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Evaluation of Anti-corrosive Efficacy of Prosopis Cineraria Extract on the Nitric Acid Corrosion of Copper

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Abstract

Anti-corrosive propensity of Prosopis cineraria extract on the corrosion behavior of copper (Cu) in nitric acid (HNO_3) medium was investigated by applying gravimetric technique. Corrosion inhibition efficiency of Prosopis cineraria was observed to enhance with increasing concentration of extract and reduce with elevation in temperature. The inhibitor underwent physisorption on the Cu metal surface. Adsorption characteristics were approximated by Langmuir adsorption isotherm. Highest inhibition efficiency (η%) 86.12 % was obtained at 303±1 K in fruit extract. It was observed that the extract acts as a benign potential corrosion inhibitor for Cu corrosion in 1.0 M HNO3 acid solution. Results revealed that existence of Prosopis cineraria extract enhances the energy of activation (E_a) of corrosion reaction. Adsorption parameters such as kinetic and thermodynamic [Gibbs free energy change (ΔG0ads) and adsorption equilibrium constant (K_{ads})] of adsorption process were determined from experimental data. These parameters show a strong interaction between surface of copper metal and inhibitor extract. The inhibitor adsorption process on surface of copper was found to be physical, exothermic and spontaneous. The surface morphology and characterization of copper was done by applying scanning electron microscope (SEM).

Keywords

Acid corrosion, Prosopis cineraria, Copper, Adsorption parameter, Langmuir adsorption

1. Introduction

Corrosion is the disintegration of substance outcomes from an immersion and interaction (mechanism of adsorption) with the environment. It is a prime problem that must be encountered in order to protection, economic and environmental causes

[1] in different mechanical, chemical, metallurgical, medical and biochemical engineering applications and more considerably in the design of a much more varied number of mechanical parts which equally vary in functionality, size and useful lifespan. Pure copper is highly and extremely ductile, very malleable and soft metal. It is alloyed with mini extent of metals namely Be, Ag, As, Cd and Cr to renovate the characteristics in order to individual uses while retaining huge of the properties of the pure copper metal. Furthermore, copper is seen as eco-friendly in view of its potential to be 100% recycled [2]. Copper tolerate from common corrosion in nitric acid, the rate of corrosion is quite high both in strong and weak nitric acid due to more solubility of $Cu(NO_3)_2$ copper nitrate.

Copper is of the significant classes of stuff owing to their broad limit of household products and industrial applications. Copper (ductile and malleable) a relatively passive metal is quietly corroded by water and air in the existence of weak acids [3]. Copper disintegration in nitrate medium is much significant in the electromachining, electrical equipment and electropolishing industries. Owing to these causes, attention has focused on the character of copper in nitrate medium. In the absence of various complexing agents in the aggressive solution, like NO3- ions, anodic dissolution of copper leads as follows in two steps.

$$Cu \rightarrow Cu^{+} + e^{-} \quad \text{(i)}$$

$$Cu+ \rightarrow Cu^{+2} + e^{-} \quad \text{(ii)}$$

Presence of oxygen (O2) in neutral aqueous medium, the overall anodic disintegration reaction of copper leads in following step:

$$Cu + \frac{1}{2} O_2 + H_2O \rightarrow Cu^{+2} + 2\,OH^- \quad \text{(iii)}$$

When nitrate ions NO_3- (complexing agents) are present in the aggressive aqueous solution, complex copper ions, like $Cu(NO_3)_2$, must be considered. In the near- neutral pH limit of oxygen- containing solution, the anodic reactions (at least at the exposure period) are as follows

$$Cu + NO_3^- \leftrightarrow CuNO_{3ads} + e^- \quad \text{(iv)}$$

$$CuNO3_{ads} + NO_3^- \leftrightarrow Cu(NO_3)_2 \quad \text{(v)}$$

Numerous naturally occurring substances such as Tamarindus indica [4], Capparis decidua [5], Datura stromonium [6], Prosopis juliflora [7], Ficus religeosa [8] have been detected as probable corrosion inhibitors. The present research work is directed to detect the extract of Prosopis cineraria as potential acid corrosion inhibitors in nitric acid (HNO_3) for copper.

Prosopis cineraria comprises specigerine, tannins, steroids namely campesterol, cholesterol, sitosterol, stigmasterol, gallic acid, tricosan-1-ol, methyldocosanoate [9-10] whereas pods and leaves contain histidine, alanine, aspartic acid, flavone derivative, serine, leucine and lysine [11-12].

2. Experimental (Materials and Methods)

2.1. Preparation of Prosopis cineraria extract

Air dried for two weeks, then different parts of Prosopis cineraria ground by electrical grinder to a fine powder. It was taken in 500 ml round bottom flask and soaked in appropriate extent of distilled ethyl alcohol (C_2H_5OH). Later on, it was extracted by standard mechanism [13-14].

2.2. Preparation of test coupons

Copper coupons comprises 99.5 wt.% Cu, 0.001 wt.% Ni, 0.019 wt.% Al, 0.004 wt.% Mn, 0.116 wt.% Si and balance impurities were used. The copper strips employed have a rectangular shape (2.54 cm × 1.52 cm × 0.029 cm) with mini holes of almost 2 mm diameter towards the upper edge in order to suspension has been employed. Before experimentation, each strip was

degressed in absolute alcohol, dried in acetone, weighed as per standard method [13-14]. After immersion period, strips are removed from corroded environment and were cleaned chromate- phosphate mixture medium.

2.3. Test solution

The corrosive medium (1.0M HNO3) was prepared by dilution of Analar Grade 69 % nitric acid (HNO_3) with bi-distilled water. Copper strips were immersed in isolate beakers involving aggressive mediums and varying inhibitor concentration (ranging from 0.09 to 0.45%) for immersion time 12 hrs at 303± 1 K temperature. From the Gravimetric technique, various corrosion parameters, viz., Weight loss (ΔM), Fractional surface coverage (θ), corrosion rate (ρ_{corr}) and Percentage inhibition efficiency (η%) were calculated using standard equation [13-14].

Table 1. Weight loss parameters on corrosion of copper in 1.0M HNO_3 with ethanolic extract of various concentration of fruit, stem bark and root bark of Prosopis cineraria at 303 ± 1 K.

Effective area of Coupon: 7.72 cm^2 Immersion time: 12 hrs.

Inhibitor Concentration (%)	Mass loss ΔM (mg)	Corrosion Rate (ρ_{corr}) (mmy-1)	Fractional Surface Coverage (θ)	Inhibition Efficiency (η %)	$\log(\frac{\theta}{1-\theta})$
Uninhibited	140.5	196.82	-	-	-
Fruit Extract					
0.09	51.4	72.00	0.6341	63.41	0.2387
0.18	41.6	58.27	0.7039	70.39	0.3760
0.27	34.7	48.61	0.7530	75.30	0.4840
0.36	27.3	38.24	0.8056	80.56	0.6174
0.45	19.5	27.31	0.8612	86.12	0.7927
Stem bark extract					
0.09	54.2	75.92	0.6142	61.42	0.2019
0.18	44.4	62.20	0.6839	68.39	0.3351
0.27	37.6	52.67	0.7323	73.23	0.4370
0.36	31.8	44.54	0.7736	77.36	0.5336
0.45	21.5	30.11	0.8469	84.69	0.7428
Root bark Extract					
0.09	55.7	78.03	0.6035	60.35	0.1824
0.18	47.5	66.54	0.6619	66.19	0.2917
0.27	40.3	56.45	0.7131	71.31	0.3954
0.36	32.6	45.66	0.7679	76.79	0.5196
0.45	24.5	34.32	0.8256	82.56	0.6752

3. Results and Discussion

Values of weight loss (ΔM), corrosion inhibition efficiency (η%), surface coverage(θ) and corrosion rate (ρ_{corr}) were explored from gravimetric method in order to different inhibitor extract concentration and 1.0M HNO_3 nitric acid medium are demonstrated in Table 1. It is revealed from experimental data that the percentage inhibition efficiency (η%) reduces with increases in nitric acid (HNO3) strength and enhances with increase in the extract concentration.

Each corrosion inhibitor diminished the corrosion rate to a prominent amount. The rate of corrosion reduces with increases in inhibitors extract concentration. Corrosion rate values outcomes from experimental data revealed that corrosion rate (ρ_{corr}) is directly inverse proportional to concentration of inhibitor. The highest inhibition efficiency (η%) was enlisted in fruit extract

86.12 % in 1.0M HNO3 acid solution.

3.1. Langmuir Adsorption Isotherm

Numerous adsorption isotherms were employed yet the optimal fit in order to adsorption of Prosopis cineraria is Langmuir adsorption isotherm. The affinity between the inhibitors extract concentration in % and surface coverage can be manifested from the under mentioned Langmuir adsorption isotherm:

$$\log\left(\frac{\theta}{1-\theta}\right) = \log K_{ads} + \log C \quad \text{(vi)}$$

The plot of log (θ / 1-θ) versus log C displayed a straight line of unit gradient in order to tested inhibitor. The linear plot Fig.2 with high correlation coefficient (0.998). The slopes of almost unity clearly manifested that the surface adsorption process of Prosopis cineraria on to the surface of copper metal obey Langmuir adsorption isotherm. K_{ads} value can be determined by the intercept line on the log (θ / 1-θ) axis. K_{ads} is concerned to the standard free energy of adsorption (ΔG_{ads}) as

$$\Delta G^0_{ads} = -2.303\ RT \log (55.5\ K_{ads}) \quad \text{(vii)}$$

Values of ΔG^0 ads are negative in all cases ensure the stability of the adsorption oxide film and spontaneity of the adsorption reaction which is made by Prosopis cineraria onto the surface of copper metal.

4. Conclusions

Principle conclusions are:

1. The percentage inhibition efficiency enhanced with respect to the inhibitor extract concentration and diminished with elevation in temperature in order to copper metal.
2. The adsorption process is spontaneous and adheres Langmuir adsorption isotherm in HNO_3 acid solution and corrosion rate may be enhanced with temperature owing to thermal activated kinetics.
3. Prosopis cineraria extract is an eco-friendly, cheap, readily available, benign potential corrosion inhibitor for copper in HNO_3 acid solution.
4. SEM analysis further supports the creation of the protective oxide film.

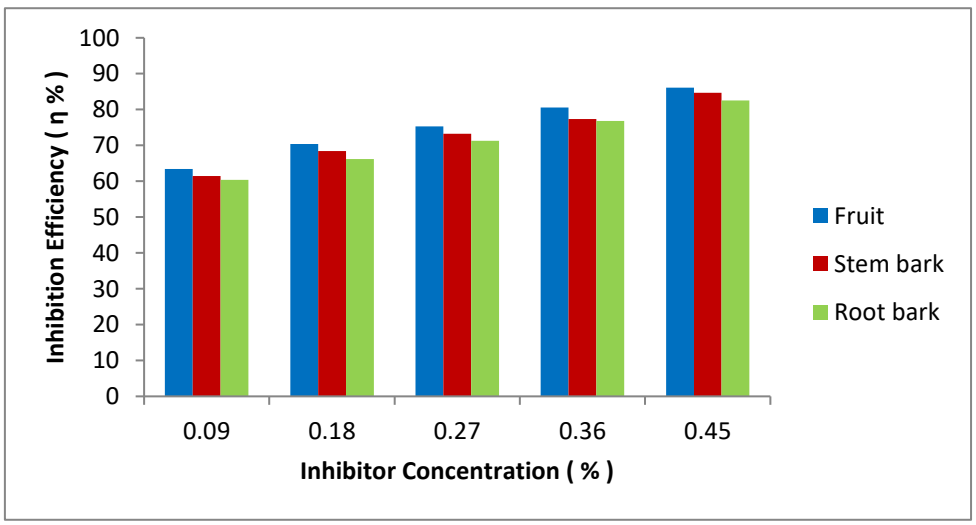

Figure 1. Influence of inhibition efficiency of Prosopis cineraria extract for copper in 1.0M HNO3 at 12 hrs exposure time.

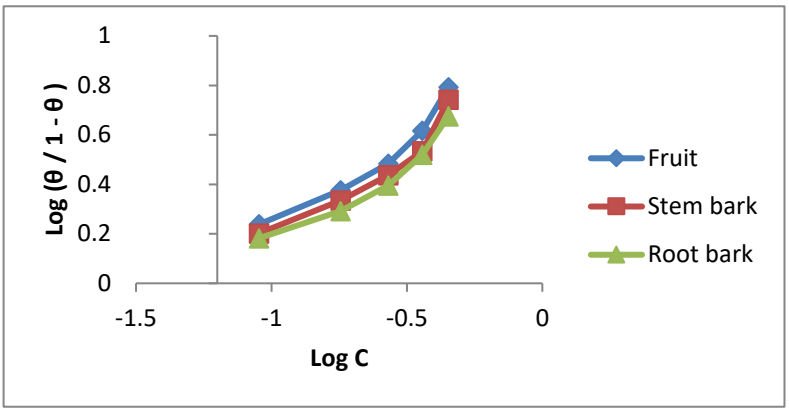

Figure 2. Plot of log (θ / 1-θ) against log C for Prosopis cineraria extract for copper in 1.0M HNO3 at 12 hrs immersion period.

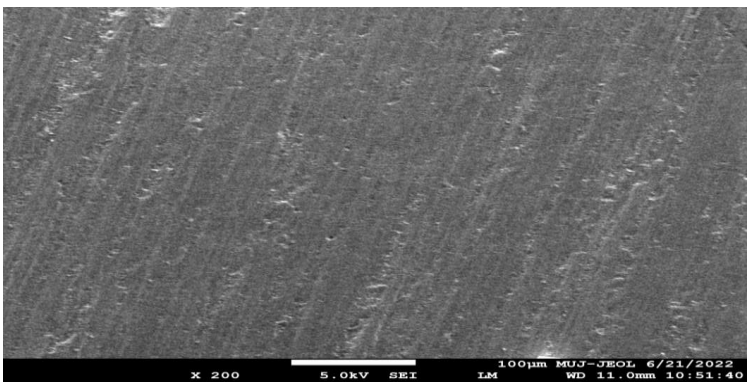

Figure 3. SEM image of pure copper metal

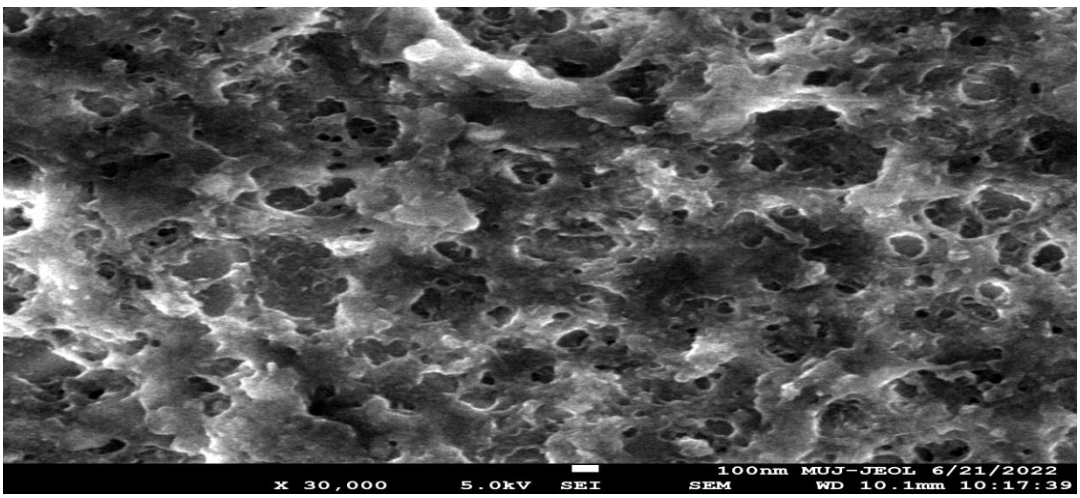

Figure 4. SEM image of copper in uninhibited (acid).

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