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RESEARCH ARTICLE

CORROSION INHIBITION AND ADSORPTION PROPERTIES OF AZADIRACHTA INDICA (NEEM) LEAVES EXTRACT AS A GREEN INHIBITOR FOR ZINC IN H_2SO_4

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ABSTRACT

The corrosion inhibition of Neem, Azadirachta indica (AZI) leaves extract as a green inhibitor of zinc corrosion in H_2SO_4 has been studied using the gravimetric method. The results of the study reveal that the different concentrations of the AZI extract inhibit zinc corrosion and that inhibition efficiency of the extract varies with concentration and temperature.

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INTRODUCTION

Corrosion is the destruction of material resulting from exposure and interaction with the environment. It is a major problem that must be confronted for safety, environment, and economic reasons (Thompson et al., 2007). Several efforts have been made using corrosion preventive practices and the use of green corrosion inhibitors is one of them (Anuradha et al., 2008). The use of green inhibitors for the control of corrosion of metals (Valdez et al., 2003) and alloys which are in contact with aggressive environment is an accepted and growing practice (Taylor et al., 2007; Khaled, 2008). Large numbers of organic compounds are under study to investigate their corrosion inhibition potential. All these studies have revealed that organic compounds, especially those with N, S, and O, show significant inhibition efficiency. However, most of these compounds are not only expensive, but also toxic to living beings (Bothi Raja, 2008). It is needless to point out the importance of cheap and safe inhibitors of corrosion. Plant extracts and organic species have therefore become important as an environmentally acceptable, readily available, and renewable source for a wide range of inhibitors (Rajendran et al., 2004; Mesbah et al., 2007; Okafor et al., 2007; Lebrini et al., 2008; Radoj et al., 2008; Refaey et al., 2008).

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They are the rich sources of ingredients which have very high inhibition efficiency (Bothi Raja, 2008) and are hence termed ''Green Inhibitors'' (Lebrini et al., 2010). Green corrosion inhibitors (Sharma et al., 2009) are biodegradable and do not contain heavy metals or other toxic compounds. The successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment has been reported by some research groups (Abdel-Gaber et al., 2008; Khamis et al., 2007; Umoren, 2008; Okafor, 2007; El-Etre, 2006; Umoren et al., 2006; Bendahou et al., 2006). Research efforts to find naturally organic substances or biodegradable organic materials to be used as effective corrosion inhibitors of a wide number of metals has been one of the key areas in research (Sharma et al., 2008).

Azadirachta indica (AZI) - The Neem plant

The principal focus in this paper is on Azadirachtaindica ((AZI), Neem), specifically the extract from Neem leaves. Several studies have been carried out and have remained focused on the Neem plant parts for their various pharmacological activities (anti- inflammatory, anti-pyretic, analgesic, immunostimulant, anti-fertility, anti-carcinogenic, anti-malarial, and hepatoprotective) (Subapriya, 2005; Dasgupta et al., 2004; Biswas et al., 2002) and medicinal properties (Biswas et al., 2002).

The Neem extract has been only very occasionally involved in environmental engineering and environmental chemistry research with the analysis of the adsorption of Pb(II) from aqueous solution by AZI leaf powder by Bhattacharyya and Sharma (Bhattacharyya et al., 2004), the adsorption and corrosion inhibitive properties of AZI in acid solutions (Oguzie, 2006) and the study of copper corrosion inhibition by AZI leaves extract in 0.5M Sulfuric acid by Valek (Valek, 2007). AZI has been well known in India and its neighboring countries for more than 2000 years as one of the most versatile medicinal plants having a wide spectrum of biological activity (24). Neem is an evergreen tree, cultivated in various parts of the Indian subcontinent. Neem has been extensively used in ayurveda (Subapriya, 2005), unani, and homoeopathic medicine and has become a cynosure of modern medicine. The Sanskrit name of the Neem tree is ‘‘Arishtha’’ meaning ‘‘reliever of sickness’’ and hence is considered as ‘‘Sarbaroganibarini’’ (Biswas et al., 2002). The tree is still regarded as a ‘‘village dispensary’’ in India. The importance of the Neem tree has been recognized by the US National Academy of Sciences, which published a report in 1992 entitled ‘‘Neem a tree for solving global problems.’’ Chemical investigation on the products of the Neem tree was extensively undertaken in the middle of the twentieth century. Nimbin was the first bitter compound isolated from Neem oil, and thereafter more than 135 compounds have been isolated from different parts of Neem and several reviews have also been published on the chemistry and structural diversity of these compounds which are divided into two major classes: isoprenoids (Roy et al., 2007) and others. Neem extracts contain significant amounts of water soluble, electrochemically active compounds, as well as high concentrations of alkaloids, fatty acids, and nitrogen and oxygen-containing compounds. Neem is bitter in taste. The bitterness is due to an array of complex compounds called ‘‘triterpenes’’ or more specifically ‘‘limonoids.’’

Nearly 100 protolimonoids, limonoids or tetranortriterpenoids, pentanortriterpenoids, hexanortriterpenoids, and some non-terpenoid constituents have been isolated from various parts of the Neem tree (Sawchuk, 1994; Koul, 1990); still more are being isolated. The most important bioactive principal is azadirachtin; at least 10 other limonoids possess insect growth in regulating activity (Saxena, 1997; Schmutterer, 1995). Neem fruits, seeds, oil, leaves, bark, and roots have such uses as general antiseptics, anti-microbials, treatment of urinary disorders, diarrhea, fever and bronchitis, skin diseases, septic sores, infected burns, hypertensions, and inflammatory diseases. Neem oil and its isolates nimbidin, nimbidiol, and nimbin inhibit fungal growth on humans and animals (Suresh et al., 2007). Neem leaf extracts and teas can treat malaria and the anti-malarial action is attributable to gedunin, a limonoid. Given the wide spectrum of chemical species present in Neem leaves and their respective multifaceted chemical and biological properties, we therefore articulated that channeling Neem leaf extract for yet another use into green inhibition of corrosion studies may yield some interesting results. All the more, Neem extract has been only very occasionally involved in environmental engineering and environmental chemistry research with the analysis of the adsorption of Pb (II) from aqueous solution by Neem leaf powder by Bhattacharyya and Sharma (Bhattacharyya, 2004), the adsorption and corrosion inhibitive properties of AZI in acid solutions (Oguzie, 2006; Eddy, 2008; Sharma, 2010) and the study of copper corrosion inhibition by AZI leaves extract in 0.5M Sulfuric acid by Valek and Martinez (Valek, 2007).

Research objectives

Due to its position in the electrochemical series, zinc with an oxidation potential of 0.76 eV is much prone to corrosion, especially in acidic medium. The corrosion of Zn in acidic medium is believed to occur according to “Hydrogen evolution Mechanism.” In the present study, we are trying to study corrosion of zinc and the inhibition of the corrosion process by AZI extract. To the best of our knowledge, nothing has been specifically reported on the use of AZI extract for the inhibition of zinc corrosion in acidic medium. AZI leaves are often used in the medicinal and pharmaceutical industry. An additional beneficial use of Neem leaves to curb corrosion of zinc would surely imply the successful utilization of this powerful and versatile natural resource in the metallurgical, materials science, and chemical engineering industries. The present study therefore seeks to investigate the inhibitive properties of AZI leaves extract for zinc corrosion using a gravimetric technique in an acidic media (H_2SO_4 acid) with and without the extract at two temperatures. Any positive result would help reduce the economic cost of corrosion control as well as decrease the subsequent environmental threats from inhibitor usage because Neem leaves extract is non-toxic and biodegradable.

MATERIALS AND METHODS

Preparation of stock solution of Neem *Azadirachta indica* (AZI) leaves extract

Stock solution of the AZI leaves extract was prepared by boiling 0.5 kg of air-dried Neem leaves in deionized water and left overnight. The contents of the extraction process were then mixed in a graduated cylinder, filtered, and the resulting solution was kept in a refrigerator at low temperatures of 2°C in order to prevent the contents from being altered due to the chemical, physical, and biological reactions it might otherwise undergo (Sliwka-Kaszynska et al., 2003).

Specimen preparation

Rectangular specimen sheets of zinc were mechanically pressed cut to form different coupons, each of dimension 5.0×2.5×0.04 cm. Each coupon was degreased by washing with ethanol, dried in acetone, and preserved in a dessicator. All reagents used for the study were Analar grade and double distilled water was used for their preparation. Specimens containing a small hole of 2 mm diameter near the upper edge were used for the determination of CR. The working surfaces of the zinc coupons were carefully and lightly polished with grade P600 SiC polishing paper in order to remove the oxide layer and eliminate the reactions that would have otherwise taken place with the acid and this zinc oxide layer.

Calculation of inhibition efficiency (%I) and degree of surface coverage (θ)

The mass loss method was employed for a room temperature (303 K) and 333 K. The temperature for each run of the experiments was kept constant using a thermostat. In this procedure, the mass loss of the metal in uninhibited (with no AZI extract) and inhibited solutions were monitored and recorded. About 50 mL of test solutions were analyzed. From these data, the inhibition efficiency (%*I*) and degree of surface coverage (θ) were calculated (Eddy, 2008) using Equations 1 and 2, respectively

$$\%I = \left(1 - \frac{\Delta M_i}{\Delta M_u}\right) \times 100 \quad (1)$$

where ΔM_u and ΔM_i are the mass loss of zinc in uninhibited solution and inhibited solution, respectively.

$$\theta = \left(1 - \frac{\Delta M_i}{\Delta M_u}\right). \quad (2)$$

The CR in mmpy (millimetres per year) has been calculated from Equation 3.

$$CR = \frac{(MassLoss) \times 87.6}{(Area)(Time)(MetalDensity)} \quad (3)$$

where mass loss is expressed in mg, area is expressed in cm^2 of metal surface exposed, time is expressed in hours of exposure and metal density is expressed in g/cm^3 and 87.6 is a conversion factor.

RESULTS AND DISCUSSION

Table 1 shows values of corrosion rate (CR) of zinc in all the concentrations of H_2SO_4 studied and it shows that CR increases with increase in H_2SO_4 concentration. Table 2 shows the CR for the corrosion of zinc at 2.0N H_2SO_4 in the absence and presence of AZI extract at 303 and 333 K. Addition of increasing concentration of the inhibitor generally retards the CR of zinc in the solutions. This is clearly seen from the decreasing change in mass loss taking place (Figure 1A and B) at a particular acid concentration corresponding with an increase in inhibitor concentration. Table 3 shows values of inhibition efficiency of the different concentrations of AZI extract at 303 and 333 K.

Table 1. Corrosion rate (gravimetric) for corrosion of zinc in H_2SO_4 at 303K

Concentration of H_2SO_4 (N)	CR (mmpy)
0.5	1.18
1.0	1.32
2.0	1.48

Table 2. Corrosion rates for the corrosion of zinc in 2.0 N H_2SO_4 solutions containing AZI extract

Concentration of AZI extract in 2.0N H_2SO_4 (x 10^{-3} g/L)	CR (mmpy) at 303 K	CR (mmpy) at 333 K
Uninhibited	1.48	1.73
9.09	0.87	1.21
16.66	0.83	0.87
23.08	0.78	0.86
28.57	0.68	0.83
33.33	0.48	0.81
37.50	0.31	0.62

Table 3. Inhibition efficiency (%I) for the corrosion of zinc in 2.0N H_2SO_4 solutions containing AZI extract

Concentration of AZI extract (x 10^{-3} g/L)	Gravimetric	
	%I (303 K)	%I (333 K)
9.09	29.85	30
16.66	34.32	43.75
23.08	40.3	48.75
28.57	50.75	51.25
33.33	73.13	56.25
37.5	83.58	81.25

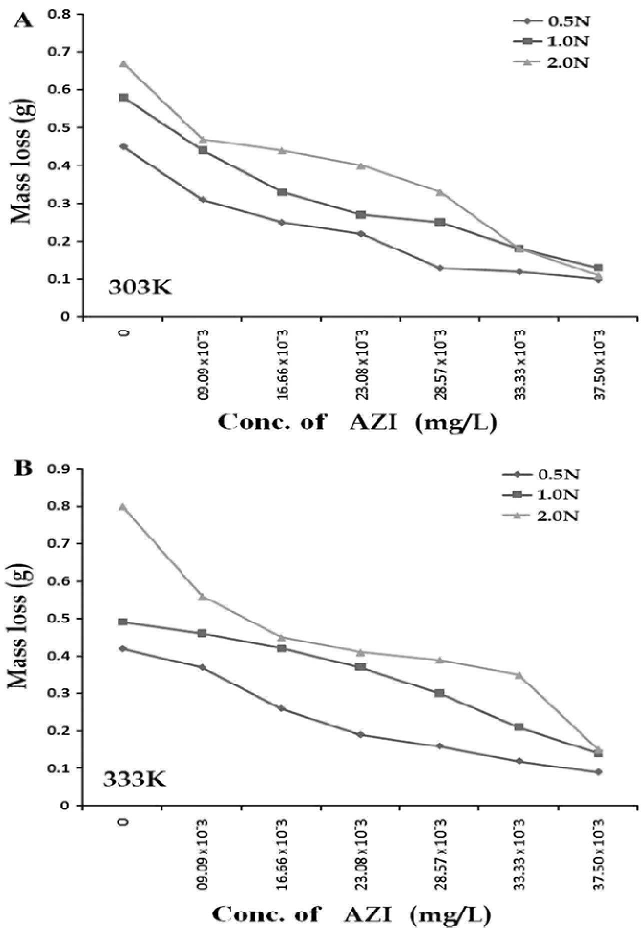

Figure 1. Variation of mass loss change with increase in concentration of AZI leaves extract for various acid concentrations at the two temperatures investigated

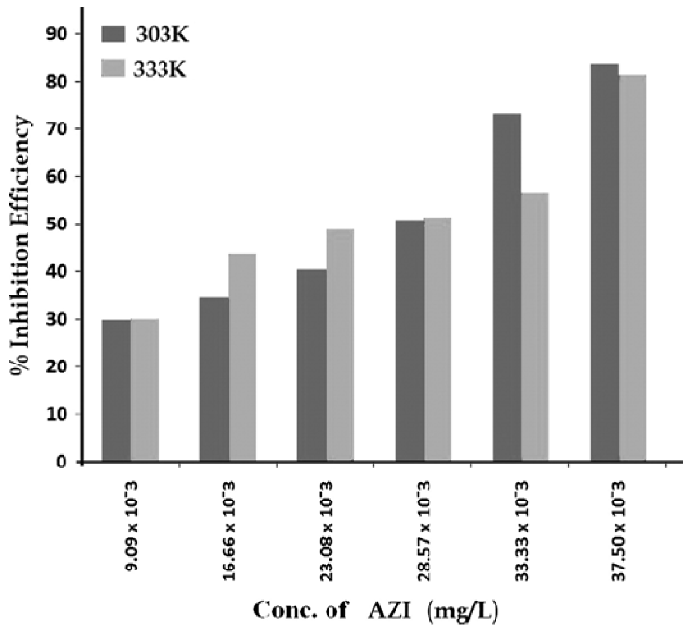

Figure 2. Variation of inhibition efficiency with concentration of AZI leaves extract

Effect of concentration

From Table 1 and 2, it is found that the rate of corrosion of zinc is affected by concentration of H_2SO_4, temperature, and concentration of AZI extract.

The rate of zinc corrosion increases as the concentration of H_2SO_4 increases and also increases as the temperature is increased (Figure 1). Analysis and interpretation of trends in Figure 1 show that corrosion increases as the concentration of the acid increases confirming that the rate of corrosion of zinc in H_2SO_4 increases with concentration. The mass loss taking place and recorded at the different concentrations of the AZI extract are lower than that of the blank solution (for the 2.0N H_2SO_4) indicating that different concentrations of the AZI extract retard the corrosion of zinc. It is supposed to be due to adsorption of AZI extract on the surface of Zn. This hypothesis shall be verified in a future study with details of the electrochemical studies reported and discussed therein.

Effect of temperature

Figure 1 hence shows mass loss plots for the corrosion of zinc in the presence of different concentration of the AZI extract at 303 K (A) and 333 K (B), respectively. Comparing Figure 1 A and B, it is found that at a fixed concentration of the inhibitor and a fixed acid concentration, the mass loss taking place at 333 K is in most of the instances higher than that occurring 303 K indicating that the inhibition efficiency of AZI extract decreases with increase in temperature. The decrease may be due to competition between forces of adsorption and desorption. These very same competing forces of adsorption and desorption may also actually explain the occasional discrepancies in mass loss change observed in Figure 1. From Table 3, it can also be seen that inhibition efficiency of AZI extract varies with its concentration. Optimum value of inhibition efficiency (83.58%) was obtained at an extract concentration of 37.50 mg/L, while the least value was obtained at an extract concentration of 9.09 mg/L. Figure 2 shows the variation of inhibition efficiency against the different concentrations of AZI extract at both 303 and 333 K. The significant difference between values of inhibition efficiency of AZI extract obtained at 303 and 333 K for especially the higher concentrations of the extract suggests that the mechanism of adsorption of the inhibitor on the zinc surface is by physical adsorption. For a physical adsorption mechanism, inhibition efficiency of an inhibitor decreases with temperature while for a chemical adsorption mechanism, values of inhibition efficiency increase with temperature (34, 35).

Conclusion

From the present study, it is found that the neem (AZI) leaves extract can be used as an inhibitor for zinc corrosion in H_2SO_4 medium. While the green inhibitor molecules most supposedly act by being adsorbed on zinc surface, the overall inhibition is provided by a synergistic effect. It has also been found that the inhibitive action of AZI leaves extract is basically controlled by temperature and the concentration of the inhibitor. A probable sequel to the present study would be to depict the active components of the AZI leaves extract involved in the corrosion inhibition reaction, and also elucidate the corrosion inhibition mechanism.

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