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Inhibition of Mild Copper Metal Corrosion in HNO_3 Medium by Acid Extract of *Azadirachta Indica* Seed

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Abstract: Efficiency of acid extract of dry *azadirachta indica* seed as corrosion inhibitor for mild copper metal in various concentration of (1 N,2 N and 3N) HNO_3 medium was investigated in the present study. Experimental methods include weight loss, determination of corrosion rate, inhibition efficiency and phytochemical analysis was studied. The results indicate *azadirachta indica* seed to be a good corrosion inhibitor of a mixed type and having efficiency as high as 95% at 1% inhibitor concentration in different time duration.

Keywords: *Azadirachta indica*, Corrosion inhibitor, Plant products, Mild copper metal, Acid medium

Introduction

Corrosion is a natural process. When products are fabricated out of iron, steel or other metal, it is natural for them to return to their original state. The process is called corrosion and may be the only time when 'Nature' can cause tremendous concern. An ancient scriptures show more than 2500 years ago Bhagavan Buddha could know of the corrosion of iron when he state, "As rust sprung from iron straight away corrodes and destroys the very pure iron itself, so do impure deals of evildoers bring them to self-destruction[1]. All metals except Gold and platinum exist in nature in the forms of their oxides, carbonates, sulphides, sulphates *etc*. These combined form of metals represent their thermodynamically stable state. It is their natural tendency to go back to the lower energy state (*i.e.*) combined state by recombining with the elements present in the environment. If the metal or alloy structure is not properly maintained, they deteriorate slowly by the action of atmospheric gases, moisture and other chemicals. This is the main reason for metallic corrosion. Corrosion and its cost have been deplored since ancient times, but only recently have serious attempts been made to estimate the total cost to the community at large[2]. Our economy would be drastically changed if there were no corrosion. But corrosion touches all inside and outside the home, on the road, on the sea, in the plant and in aerospace vehicles[3].

Defined[2] corrosion inhibitors as some chemical substances known as inhibitors are added to corrosive environment in small quantities. These substances substantially reduce the rate of corrosion pure synthetic chemicals are costly, some of them are not easily biodegradable and their disposal creates pollution problems. Plant extracts are environment friendly, bio-degradable, non-toxic, easily available and of potentially low cost. Most of the naturally occurring substances are safe and can be extracted by simple procedures. Recent literature is full of researches which test different extracts for corrosion inhibition applications. The examples are numerous such as fenugreek[4], Henna[5,6] Olive[7], Jojoba[8], Black pepper[9] (Pandian), *Occimum viridis*[10], *Andrographis paniculata*[11], *Phyllanthus amarus*[12], Onion, garlic[13], *Eugenia jambolans*[14], *Pongamia glabra*[15], Opuntia[16] and Eugenol[17] *etc*. Many of these naturally occurring substances proved their ability to act as corrosion inhibitors for the corrosion of different metals and alloys in different aggressive media.

The aim of the present study is to investigate the corrosion inhibition effect of *Azadirachta indica* seed as a cheap and environment friendly corrosion inhibitor for mild copper in various concentration of HNO_3 medium by weight loss, determination of corrosion rate, determination of inhibition efficiency and phytochemical analysis.

Experimental

Sheet of mild copper metal obtained locally and of 2 mm thickness was mechanically cut in to coupons of 5x1 cm^2 size, having a hole of uniform diameter to facilitate suspension of the coupon in the test solution. The coupons were mechanically cleaned followed by polishing with emery sheet of fine quality to expose shining polished surface. To remove any oil and organic impurities coupons were degreased with acetone and finally with de-ionized water, dried and stored in a desiccators. Accurate weight of the samples was taken using electronic balance.

Inhibitior preparation

5% Stock solution of the inhibitor materials *Azadirachta indica* seed extracts was prepared by refluxing 25 g dry powder with 250 mL of 1 N, 2 N and 3 N, nitric acid for 3 h. The refluxed solution was allowed to stand overnight and filtered through ordinary filter paper. The residue was repeatedly washed with small amounts of 1 N HNO_3 and the filtrate made up to 500 mL. From this solution, different concentrations of inhibitor solutions ranging from 0.01 to 1% were diluted. The chemicals used were of analytical grade.

Phytochemical analysis

Phytochemical analysis of the ethanol and aqueous extracts of *azadirachta indica* leaves and seeds was carried out according to the method reported[18]. The pulverized plant materials (325.60 g) were defatted using redistilled petroleum spirit (333 - 353 K) of fatty acid and their derivatives. The defatted pulverized plant materials were then successively and exhaustively extracted with ethanol. Frothing and Na_2CO_3 tests were used for the identification of saponin, bromine water, ferric chloride tests were used for the identification of tannin, and Leberman's and Salkowski's tests were used for the identification of cardiac glycodises, while dragendorf, Hagger and Meyer reagent tests were used for the identification of alkaloid.

Weight loss method

Pre weighed mild copper metal specimens (in triplicate) were suspended in 1 N HNO_3 test solution for a predetermined period of time, with and without the inhibitor in different

concentrations ranging from 0.01 to 1% at different time interval. The coupons were removed from test solution, thoroughly washed with NaHCO3 solution and de-ionized water, dried well and then weighed. The percentage of inhibitor efficiency (IE %) for various concentrations of the inhibitor were calculated as I.E.% = Weight loss without inhibitor – weight. loss with inhibitor x 100

Determination of corrosion rate

The corrosion rate expressed as mills per year was calculated using formula

$$\text{C.}R = \frac{534 \times W \times 1000}{A \times T \times D}$$

Where, W - Weight Loss in gm, A – Area of the specimen in cm^2, T – exposure time in hours.

Determination of inhibition efficiency

Inhibition efficiency was calculated by using the formula

$$I.E(\%) = \frac{W_0 - W}{W_0} \times 100$$

Where, W_0 - Weight loss without inhibitor, W - Weight loss with inhibitor.

Surface coverage

The degree of surface coverage (θ) for different concentration of the inhibitor in acidic media have been evaluated from weight loss experiments using the equation

$$\theta = \frac{W_0 - W}{W_0}$$

Where,W_0 - Weight loss without inhibitor ,W - Weight loss with inhibitor

Results and Discussion

Green corrosion inhibitors have been designed by understanding the relationships between the structure of organic compounds and toxicity as well as corrosion inhibition efficiency. The predicted structures with reduced toxicity and improved corrosion inhibition efficiency are then tested experimentally for these properties, thus leading to green inhibitors. Weight loss measurements were carried out for metallic copper both in the absence and presence of acid extracts of *Azadirachta indica* seed in 1 N, 2 N and 3 N HNO_3 medium.

Efficacy of the *Azadirachta indica* in the nitric acid medium (1 N, 2 N and 3 N HNO_3) with respect to the concentration of the inhibitor, experiments have been carried out by varying the concentration range from 0.2-1.0%. The results were obtained and shown in Table 1-4 the results were reveal that the corrosion rate decreased with the increasing concentration of *Azadirachta indica* extract in 1 N HNO_3 in all the concentration ranging from (0.2-1.0%).The inhibition efficiency increased with increase in concentration of the extract and increasing in the time of contact. For this investigation we found that the inhibitor efficiency of *Azadirachta indica* seed extract was increased from 53.3 to 82.96% for 6 h with 1 N HNO_3 medium. The Maximum inhibition efficiency was recorded in 95.69% in 1 N HNO_3 92.54%, in 2 N HNO_3 and 95.47% in 3 N HNO_3 was exhibited by 1% concentration of *Azadirachta indica* seed extract.

Table 1. Weight loss as the function of exposure time on copper metal in different normality of HNO_3 using *Azadirachta indica* seed extract at room temperature

Conc	1 N				2 N				3 N			
(A.i)	1 h	2 h	3 h	6 h	1 h	2 h	3 h	6 h	1 h	2 h	3 h	6 h
Blank	0.093	0.168	0.198	0.270	0.124	0.356	0.429	0.632	0.153	0.312	0.398	0.982
0.2	0.048	0.107	0.113	0.126	0.062	0.139	0.113	0.381	0.042	0.104	0.076	0.261
0.4	0.024	0.093	0.098	0.101	0.048	0.097	0.078	0.253	0.039	0.089	0.053	0.159
0.6	0.013	0.052	0.048	0.163	0.041	0.083	0.064	0.197	0.026	0.073	0.034	0.124
0.8	0.009	0.021	0.029	0.052	0.032	0.075	0.057	0.143	0.019	0.067	0.030	0.107
1.0	0.004	0.013	0.021	0.046	0.017	0.062	0.032	0.107	0.012	0.058	0.018	0.096

Note :A.i (Azadirachta indica)

Table 2. Inhibitor efficiency and corrosion rate in HNO_3 as the function of exposure time on copper metal in 1 N HNO_3 using *Azadirachta indica* seed extract

Conc.	1 h		2 h		3 h		6 h	
(A.i)	C. r	Efficiency	C.rate	Efficiency	C. rate	Efficiency	C. r	Efficiency
Blank	1.109		1.002		0.7875		0.5369	
0.2	0.5727	48.38	0.6384	36.30	0.4494	42.92	0.2505	53.33
0.4	0.2863	74.19	0.5548	44.64	0.3898	50.50	0.2008	62.59
0.6	0.1551	86.02	0.3102	69.0	0.1909	75.75	0.1252	76.66
0.8	0.1073	89.39	0.1252	87.5	0.1153	85.35	0.1034	80.74
Conc. (A.i)	0.0477	90.32	0.077	92.26	0.0835	95.69	0.0914	82.96

Note: A.i (Azadirachta indica) , C.r (Corrosion rate)

Table 3. Inhibitor efficiency and corrosion rate in HNO_3 as the function of exposure time on copper metal in 2 N HNO_3 using *Azadirachta indica* seed extract

Conc.	1 h		2 h		3 h		6 h	
	C. r	Efficiency	C. r	Efficiency	C. r	Efficiency	C. r	Efficiency
Blank	1.4796		2.124		1.7064		1.256	
0.2	0.7398	50.0	0.8293	60.95	0.4494	73.65	0.7577	39.71
0.4	0.5727	61.29	0.5787	72.75	0.3102	81.81	0.5031	59.96
0.6	0.4892	66.93	0.4952	76.68	0.2545	85.08	0.3917	68.82
0.8	0.3818	74.19	0.4474	78.93	0.2267	86.71	0.2844	77.37
1.0	0.2028	86.29	0.3699	82.58	0.2128	83.06	0.1272	92.54

Note :A.i (Azadirachta indica), C.r (Corrosion rate)

Table 4. Inhibitor efficiency and corrosion rate in HNO_3 as the function of exposure time on copper metal in 3 N HNO_3 using *Azadirachta indica* seed extract

Conc.	1 h		2 h		3 h		6 h	
	C. r	Efficiency	C. r	Efficiency	C. r	Efficiency	C. r	Efficiency
Blank	1.8257		1.8615		1.583		1.9530	
0.2	0.5011	72.54	0.6205	66.66	0.3023	80.90	0.5190	73.42
0.4	0.4653	74.50	0.5310	71.47	0.2108	86.68	0.3162	83.80
0.6	0.3102	83.00	0.4355	76.60	0.1352	91.45	0.2466	87.37
0.8	0.2267	87.58	0.3997	78.52	0.1193	92.46	0.2128	89.10
1.0	0.1431	92.15	0.3460	81.41	0.1909	90.22	0.0715	95.47

Note: A.i (Azadirachta indica) , C.r (Corrosion rate)

Impact of immersion time

The free dissolution of metallic copper in 1 N, 2 N and 3 N HNO_3 with and without inhibitors such as *Azadirachta indica* for different immersion time (1 h, 2 h and 3 h) was carried out. The variation in corrosion rate and inhibition efficiency with time was given in Table 2-4. Corrosion rate gradually decreased from 1hr to 6 h shown inverse relationship to the time of immersion, the optimum time of immersion was found to be 6 h in 1 N HNO_3. Maximum inhibition efficiency 95.69% of with 1% concentration of the extract was observed at 3 h the results were shown in the Table 2, followed by the rate of inhibition efficiency gradually increased up to 3 h in the 2 N, 3 N HNO_3 medium the results were shown in the Table 3 and 4. The data indicates 3 h as the optimum period of immersion at which the maximum efficiency of 95.47% was recorded with 1.0% extract concentration.

The inhibitive effect on corrosion of mild copper, Al, Zn and Cu in HCl and H_2SO_4 solutions by aqueous extracts of Fengugreek, lupine seeds, doum, beatroot and Solanum melongena fruits using weight loss methods have been reported[19]. The inhibition efficiency increased with an increase of additive concentration in all cases except for Fengugreek extract with Zn and Cu and dry extract in the case of Zn, observed the corrosion inhibitive capacity on copper of natural products such as neem tree bark, jamun bark, neem leat black berry and red sanders wood. The result suggested that some of the natural products have good potential as corrosion inhibitors for use on copper artifacts. Investigated[20] the inhibitive effect of mango bark and leaf extract solution on mild steel in 0.2 sulphric acid medium by weight loss method and potential measurement. The results obtained form the combination of the two, gave very good results. Noted[21] that the phytochemical constituents of plant extract, such as saponnin, tannin, alkaloid, glycoside, anthraquinone and flavanoid, are the major factors that determine the inhibition efficiency of the plant extract. Table 5 shows the phytochemical constituents of ethanol extract of seeds of *Azadirachta indica*.

Table 5. Phytochemical composition of ethanol extract of *Azadirachta indica* seeds

Photochemicals	Seed
Saponin	+++ ++
Phlobatanin	++ +
Tannin	+++ ++
Anthraquinone	+ -
Cardiac glycosides	+++ +++
Flavanoid	+ +
Terpene	+++ +++
Alkaloid	+++ ++

Note: = - absent, + present in trace quantity, ++ = moderately present, +++ = present in large quantity

Conclusion

Acid extract of *Azadirachta indica* seed acts as good corrosion inhibitor for mild copper metal in 1 N HNO_3 medium. Inhibition efficiency increases with inhibitor concentration and maximum inhibition efficiency was 95% at the inhibitor concentration 1% v/v. Corrosion inhibition may be due to the adsorption of the plant phytochemical constituents on the mild copper surface.

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