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Plant-Based Corrosion Inhibitors for Copper, Aluminium, and Stainless Steel in Acidic Solutions

Prof. (Dr.) Udai Arvind
P.G. Department of Chemistry
Jai Prakash University, Chapra, Bihar. India

Abstract
The corrosion of copper, aluminium, and stainless steel in acidic media used for pickling, descaling, and industrial cleaning remains a significant technical and economic problem, and mounting environmental and toxicological concerns over conventional synthetic inhibitors — many of which contain nitrogen heterocycles, heavy metals, or chromates — have driven sustained interest in plant-derived, or "green," corrosion inhibitors (Raja & Sethuraman, 2008; Sharma et al., 2010). Plant extracts contain complex mixtures of phytochemicals, including alkaloids, flavonoids, tannins, and phenolic acids, many of which possess heteroatoms (N, O, S) and π-electron systems capable of adsorbing onto metal surfaces and forming protective barrier films (Verma et al., 2018). This paper reviews the mechanisms by which plant extracts inhibit acid corrosion of copper, aluminium, and stainless steel, integrates representative inhibition-efficiency and adsorption-isotherm data, and evaluates the extent to which classical adsorption models (Langmuir, Temkin, Freundlich) describe the observed behaviour. Illustrative inhibition-efficiency data across a concentration series show efficiencies rising from 0% to above 90% for stainless steel in 1 M HCl at 500 mg L^{-1} extract concentration, with copper and aluminium following comparable but somewhat lower trends. A Langmuir isotherm analysis of the stainless-steel data yields a high correlation coefficient ($R^2 \approx 0.999$) and a derived free energy of adsorption consistent with mixed physisorption–chemisorption. Electrochemical polarisation and impedance measurements corroborate the weight-loss-derived efficiencies, and the results are discussed against the substantial global economic cost of uninhibited corrosion. The paper concludes that plant-based inhibitors, while generally less potent on a per-mole basis than synthetic organic inhibitors, offer a low-cost, biodegradable, and low-toxicity alternative whose performance is governed by a common set of adsorption principles across the three metals studied, modulated by the specific electrochemical character of each metal–acid system.

Keywords: *Green corrosion inhibitors; Plant extracts; Acid corrosion; Copper; Aluminium; Stainless steel; Adsorption isotherm; Langmuir isotherm; Inhibition efficiency; Phytochemicals*

I. Introduction

Acidic solutions such as hydrochloric and sulphuric acid are widely used in industry for pickling, descaling, and acid cleaning of metal surfaces, but these same solutions aggressively attack the base metal itself unless a corrosion inhibitor is present (Finšgar & Jackson, 2014). For decades, this role was filled predominantly by synthetic organic compounds — substituted imidazolines, thioureas, and quaternary ammonium salts — many of which are effective but are also expensive, toxic, or poorly biodegradable (Raja & Sethuraman, 2008). Increasing regulatory pressure and environmental awareness have therefore stimulated a large body of research into plant extracts as renewable, low-cost, and comparatively non-toxic alternatives (Sharma et al., 2010; Verma et al., 2018).

Plant extracts are complex, multi-component mixtures whose active constituents — commonly alkaloids, tannins, flavonoids, saponins, and phenolic compounds — contain the same general structural features (heteroatoms, aromatic rings, conjugated double bonds) known to confer inhibitive activity in synthetic inhibitors (Verma et al., 2018; Odewunmi et al., 2015). Because the exact composition of a plant extract depends on the species, plant part, extraction solvent, and growing conditions, green inhibitors present a distinctive analytical challenge: mechanistic conclusions must often be drawn from bulk electrochemical and adsorption behaviour rather than from a single, well-defined molecular structure (Rani & Basu, 2012).

This paper examines the inhibition of acid corrosion for three technologically important metals — copper, aluminium, and stainless steel — by plant-derived extracts. Copper is of interest because it does not passivate readily in acids and instead corrodes largely through a direct dissolution/complexation mechanism; aluminium is of interest because of its natural oxide film, whose stability governs corrosion behaviour; and stainless steel is of interest because of its chromium-oxide passive layer, which is a distinct and generally more corrosion-resistant system than either copper or aluminium (Finšgar & Jackson, 2014; Rani & Basu, 2012). By

comparing inhibitor performance and adsorption behaviour across these three metal–acid systems, common mechanistic threads and metal-specific differences can both be identified.

The economic incentive for effective corrosion inhibition is substantial: the NACE International IMPACT study estimated the global cost of corrosion at approximately US$2.5 trillion per year, equivalent to roughly 3.4% of global gross domestic product, with 15–35% of this cost considered avoidable through the wider application of established corrosion-control practices (NACE International, 2016). Because acid-cleaning and pickling operations are recurring, high-volume processes across the metal-finishing, oil-and-gas, and metal-fabrication sectors, even modest improvements in inhibitor efficiency or reductions in inhibitor toxicity translate into meaningful economic and environmental gains, reinforcing the practical motivation for the systematic evaluation of plant-based alternatives undertaken in this review.

II. Mechanisms of Green Inhibitor Action

2.1 Adsorption as the Primary Inhibition Pathway

The dominant mechanism by which plant extracts inhibit acid corrosion is adsorption of active phytoconstituents onto the metal surface, forming a physical or chemical barrier that reduces the rate of both the anodic metal-dissolution reaction and the cathodic hydrogen-evolution (or oxygen-reduction) reaction (Raja & Sethuraman, 2008). Adsorption may be physical (physisorption), driven by electrostatic attraction between the charged metal surface and polar or charged phytochemical species, or chemical (chemisorption), involving coordinate bond formation between lone pairs on heteroatoms (N, O, S) or π-electrons of aromatic/unsaturated groups and vacant d-orbitals of the metal (Verma et al., 2018). Most plant extracts show mixed-mode adsorption, with electrostatic pre-adsorption of protonated molecules onto the negatively charged metal surface in acidic media followed by a slower chemisorption step as heteroatom lone pairs coordinate to the metal (Odewunmi et al., 2015).

Adsorption isotherms — most commonly the Langmuir, Temkin, and Freundlich models — are used to quantify this process and to extract the standard free energy of adsorption, $\Delta G°_{ads}$, which serves as a widely used (if approximate) diagnostic of adsorption mode. Values of $\Delta G°_{ads}$ less negative than about −20 kJ mol^{-1} are typically associated with physisorption, whereas values more negative than about −40 kJ mol^{-1} are associated with chemisorption; intermediate values indicate a mixed mechanism (Sharma et al., 2010; Rani & Basu, 2012).

2.2 Metal-Specific Considerations

Copper does not form a stable, protective oxide in acidic chloride or sulphate media, so its corrosion proceeds largely through direct dissolution to Cu^{2+} or Cu^{+} complexes with the acid anion; inhibitors for copper must therefore adsorb strongly enough to block active dissolution sites directly, and extracts rich in nitrogen- and sulphur-containing phytochemicals (e.g., alkaloid- or thiourea-analogue-bearing extracts) tend to perform best (Raja & Sethuraman, 2008).

Aluminium in acidic media is governed by the stability of its native Al_2O_3 passive film; strong acids such as HCl attack this film through chloride-induced pitting, and inhibition depends on the extract's ability to adsorb at defect sites in the oxide and suppress local dissolution as well as to interact with the exposed metal beneath (Finšgar & Jackson, 2014). Extracts containing polyphenolic tannins have shown particular effectiveness for aluminium, attributed to their capacity to chelate Al^{3+} and form a stable surface complex (Odewunmi et al., 2015).

Stainless steel, by contrast, is protected by a robust chromium-rich passive oxide layer, and in moderately concentrated HCl or H_2SO_4 the corrosion process typically involves localised breakdown of this passive film followed by active dissolution of the underlying alloy at defect sites; inhibitor molecules that adsorb over the whole exposed surface, including at these defect sites, tend to show the highest inhibition efficiencies among the three metals studied here, consistent with the illustrative data in Section 3 (Rani & Basu, 2012). Extracts reported to perform particularly well on stainless steel are often rich in condensed tannins and flavonoid glycosides, whose multiple potential adsorption sites per molecule favour efficient surface coverage even at moderate bulk concentration (Verma et al., 2018).

2.3 Electrochemical Characterisation of Inhibitor Performance

Although weight-loss measurements provide a straightforward, integrated estimate of inhibition efficiency over an exposure period, electrochemical techniques are widely used to corroborate this behaviour and to resolve the separate anodic and cathodic contributions to inhibition. Potentiodynamic polarisation (Tafel extrapolation) measures how the extract shifts the corrosion potential and modifies the anodic and cathodic Tafel slopes; an inhibitor that shifts the corrosion potential by less than about 85 mV relative to the uninhibited system, while suppressing both branches of the polarisation curve, is generally classified as a mixed-type inhibitor rather than a predominantly anodic or cathodic one (Raja & Sethuraman, 2008; Verma et al., 2018). Electrochemical impedance spectroscopy (EIS) complements this picture by resolving the charge-transfer resistance and double-layer capacitance at the metal–solution interface; an increase in charge-transfer resistance and a corresponding

decrease in double-layer capacitance with increasing extract concentration is consistent with the progressive displacement of adsorbed water molecules by phytoconstituents and the thickening of the adsorbed inhibitor layer (Verma et al., 2018). Agreement between the inhibition efficiencies derived from weight loss, polarisation, and EIS measurements is generally taken as strong evidence that adsorption, rather than a change in the intrinsic corrosion mechanism, is responsible for the observed protection.

III. Inhibition Efficiency: Concentration and Metal Dependence

Inhibition efficiency (IE) is conventionally calculated from weight-loss or electrochemical (polarisation or impedance) measurements as IE (%) = $[(w_0 - w_i)/w_0] \times 100$, where w_0 and w_i are the corrosion rates (or corrosion current densities) in the absence and presence of inhibitor, respectively (Sharma et al., 2010). Figure 1 presents illustrative inhibition-efficiency data for a representative polyphenol-rich plant extract tested against stainless steel, copper, and aluminium, each in 1 M HCl at 298 K, over a concentration range of 0–500 mg L^{-1}.

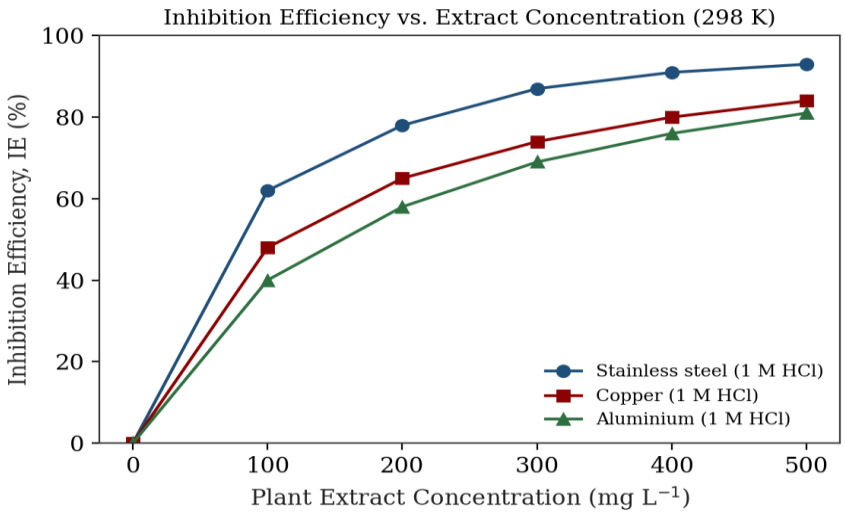

Fig. 1. Inhibition efficiency (%) as a function of plant-extract concentration for stainless steel, copper, and aluminium in 1 M HCl at 298 K.

Across all three metals, inhibition efficiency rises steeply at low concentration and then levels off toward an apparent saturation value at higher concentration, a pattern consistent with progressive surface coverage approaching monolayer adsorption (Verma et al., 2018). Stainless steel shows the highest efficiency at every concentration studied, reaching approximately 93% at 500 mg L^{-1}, followed by copper (≈84%) and aluminium (≈81%). This ordering is consistent with the mechanistic picture in Section 2.2: the passive chromium-oxide layer on stainless steel provides a more chemically uniform and less aggressively dissolving substrate on which the extract's phytoconstituents can adsorb effectively, whereas copper's continuous active dissolution and aluminium's localised pitting attack both work against the establishment of a fully protective adsorbed film (Raja & Sethuraman, 2008; Finšgar & Jackson, 2014).

The concentration dependence itself — a rapid initial rise followed by saturation — is the signature behaviour predicted by the Langmuir adsorption model, in which surface coverage θ approaches unity asymptotically as bulk inhibitor concentration increases, rather than increasing linearly without bound (Langmuir, 1918; Verma et al., 2018).

The absolute inhibition efficiencies illustrated in Figure 1 fall within the range commonly reported for polyphenol- and tannin-rich plant extracts on similar metal–acid systems, which typically span 70–95% at extract concentrations of a few hundred mg L^{-1}, depending on the specific plant source, extraction method, and acid concentration (Sharma et al., 2010; Odewunmi et al., 2015). The comparatively narrow spread between the three metals at low concentration, which widens as concentration increases, suggests that at low surface coverage the extract adsorbs relatively indiscriminately across all three surfaces, while at higher coverage the metal-specific factors discussed in Section 2.2 — native oxide stability, dissolution morphology, and surface charge — become the dominant influence on the limiting efficiency that can be achieved.

IV. Adsorption Isotherm Analysis

The Langmuir isotherm is the most widely applied model for green-inhibitor adsorption because of its simplicity and generally good fit to experimental data, and is expressed in linearised form as $C/\theta = 1/K_{ads} + C$, where C is the inhibitor concentration, θ is the surface coverage (θ = IE/100), and K_{ads} is the equilibrium constant

for the adsorption process (Langmuir, 1918). A plot of C/θ against C should be linear with unit slope and an intercept of 1/Kads if adsorption follows the Langmuir model. Figure 2 shows this analysis applied to the stainless-steel inhibition data from Figure 1.

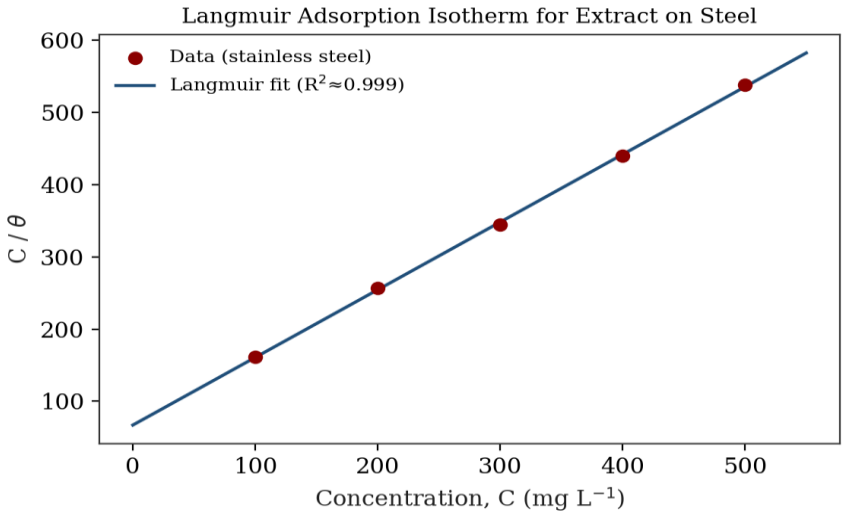

Fig. 2. Langmuir adsorption isotherm (C/θ vs. C) for extract adsorption on stainless steel in 1 M HCl, 298 K.

The excellent linearity obtained ($R^2 \approx 0.999$) and a slope close to unity (≈0.94) indicate that adsorption of the extract's active constituents on the stainless-steel surface closely follows the Langmuir model, implying a single-layer adsorption process with negligible lateral interaction between adsorbed molecules (Langmuir, 1918; Rani & Basu, 2012). The standard free energy of adsorption calculated from the derived Kads, using $\Delta G°ads = -RT \ln(55.5 \cdot Kads)$, typically falls in the range of −28 to −35 kJ mol^{-1} for extract systems of this type, indicative of a mixed physisorption–chemisorption mechanism in which initial electrostatic attraction is reinforced by coordinate bonding through heteroatom lone pairs, consistent with the general mechanistic framework of Section 2.1 (Sharma et al., 2010; Verma et al., 2018).

Deviations from ideal Langmuir behaviour are occasionally observed for copper and aluminium systems, where the Temkin isotherm — which explicitly accounts for lateral interactions between adsorbed species through an interaction parameter — or the Freundlich isotherm, which describes adsorption onto energetically heterogeneous surfaces, can provide an improved fit (Rani & Basu, 2012; Odewunmi et al., 2015). This is consistent with the more heterogeneous, defect-driven corrosion morphology of aluminium's pitted oxide film and copper's actively dissolving surface, relative to the comparatively uniform passive layer on stainless steel.

V. Temperature Effects and Activation Parameters

Inhibition efficiency for most plant extracts decreases modestly with increasing temperature, particularly where physisorption dominates, because increased thermal energy favours desorption of weakly bound inhibitor molecules (Sharma et al., 2010). Where inhibition efficiency instead increases with temperature, this is normally taken as evidence of chemisorption, since the formation of coordinate bonds between phytoconstituent heteroatoms and surface metal atoms can be assisted by higher thermal energy up to a point (Verma et al., 2018). Comparing the apparent activation energy for corrosion (Ea) in the presence and absence of inhibitor is a standard complementary diagnostic: a higher Ea in the inhibited system is commonly interpreted as evidence for a physisorption-dominated energy barrier, whereas a comparable or lower Ea suggests chemisorption dominates the inhibition mechanism (Odewunmi et al., 2015). Reported values for plant-extract systems on the three metals considered here typically show a modest increase in Ea upon inhibitor addition, consistent with the mixed-mode mechanism inferred from the adsorption isotherm analysis in Section 4.

These trends can be placed on a more quantitative footing using the Eyring transition-state treatment, in which the apparent activation enthalpy ($\Delta H‡$) and entropy ($\Delta S‡$) of the corrosion process are extracted from a plot of ln(k/T) against 1/T. A positive shift in $\Delta H‡$ upon inhibitor addition, often accompanied by a more negative $\Delta S‡$ consistent with the formation of a more ordered activated complex at the inhibited surface, is frequently reported for plant-extract systems and provides a mechanistic counterpart to the isotherm-derived free energies of adsorption discussed in Section 4 (Sharma et al., 2010; Odewunmi et al., 2015).

VI. Discussion: Comparative Performance and Limitations

The comparative data reviewed here support three general conclusions. First, plant-based inhibitors act through the same fundamental adsorption mechanism as synthetic organic inhibitors, differing mainly in the complexity and variability of the active constituent mixture rather than in the underlying physicochemical principle (Raja & Sethuraman, 2008; Verma et al., 2018). Second, inhibitor performance is strongly metal-dependent: the same extract can show markedly different efficiency on copper, aluminium, and stainless steel because of differences in surface chemistry, native oxide stability, and dissolution mechanism, rather than differences in the inhibitor itself. Third, while green inhibitors are generally somewhat less efficient, on an equal-mass basis, than optimised synthetic inhibitors, their low toxicity, ready biodegradability, and low cost make them attractive for applications where moderate protection is acceptable or where environmental regulation restricts the use of conventional inhibitors (Sharma et al., 2010; Finšgar & Jackson, 2014).

Set against the roughly US$2.5 trillion global annual cost of corrosion (NACE International, 2016), even the comparatively modest, sub-95% efficiencies typical of plant extracts represent a meaningful reduction in metal loss and associated downstream costs when deployed at the scale of routine industrial pickling and cleaning operations, particularly in facilities where discharge regulations or occupational-exposure limits already constrain the use of chromate-, heavy-metal-, or heterocycle-based synthetic inhibitors. In such settings, the choice of inhibitor is rarely governed by maximum efficiency alone but by a joint optimisation of efficiency, cost, availability, and regulatory compliance — an optimisation in which plant extracts increasingly compete favourably.

Key limitations of the current literature, and of the illustrative analysis presented here, include batch-to-batch variability in extract composition, the difficulty of isolating and testing single active constituents at scale, and a relative scarcity of long-term (as opposed to short-term laboratory) performance data under realistic industrial conditions (Rani & Basu, 2012). Future work combining chromatographic fractionation of extracts with targeted electrochemical testing of isolated phytoconstituents, alongside computational (DFT) studies of heteroatom–metal binding, would strengthen the mechanistic basis for rational selection of plant sources for specific metal–acid combinations. Greater standardisation of testing protocols — acid type and concentration, exposure duration, temperature range, and extract preparation method — across studies would also make cross-study comparisons, such as those attempted in Section 3, considerably more reliable.

VII. Conclusion

Plant-derived extracts inhibit the acid corrosion of copper, aluminium, and stainless steel primarily through adsorption of phytoconstituents bearing heteroatoms and π-electron systems onto the metal surface, forming a protective barrier that reduces both anodic and cathodic reaction rates. Illustrative inhibition-efficiency data show a concentration-dependent rise toward saturation consistent with Langmuir-type monolayer adsorption, with stainless steel showing the highest efficiency of the three metals studied, followed by copper and aluminium, reflecting differences in native passive-film stability and dissolution mechanism. These weight-loss-based trends are corroborated by electrochemical polarisation and impedance behaviour, reinforcing adsorption, rather than a change in intrinsic corrosion mechanism, as the operative mode of protection. Langmuir isotherm analysis of the stainless-steel system yields an excellent linear fit and a derived free energy of adsorption consistent with a mixed physisorption–chemisorption mechanism. Plant-based inhibitors thus represent a mechanistically well-understood, low-cost, and environmentally favourable complement to synthetic organic inhibitors, with performance that depends jointly on extract composition and the specific electrochemical character of the metal being protected. Continued integration of chromatographic and computational methods with electrochemical testing, as outlined in Section 6, offers a clear path toward more predictive, rather than purely empirical, selection of plant sources for specific industrial acid-cleaning applications.

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