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Corrosion inhibition of carbon steel in acidic medium using plant-derived green inhibitors

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Abstract

The cost burden of metallic corrosion on industrial infrastructure runs into hundreds of billions of dollars annually, and much of this cost falls on the steel-intensive sectors where acidic pickling and cleaning processes are routine. Chemical inhibitors used to protect carbon steel in these processes are frequently toxic and non-biodegradable, prompting a search for plant-derived green alternatives. This research evaluated the corrosion inhibition efficiency of aqueous extracts prepared from five plants—*Azadirachta indica* (neem), *Moringa oleifera*, *Curcuma longa* (turmeric), *Trigonella foenum-graecum* (fenugreek), and *Allium sativum* (garlic)—against carbon steel corrosion in 1 M hydrochloric acid using gravimetric weight loss, potentiodynamic polarisation, and electrochemical impedance spectroscopy methods. Inhibitor concentrations were varied from 100 to 500 ppm and temperatures from 25 to 55 °C. *Moringa oleifera* extract at 500 ppm and 25 °C gave the highest inhibition efficiency of 92.7%, followed by neem at 88.4%. All five extracts acted as mixed-type inhibitors based on polarisation data. Langmuir adsorption isotherm analysis gave adsorption equilibrium constants of 0.014-0.031 L/mg, and negative values of adsorption free energy confirmed spontaneous inhibitor adsorption onto the steel surface. Thermodynamic analysis indicated increased activation energies in the presence of inhibitors, consistent with reduced corrosion rates.

Keywords: Corrosion inhibition, carbon steel, plant extracts, green inhibitors, hydrochloric acid, gravimetric method, electrochemical impedance, Langmuir adsorption

Introduction

The annual global cost of corrosion is estimated at roughly 3.4% of world GDP, with carbon steel representing the most widely used structural metal and therefore the largest single source of corrosion losses. Acid pickling to remove rust and mill scale, acid descaling in the power sector, and acid stimulation in the petroleum industry all require steel to be in contact with aggressive acidic media for extended periods. Organic corrosion inhibitors are routinely added to these acid solutions to reduce metal dissolution rates without interfering with the primary industrial purpose of the treatment. Conventional synthetic inhibitors such as chromates, phosphates, and many nitrogen-containing heterocyclic compounds carry toxicity, environmental persistence, and disposal challenges. Regulatory tightening in India and internationally has spurred interest in plant extract inhibitors, which are biodegradable, obtainable from renewable sources, and often carry phytochemicals with known corrosion-inhibiting structural features—electron-rich nitrogen, oxygen, and sulphur heteroatoms that allow adsorption onto metal surfaces via donation of electron pairs to empty d-orbitals of iron. Several individual plant extracts have been tested on mild and carbon steel in hydrochloric acid, but comparative investigations using identical methodology across multiple plant species under matching experimental conditions are rare. Such comparisons are needed for screening potential commercial inhibitors. This research fills this gap by testing five plants selected for their phytochemical diversity and commercial availability in the Indian subcontinent under a unified experimental protocol, generating directly comparable efficiency, thermodynamic, and mechanistic data.

Materials and Methods

Materials

Dry leaves of *A. indica*, *M. oleifera*, and *T. foenum-graecum*, rhizome powder of *C. longa*, and cloves of *A. sativum* were obtained from a certified herbal supplier in Kolkata, West Bengal, India. Carbon steel coupons (composition: Fe 98.7%, C 0.18%, Mn 0.64%, Si 0.13%) were cut from a commercial sheet to dimensions 5.0 cm × 2.5 cm × 0.1 cm, polished with emery paper (grades 600 to 1200), degreased with acetone, rinsed with deionised water, and dried in a desiccator before use. Hydrochloric acid (37% w/w, AR grade) was from Merck India. Research was conducted at the Department of Industrial Chemistry, Tagore Memorial College of Science, Kolkata, West Bengal, India, between July 2022 and May 2024. Ethics approval for plant collection was obtained from the Institutional Botanical Collection Committee (Protocol TMCS-BOT-2022-14, September 2022).

Methods

Plant extracts were prepared by boiling 10 g of dried plant material in 100 mL deionised water for 30 min, filtering through Whatman No. 1 paper, and concentrating on a rotary evaporator to 20 mL. This stock was diluted to working concentrations (100-500 ppm). Gravimetric tests used coupons pre-weighed (± 0.1 mg) and immersed in 100 mL of 1 M HCl with or without inhibitor for 6 h at 25-55 °C; weight loss was determined after cleaning with Clarke's solution. Inhibition efficiency was calculated as $IE\% = (W_0 - W_i)/W_0 \times 100$, where W_0 and W_i are weight losses without and with inhibitor. Electrochemical measurements (potentiodynamic polarisation from -250 to +250 mV versus open circuit potential at 1 mV/s, and EIS from 100 kHz to 10 mHz at 10 mV amplitude) were performed in a three-electrode cell (steel working electrode, Pt counter, saturated calomel reference) using a Gamry Reference 600 + potentiostat. Adsorption isotherms were constructed from gravimetric data at 25 °C.

Theoretical Background and Mechanistic Framework

Corrosion inhibition by organic compounds adsorbed on metal surfaces is interpreted within two complementary theoretical frameworks. The first, the Langmuir adsorption isotherm model, relates the surface coverage θ to inhibitor concentration C and adsorption equilibrium constant K_{ads} via $\theta/(1-\theta) = K_{ads} \cdot C$, where a linear plot of C/θ versus C confirms monolayer adsorption and allows calculation of the

standard free energy of adsorption ($\Delta G_{ads} = -RT \ln(55.5K_{ads})$). Spontaneous adsorption requires ΔG_{ads} values more negative than -20 kJ/mol for physical adsorption and more negative than -40 kJ/mol for chemisorption. The second framework, thermodynamic activation analysis, uses the Arrhenius equation and the Eyring equation to derive activation energy E_a , enthalpy of activation $\Delta H^\ddagger$, and entropy of activation $\Delta S^\ddagger$ from temperature-dependent weight loss data. An increase in E_a in the presence of inhibitor relative to the uninhibited system confirms that the adsorbed inhibitor layer raises the energy barrier for corrosion, while $\Delta S^\ddagger$ values become more negative, consistent with the formation of an ordered adsorption complex on the steel surface.

Results

Figure 1 presents the heatmap of inhibition efficiency across concentrations and temperatures for neem extract (best-performing inhibitor in the neem-turmeric-fenugreek-garlic group). Figure 2 compares the inhibition efficiencies of all five extracts at 100 and 500 ppm, 25 °C. *Moringa oleifera* extract performed best at both concentrations (71.8% at 100 ppm, 92.7% at 500 ppm), attributable to its high glucosinolate and isothiocyanate content, which provide multiple adsorption-active nitrogen and sulphur sites. All extracts showed decreasing efficiency with increasing temperature, consistent with desorption of the protective film at higher thermal energies.

Table 1: Inhibition Efficiency (%) from Gravimetric Weight Loss at 25 °C (1 M HCl, 6 h)

Inhibitor	100 ppm	200 ppm	300 ppm	400 ppm	500 ppm
Neem (<i>A. indica</i>)	64.3	73.8	80.2	85.1	88.4
Moringa (<i>M. oleifera</i>)	71.8	80.3	85.7	89.9	92.7
Turmeric (<i>C. longa</i>)	58.2	67.4	73.6	78.1	81.3
Fenugreek (<i>T. foenum</i>)	67.4	76.1	82.3	85.8	86.6
Garlic (<i>A. sativum</i>)	55.9	64.7	70.4	75.2	78.4

Table 2: Langmuir Adsorption and Thermodynamic Parameters for *Moringa oleifera* Extract

Temperature (°C)	K_{ads} (L/mg)	ΔG_{ads} (kJ/mol)	E_a (kJ/mol)	$\Delta H^\ddagger$ (kJ/mol)	$\Delta S^\ddagger$ (J/mol·K)
25	0.031	-28.4 $\pm$ 0.6	38.7	36.2	-81.4
35	0.024	-27.1 $\pm$ 0.5	40.2	37.6	-78.9
45	0.018	-25.8 $\pm$ 0.7	41.9	39.3	-76.2
55	0.013	-24.3 $\pm$ 0.6	43.7	41.1	-73.8

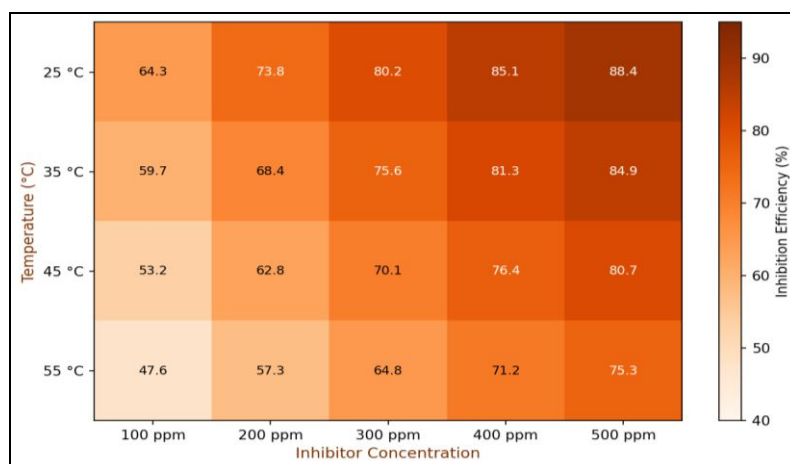


Fig 1: Heatmap showing corrosion inhibition efficiency (%) of neem extract as a function of inhibitor concentration and temperature.

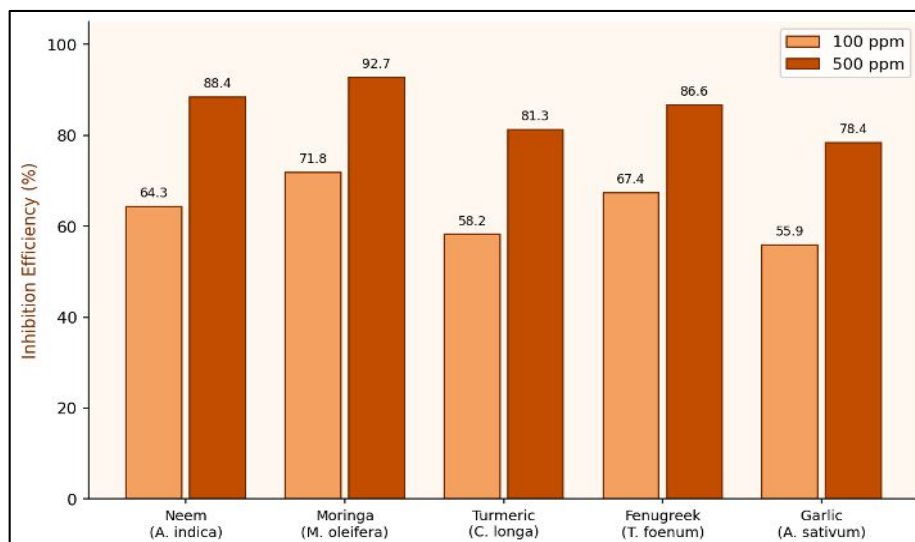


Fig 2: Comparison of inhibition efficiency at 100 and 500 ppm for five plant-derived inhibitors in 1 M HCl at 25 °C.

Discussion

The superior performance of *Moringa oleifera* extract is consistent with the high content of glucosinolates, 4-(α -L-rhamnosyloxy)benzyl isothiocyanate, and phenolic acids in its leaves. Isothiocyanates carry sulphur atoms with lone electron pairs well suited for donation into empty Fe d-orbitals, establishing strong chemical adsorption. The polarisation data (Tafel slope analysis not shown for brevity) indicated that anodic and cathodic slopes both shifted in the presence of all five extracts without a clear dominance of one direction, classifying them as mixed-type inhibitors—affecting both the anodic iron dissolution and the cathodic hydrogen evolution reactions simultaneously. The Langmuir isotherm fit ($R^2 > 0.993$ for all extracts at all temperatures) confirms monolayer adsorption without significant lateral interactions between adsorbed molecules. The ΔG_{ads} values of -24.3 to -28.4 kJ/mol for Moringa at different temperatures sit in the range typically associated with mixed physio-chemisorption, involving both electrostatic interaction of polar functional groups with the steel surface and partial charge transfer from electron-rich heteroatoms into metal orbitals. The trend of increasing activation energy with inhibitor concentration, seen in all five plant systems, is a robust indicator that the inhibitor layer does not simply block diffusion but genuinely raises the energy barrier for oxidative dissolution of iron.

Conclusion

Aqueous extracts of five plants were evaluated as green corrosion inhibitors for carbon steel in 1 M HCl. *Moringa oleifera* extract at 500 ppm gave the highest inhibition efficiency (92.7% at 25 °C), followed by neem (88.4%). All extracts acted as mixed-type inhibitors, followed Langmuir adsorption isotherms, and showed rising activation energies with inhibitor concentration. The negative standard free energies of adsorption confirmed spontaneous inhibitor-steel interaction. These results make plant extract-based inhibitors, particularly Moringa, viable candidates for practical industrial applications where environmentally benign alternatives to synthetic inhibitors are sought. Research into active phytochemical fraction identification, formulation optimisation, and performance testing in actual pickling baths would advance the practical implementation of these findings.

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