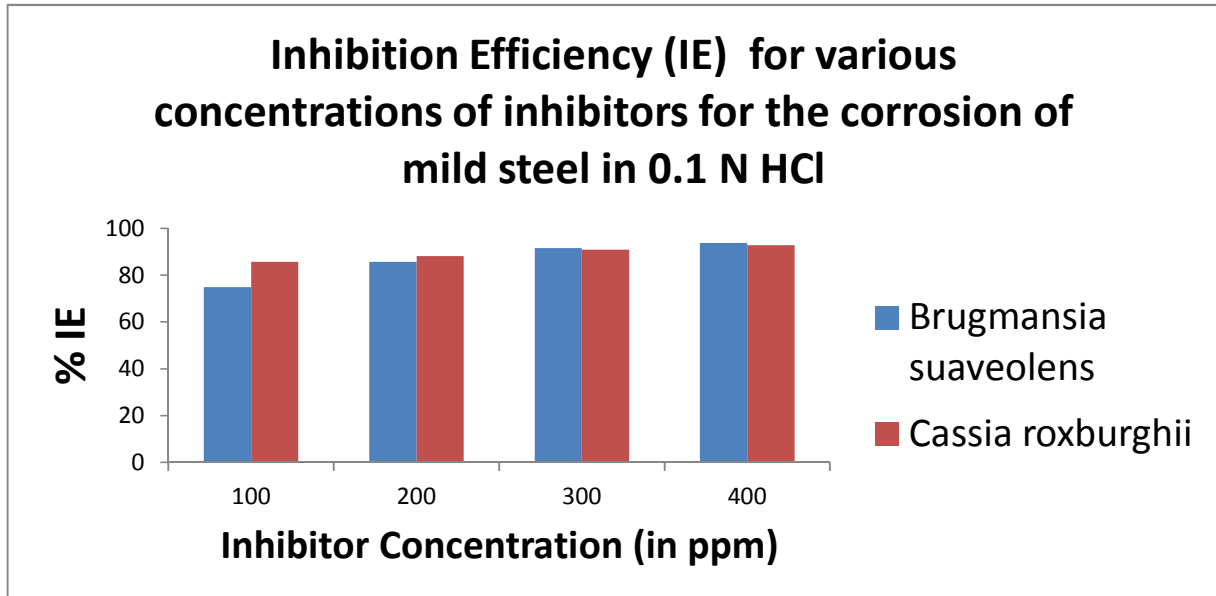
Temperature in K	% IE							
	0.1	0.3	0.5	0.7	0.9	1.1	1.3	1.5
308	19.61	21.56	37.25	39.21	40.19	45.09	52.94	64.7
318	48.88	60.74	64.07	71.11	80	80.74	81.85	83.71
328	62.44	65.89	67.36	71.13	71.65	77.4	87.23	87.45
338	38.11	45.88	52.7	54.82	58.82	61.17	64.94	69.64
348	64.93	65.26	66.54	67.63	67.91	68	75.99	78.54

**Table-5:**

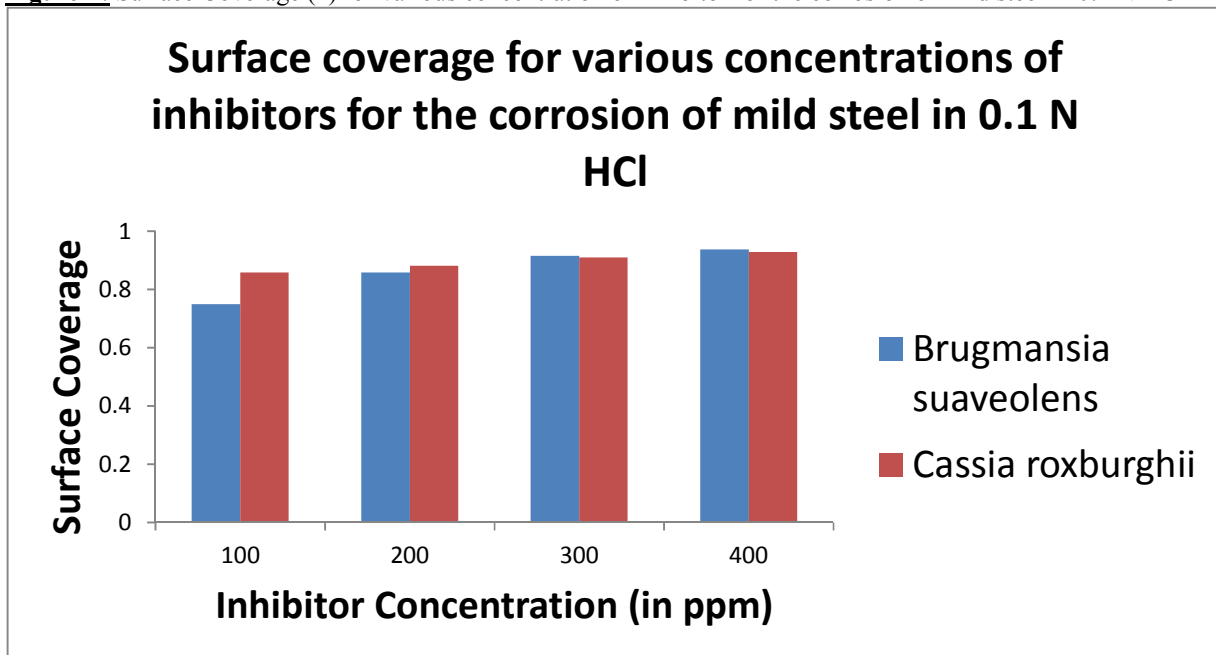
Inorganic Green Inhibitors

Inhibitor	Metal	Medium	Reference No.
La(NO <sub>3</sub> ) <sub>3</sub> , Sm(NO <sub>3</sub> ) <sub>3</sub> , LaCl <sub>3</sub> and SmCl <sub>3</sub>	AISI 434 Steel	NaCl	22 - 23
CeCl <sub>3</sub> .7 H <sub>2</sub> O	Tinned Iron	NaCl	24
CeCl <sub>3</sub>	AA5083, Galvanized Steel	NaCl	25

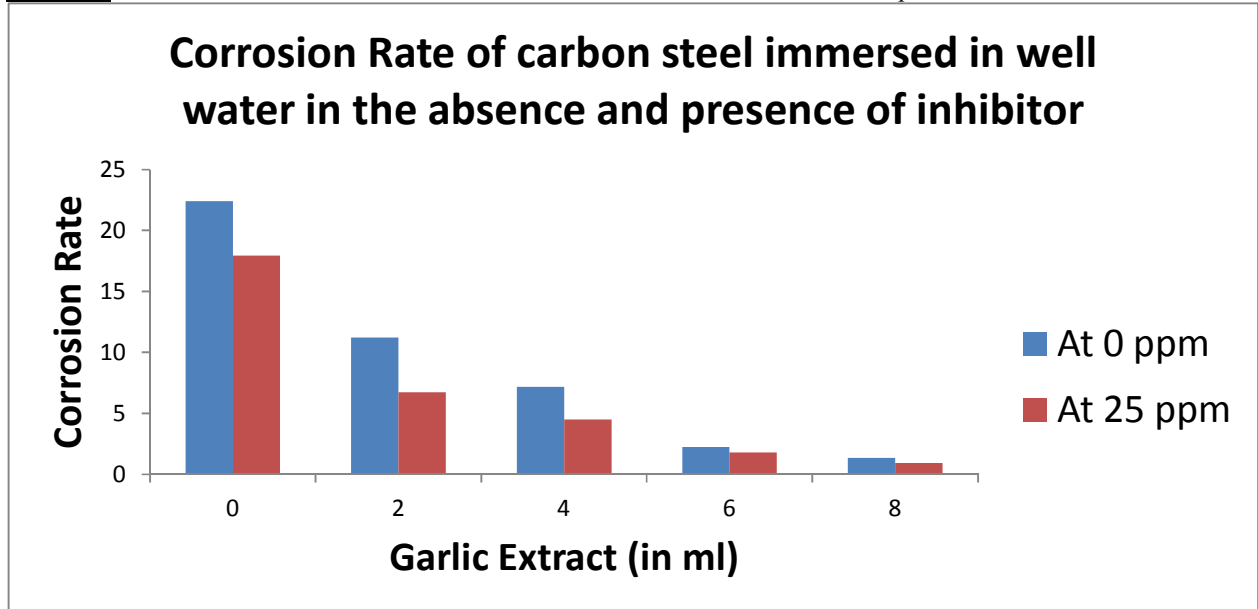
**Figure-1:** Inhibition Efficiency (IE) for various concentrations of inhibitors for the corrosion of mild steel in 0.1 N HCl



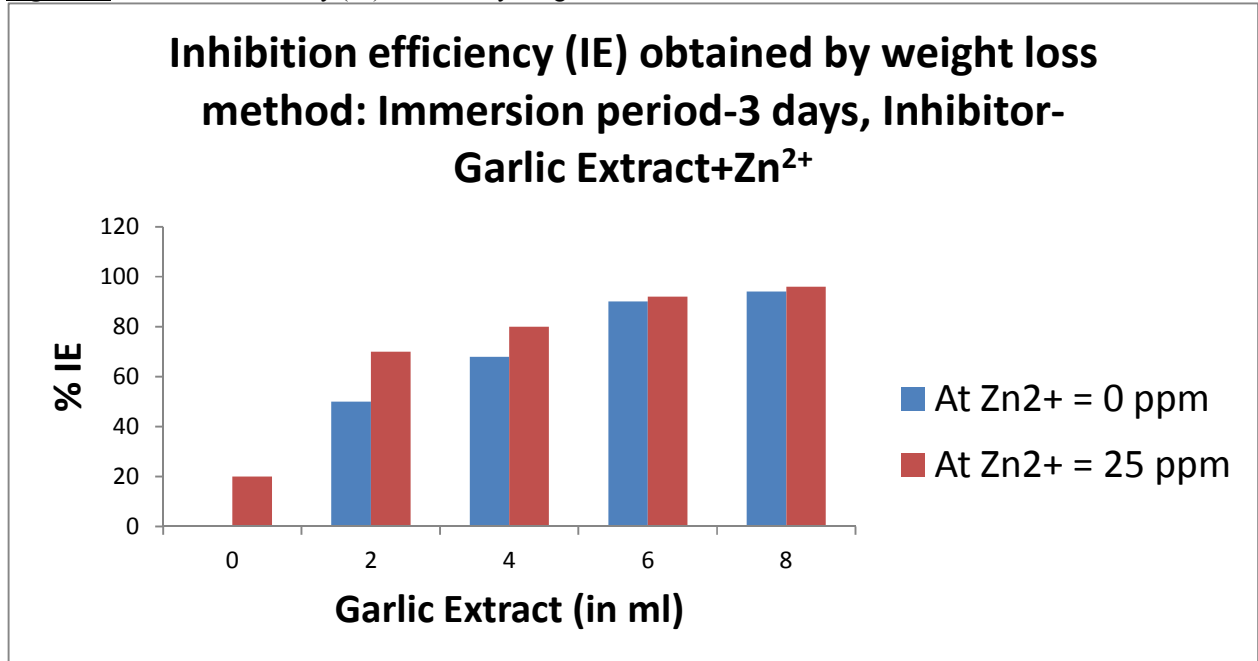
**Figure-2:** Surface Coverage (h) for various concentration of inhibitor for the corrosion of mild steel in 0.1 N HCl



**Figure-3:** Corrosion Rate of Carbon Steel immersed in well water in the absence and presence of inhibitor



**Figure-4:** Inhibition Efficiency (IE) obtained by weight loss method





**Figure-5:** % IE Vs Temperature at different concentrations

