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BIOCIDAL AND INHIBITIVE DUALITY OF NATURALLY OCCURRING SUBSTANCE AZADIRACTA INDICA ON MILD STEEL IN FRESH WATER

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This paper deals with the biocidal and inhibitive effects of aqueous extract of Azardiracta indica (neem) on mild steel in fresh water environment. The extract retards the corrosive effect to an extent, which mainly depends on the concentration and stability of the extract. The biocidal and inhibitive properties are investigated by pour plate technique and by weight loss measurements, potentiodynamic polarization and AC impedance measurements. The inhibition activity is due to the adsorption of natural compounds, which are found in A.indica extract.

Keywords: Azardiracta indica, biocide, corrosion, inhibitor, mild steel

INTRODUCTION

The inhibitors for cooling water system, which are free from environmental liabilities, are difficult to practice. But the environmental legislation imposes great restrictions on the cooling water disposal, which should be confirmed to the environmental standards prior to disposal. Efforts have been directed towards developing eco-friendly inhibitor formulations for cooling water systems.

In 1950s inorganic inhibitors such as chromates, nitrites, phosphates and zinc were used as cooling water inhibitors [1]. But they caused severe environmental problems when they were disposed to the environment.

Afterwards, phosphonates and their derivatives were used as inhibitors [2] and molybdenum based inhibitors were also widely used [3]. But they were too expensive.

Another important problem using inhibitor package to prevent corrosion in cooling water system is the interaction of biocides and inhibitors, which necessitates the additional compound or additional attention to the selection of biocide.

Thus to reduce the above problems, we shifted our attention towards investigating the eco-friendly and synergistic inhibitors. Natural organic compounds having heteroatoms are found to have higher basic properties and electron density, which assist in corrosion inhibition.

Various organic compounds such as aminoacids, alkaloids, pigments, proteins, tannins [4-7], amines [8], aldehydes [9], aniline [10], hexamine [11], thiourea [12], flavonoids, various enzymes etc. have been reported to be very good corrosion inhibitors.

Numerous naturally occurring plants like Tamarind, Tea leaves, Pomegranate [13-14], Beet root [15], Emblica officianalis, Termanalia chebula [16], Sapindas trifoliatus, Acacia conciana, Calotropis giganta [17-18], Eugenia jambolans, Swertia aungustifolia [19] have been evaluated as effective acid corrosion inhibitors.

Aqueous extracts of Eucalyptus, Hibiscus and Agaricus [20] were tried as corrosion inhibitors for cooling water systems.

The object of this paper is to investigate the utility of the aqueous extract of naturally occurring substance A.indica as a corrosion inhibitor as well as biocide in fresh water environment.

Materials and methods

The aqueous extract of A.indica was prepared from dried leaves by using Soxlet apparatus.

By using this extract the following experiments were carried out.

Biocidal property

Biocidal property has been investigated by zone formation test through pour plate technique by using nutrient agar medium. The effective concentrations of aqueous extract of A.indica on the biocidal property have also been investigated by bacterial colony counts method at various time intervals.

TABLE I: Chemical characteristics of natural pond water (control)

*p*H	7.1 - 8.1
Dissolved oxygen	4.2 - 5.1 ml/l
Total hardness	80-150 ppm
Calcium carbonate	50-100 ppm
Salinity	4000-5000 ppm
Phosphate	56 ppm
Nitrate	94 ppm
Chloride	60 ppm

Inhibitive property

Mild steel specimens of size 5 x 1 x 0.2 cm and 1 cm^2 were used to investigate the inhibition property of naturally occurring substance A.indica by weight loss measurement, potential measurement, potentiodynamic polarization measurement and AC impedance measurement. All these experiments were conducted in natural pond water (control) with and without A.indica extract. The chemical characteristics of pond water are shown in Table I.

RESULTS AND DISCUSSION

Biocidal property - Zone formation test

Fig. 1 shows the biocidal property of A.indica extract. In case of A.indica extract mixed system, the bacteria free zone of 1.3 cm dia was found out and it confirms the biocidal property of A.indica extract which contains Nimbin, nimbionone, nimboniline, nimbandial and nimbolide substances [21].

Bacterial killing efficiency

Bacterial colony counts in case of both A.indica mixed system and control system are shown in Table II. The experiment was carried out by using various concentrations of A.indica extract. In control system, the bacterial colony counts varied

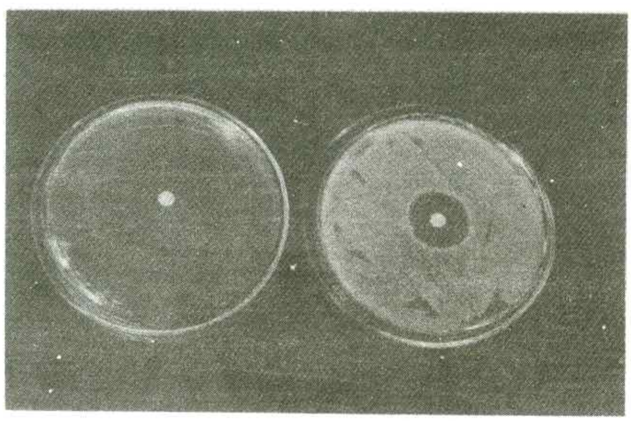

Fig. 1: Biocidal property of A.indica extract

TABLE II: Bacterial killing efficiency of A.indica extract on mild steel in fresh water environment

No of days	Bacterial colony counts in control system (CFU/ cm^2)	Bacterial attachment in A.indica extract (CFU/ cm^2) mixed system			
		10 ppm	25 ppm	50 ppm	100 ppm
1	6.8×10^6	2×10^2	TLTC	TLTC	TLTC
2	6.8×10^6	2×10^2	TLTC	TLTC	TLTC
5	6.4×10^6	2×10^3	TLTC	TLTC	TLTC
8	7.2×10^6	2×10^2	TLTC	TLTC	TLTC
10	7.1×10^6	2×10^6	2×10^2	3×10^2	2×10^3

TLTC = Too low to count.

from 6.8×10^6 to 7.2×10^6 CFU/cm^2 during 10 days exposure time. But in the presence of A.indica extract, the maximum bacterial colony count was found to be 2×10^3 CFU/cm^2 only at 10 ppm.

It is clear from the table that the 25 ppm is the minimum concentration, which is required to give 100% biocidal efficiency. More than 25 ppm concentrations also give the same effect. So we have taken 25 ppm as an optimum concentration, which is the minimum effective concentration. The presence of nimbin, nimbionone and nimboniline based compounds in the extract may be responsible for this biocidal property. The table shows that there were some bacterial colony counts on 10th day even in the presence of

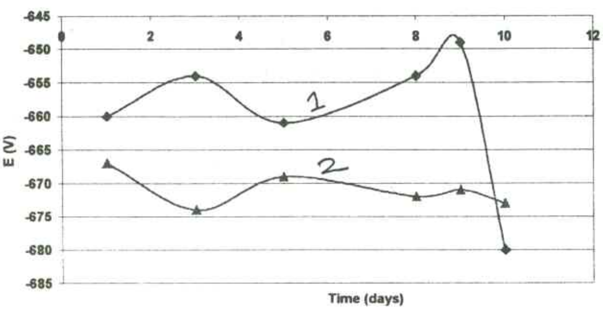

Fig. 2: Potential variation in A.indica extract mixed system and in control system
(1) A.indica extract mixed system (2) Control system

TABLE III: Corrosion rates by weight loss measurements on mild steel in A.indica extract mixed system and in control system

No of days	Weight loss (g)		Corrosion rate (mmpy)		Inhibition efficiency (%)
	A.indica mixed system	Control system	A.indica mixed system	Control system	
1	0.0021	0.0091	0.1965	0.8516	77
3	0.0036	0.0101	0.1123	0.3150	64
5	0.0045	0.0117	0.0842	0.2189	62
8	0.0059	0.0159	0.0788	0.2125	63
9	0.0064	0.0157	0.0665	0.1632	59
10	0.0188	0.0124	0.1759	0.1160	Negative

A.indica extract. It indicates the instability of A.indica extract.

Inhibition efficiency - Potential measurement

Potential variation in A.indica extract mixed system and in control systems are shown in Fig. 2. Compared to control, in the presence of A.indica extract, potential of the system is less and it is shifted towards positive direction from -669 to -649 mV vs SCE. It indicates the inhibitive activity of A.indica extract.

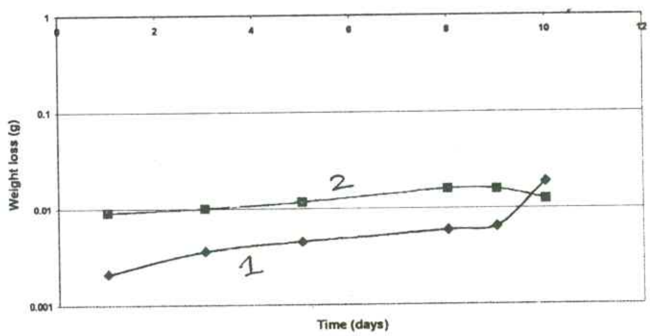

Fig. 3: Weight loss in A.indica extract mixed system and control system
(1) A.indica extract mixed system (2) Control system

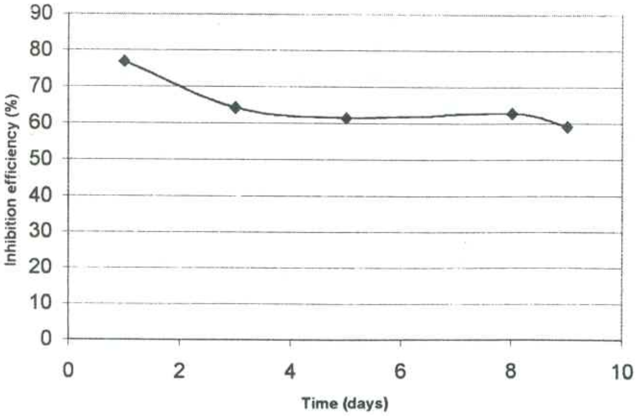

Fig. 4: Inhibition efficiency of A.indica extract mixed system

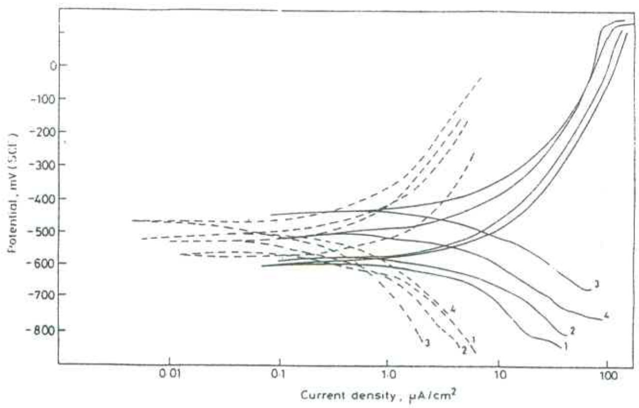

Fig. 5: Corrosion rates of mild steel in A.indica extract and its control system by polarization technique
(-----) A.indica extract system (2) (———) Control system
(1) 2nd day (2) 5th day (3) 8th day (4) 10th day

Weight loss measurement

Weight loss measurements and inhibition efficiency of A.indica extract mixed system and control systems are shown in Table III and Figs. 3 and 4. These tables show that the corrosion rate of A.indica extract mixed system was decreased from 0.1965 to 0.0665 mmpy and it is less than that of control system in which the corrosion rate was in the range of 0.1160 to 0.3150 mmpy.

The maximum inhibition efficiency of A.indica extract obtained was 77.9% and it is due to the presence of n-hexacosanal, nonacosane, protein, carbohydrates, minerals, thiamin, niacin, aminoacid etc., substances which are present in the neem leaf extract [21]. The adsorption between the metal and organic constituents of the extract could very well by chemisorption [22].

TABLE IV: Corrosion rates of mild steel in A.indica extract mixed system and in control system by potentiodynamic polarization technique

No of days	i_{corr} ($\mu A/cm^2$)		Corrosion rate (mmpy)	
	A.indica extract mixed system	Control system	A.indica extract mixed system	Control system
2	0.45	1.8	0.0005	0.020
5	0.84	2.5	0.0009	0.028
8	0.12	3.6	0.0014	0.041
10	0.84	4.0	0.0009	0.046

Potentiodynamic polarization measurements

Potentiodynamic polarization measurements of A.indica extract mixed and control systems are shown in Table IV. Fig. 5 shows the Tafel plot of both A.indica mixed and control systems. The table shows that the i_{corr} values in case of A.indica extract mixed system were reduced when it is compared to control in which the i_{corr} values were in the range of 4 $\mu A/cm^2$.

Besides the polarization curves reveals that A.indica reduces the current in both anodic and cathodic sites which act as a mixed inhibitor. Carbohydrates (22.9%), proteins (7.1%), minerals (Fe, Ca, P) thiamine (0.04%), niacin (1.4%) and vitamin C which are present in the A.indica

TABLE V: Impedance parameters for mild steel in A.indica and its control system

No of days	R_{ct} values of A.indica extract system (ohm.cm^2)	R_{ct} values of control system (ohm.cm^2)
3	4200	400
5	5630	800
10	5000	2000

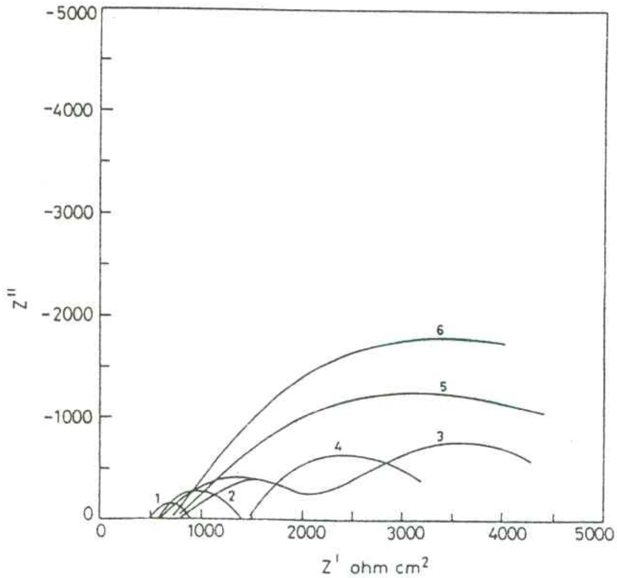

Fig. 6: Impedance parameters for mild steel in A.indica and its control system
A.indica extract system: (3) 3rd day (5) 5th day (6) 10th day
Conrol system: (1) 3rd day (2) 5th day (4) 10th day

extract may be responsible for this inhibitive property and the inhibitive property is due to adsorption of these natural compounds.

Farooqi *et al.* [23] reported that the aqueous extract of Jasiminium auriculatum and Cardia latifolia were found significantly to inhibit the corrosion of mild steel in 3% NaCl.

Impedance measurements

Table V and Fig. 6 show the R_{ct} values of A.indica extract mixed system and control system respectively. High resistance values were observed in the presence of A.indica extract mixed system, which is in the range of 5000 ohm.cm^2. Increase in resistance is due to the adsorption of natural substance, which are present in A.indica extract.

SUMMARY AND CONCLUSION

¤ Azadiracta indica was very effective biocide in a low concentration of 25 ppm.

¤ Natural compounds like nimbin, nimbione, nimboniline may be responsible for biocidal property.

¤ The maximum inhibition efficiency obtained was 77%.

¤ Apart from acting as biocide A.indica acted as inhibitor.

¤ Compounds like protein, carbohydrates, thiamine cardene, aminoacids, nonacosane and n-hexacosanal are responsible for the corrosion inhibition.

¤ The inhibitive action of this plant extract is due to the strong chemisorption of the phytochemical constituent of the extract especially heterocyclic ingredients on the surface of the mild steel. From the electrochemical studies, it is evident that this eco-friendly biodegradable inhibitors act through mixed model of inhibition.

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