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## Natural dyes as eco-friendly corrosion inhibitors: A sustainable approach to metal protection

### ABSTRACT

Natural dyes, historically celebrated for their capacity to enhance the visual appeal of textiles, foods, and artefacts, are now receiving increasing recognition for their functional applications, most significantly as eco-friendly corrosion inhibitors. Corrosion within aggressive industrial settings necessitates the formulation of an environmentally compatible inhibitor to replace conventional toxic systems. Natural dyes, extracted from botanical origins, are emerging as a sustainable alternative due to their abundant phytochemical constituents and biodegradability. Their efficacy in inhibition is primarily influenced by the presence of heteroatoms,  $\pi$ - electron density and molecular planarity, which enhance adsorption and the subsequent formation of protective films on metallic surfaces. Showing different adsorption behaviour like chemisorption, physisorption or mixed type inhibition behaviour. Comparative review reveals that dyes derived from tannins, flavonoids and quinones exhibit superior efficacy, achieving their highest stability even though their efficiency is based on medium, temperature and substrate employed. A few obstacles, like limited mechanistic validation and a lack of standardization restrict their practical application. Hence, future research must emphasize on structure activity correlations, advanced surface analysis and hybrid or modified systems to validate the role of natural dyes as a reliable alternative for toxic inhibitors.

**Keywords:** Natural dye, corrosion Inhibitor, metal protection, sustainable, surface adsorption

### 1. INTRODUCTION

Corrosion is an inherent and progressive phenomenon distinguished by the degradation of metals due to chemical or electrochemical interactions with their surrounding environment. This process typically results in the formation of more stable compounds, such as oxides, hydroxides, or sulfide. The deterioration caused by corrosion significantly compromises the mechanical integrity, safety, and functionality of metallic components, thereby reducing their operational lifespan [1]. It may manifest in various forms, including uniform corrosion, pitting corrosion, galvanic corrosion, crevice corrosion, and intergranular corrosion, often occurring simultaneously and leading to unexpected and catastrophic failures in critical systems.

The consequences of corrosion transcend simple technical issues, incorporating profound economic and ecological implications [2]. As evidenced by a pivotal study conducted by NACE International, the global financial burden associated with corrosion exceeds US \$2.5 trillion annually, constituting roughly 3.4% of the worldwide Gross Domestic Product (GDP) [3]. Moreover, it is anticipated that between 15% and 35% of these economic detriments could be alleviated through the implementation of established methodologies such as protective coatings, cathodic protection, and corrosion inhibitors [4]. Industries such as oil and gas, maritime, construction, and automotive are particularly vulnerable, facing considerable expenses related to maintenance, equipment malfunctions, environmental harm, and even human casualties. Among the various techniques available for corrosion mitigation, corrosion inhibitors have emerged as a widely adopted and cost-effective solution, particularly in scenarios involving worst-case [5]. These inhibitors operate by adhering to the metallic surface, thereby creating a protective barrier that hinders the engagement of corrosive ions, such as hydrogen

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and chloride, with the underlying metal substrate. Historically, synthetic inhibitors such as chromates, nitrites, phosphates, and amines have been utilized due to their superior effectiveness. Nevertheless, these substances are increasingly subjected to scrutiny for their toxic, carcinogenic, and non-biodegradable characteristics, which present significant threats to both human health and ecological well-being [6]. Synthetic dyes have also been evaluated for their potential in corrosion inhibition; however, they similarly exhibit comparable environmental concerns, including bioaccumulation and the generation of hazardous byproducts. In consideration of these constraints, the scientific community has shifted its focus towards natural and sustainable alternatives. Among these alternatives, natural dyes—historically utilized in textiles, food, and cosmetics—are emerging as viable eco-friendly corrosion inhibitors [7]. Derived from a variety of sources including plants, fruits, vegetables, flowers, insects, and minerals, natural dyes are characterized by their biodegradability, non-toxicity, and renewable origins. More significantly, their molecular compositions are inherently abundant in electron-donating functional groups such as hydroxyl ( $-OH$ ), carbonyl ( $C=O$ ), carboxylic ( $-COOH$ ), amino ( $-NH_2$ ), and methoxy ( $-OCH_3$ ), etc. as well as conjugated aromatic systems. These attributes facilitate robust interactions with metal surfaces through both physisorption (mediated by electrostatic and van der Waals forces) and chemisorption (through covalent or coordinate bonding), resulting in a stable, adherent protective layer that obstructs corrosive species and mitigates both anodic and cathodic reactions. A multitude of natural dyes function as mixed-type inhibitors, and their adsorption behaviour typically aligns with established isotherms such as Langmuir or Temkin, suggesting effective monolayer surface coverage [1,8,9]. A variety of studies have documented the successful application of natural dyes in inhibiting corrosion across diverse metals, including mild steel, aluminium, and copper. For instance, lawsone from *Lawsonia inermis* (henna), curcumin from *Curcuma longa*, and tannic acid from oak bark have exhibited high inhibition efficiencies in acidic and saline conditions. Other natural dyes, such as crocin and kermes, have demonstrated comparable potential due to their capacity to adsorb onto metal surfaces via polar groups and  $\pi$ -electron interactions. These inhibitors not only rival the efficacy of synthetic counterparts but also present advantages in terms of safety, biodegradability, and cost-effectiveness [10,11].

In addition to their technical advantages, the utilization of natural dyes for corrosion inhibition is in alignment with numerous United Nations Sustainable Development Goals (SDGs), thereby

underscoring their significance within global sustainability efforts. For example, SDG 12 (Responsible Consumption and Production) is fulfilled by the employment of renewable and biodegradable raw materials. SDG 13 (Climate Action) gains from the diminished carbon footprint and reduced chemical waste associated with environmentally friendly corrosion inhibitors. SDG 3 (Good Health and Well-Being) is enhanced by lowering exposure to hazardous substances, while SDG 6 (Clean Water and Sanitation) and SDG 9 (Industry, Innovation, and Infrastructure) are advanced through diminished pollution and the promotion of eco-friendly industrial technologies. India, characterized by its abundant biodiversity and rich cultural traditions involving plant-based dyes, is home to over 500 species of dye-yielding plants, providing a substantial resource for the development of sustainable corrosion control solutions. As regulatory standards tighten and industries pursue greener alternatives, natural dyes emerge as a scientifically sound, industrially scalable, and ecologically responsible option. This academic review article seeks to methodically examine the effectiveness of natural dyes as corrosion inhibitors through a comprehensive analysis of their classification, chemical characteristics, adsorption mechanisms, and relative efficacy in various corrosive settings. By synthesizing traditional knowledge with modern materials science, natural dyes could serve as a pivotal element in fostering sustainable approaches for corrosion prevention in future industrial applications [12].

## 2. TRADITIONAL CORROSION INHIBITOR-LIMITATIONS AND ENVIRONMENTAL CONCERNS

Traditional corrosion inhibitors have been extensively employed across a wide array of industrial domains, including but not limited to the oil and gas sector, power generation, water treatment, marine transportation, and various manufacturing processes. Within the oil and gas sector, inhibitors such as ammonium bisulfite and imidazolines are prevalently utilized to mitigate corrosion in pipelines, drilling fluids, and refinery apparatus, predominantly by neutralizing acidic gases such as hydrogen sulfide ( $H_2S$ ) and carbon dioxide ( $CO_2$ ). In power generation facilities and cooling water systems, nitrite-phosphonate combinations, molybdate complexes, and zinc phosphates are routinely implemented to safeguard steel and copper alloys against corrosion under conditions of elevated temperature and high fluid velocity. Chromates, including sodium chromate and dichromate, have traditionally been employed in boiler systems, condensers, and heat

exchangers owing to their remarkable efficacy in forming passive films on metallic substrates. Phosphate-based inhibitors are frequently utilized in municipal water treatment facilities and fire protection systems, while silicates and borates are incorporated within closed-loop cooling systems and antifreeze formulations. In maritime applications, particularly within ballast tanks and seawater-cooled engines, zinc salts and organic amines are applied to mitigate chloride-induced corrosion [13–15].

Despite their extensive application, these inhibitors are linked to considerable environmental and public health challenges. Chromates, notwithstanding their demonstrated high effectiveness, are recognised as carcinogenic and non-biodegradable substances, thus presenting risks during both their utilization and disposal phases. Nitrites possess the potential to generate carcinogenic nitrosamines, particularly under acidic conditions or elevated thermal environments. Phosphates are associated with the occurrence of eutrophication in aquatic ecosystems, resulting in detrimental algal blooms and oxygen depletion. Organic compounds, such as amines, thiols, and quaternary ammonium salts, may decompose into volatile organic compounds (VOCs), which present occupational health hazards, including respiratory irritation and skin sensitization. Moreover, a significant fraction of these inhibitors is non-biodegradable and demonstrate a tendency to accumulate in the environment, thereby necessitating sophisticated and costly effluent treatment processes to adhere to environmental discharge regulations. Their effectiveness is frequently affected by system parameters, including temperature, pH, flow rate, and chloride ion concentration, underscoring the necessity for meticulous monitoring. For example, molybdate-based systems, although serving as safer alternatives to chromates, entail substantial costs and require stringent dosage regulation to ensure sustained effectiveness. With the escalation of regulatory constraints and a heightened awareness of environmental risks, there exists an imperative necessity to shift towards eco-friendly, non-toxic, and biodegradable alternatives [16–18]. Natural corrosion inhibitors sourced from botanical materials, such as dyes and extracts, are garnering considerable attention for their efficacy in providing corrosion resistance while alleviating the environmental and health hazards associated with traditional synthetic formulations. These natural substances not only offer a safer and more sustainable solution but also resonate with the tenets of green chemistry and cleaner industrial methodologies.

Green corrosion inhibitors are designed to achieve performance levels that are comparable to those of conventional inhibitors while concurrently

reducing the detrimental impacts on human health and the environment. This paradigm shift has precipitated a marked increase in interest regarding plant-based and bio-derived inhibitors, including but not limited to plant extracts, essential oils, alkaloids, and particularly, natural dyes. Natural dyes represent a particularly promising category of environmentally friendly inhibitors. Sourced from renewable plant materials such as leaves, roots, bark, flowers, and fruits, these dyes are characterized by the presence of aromatic systems and functional groups—including phenols, carboxylic acids, flavonoids, and quinones—that augment their adsorption onto metallic surfaces. The aforementioned structural attributes enable natural dyes to operate as highly effective mixed-type inhibitors, engaging through both anodic and cathodic mechanisms. The utilisation of such biogenic compounds underpins the worldwide initiative aimed at promoting sustainable practices in industrial chemistry, thereby reducing dependence on petrochemical derivatives while capitalising on abundant natural resources and agricultural byproducts [19,20]. Recent investigations have demonstrated that compounds such as curcumin, quercetin, and lawsone exhibit inhibition efficiencies exceeding 90% in acidic environments, which is on par with their synthetic equivalents.

### 3. NATURAL DYES AS POTENTIAL CORROSION INHIBITORS- EMERGING FIELD

Dyes represent chromatic compounds that are capable of chemically or physically bonding to a substrate, typically through the establishment of connections with fibres, polymers, or metals. They are categorically divided into two classifications: synthetic dyes, which are produced through chemical synthesis utilizing petroleum-derived precursors, and natural dyes, which are derived from organic sources such as flora, fauna, minerals, and microorganisms. Although synthetic dyes predominate in commercial uses due to their cost-effectiveness and reproducibility, they frequently contain hazardous aromatic amines and heavy metals, and are characterized by their non-biodegradability, thereby raising significant environmental concerns. Conversely, natural dyes are fundamentally eco-friendly, renewable, and demonstrate an extensive array of functional properties, encompassing antioxidant, antimicrobial, and corrosion-inhibiting characteristics [21].

#### *Chemical composition of natural dyes*

Natural dyes are constituted of intricate organic molecules that frequently belong to a variety of phytochemical classifications, as shown in Figure 1, including flavonoids [22], anthocyanins [23], carotenoids [24], quinines [25], tannins [26], and

alkaloids [27]. These substances are abundant in functional groups such as hydroxyl ( $-OH$ ), carbonyl ( $=O$ ), amine ( $-NH_2$ ), carboxyl ( $-COOH$ ), and methoxy ( $-OCH_3$ ), which promote robust

adsorption on metallic surfaces through either physical (physisorption) or chemical (chemisorption) interactions.

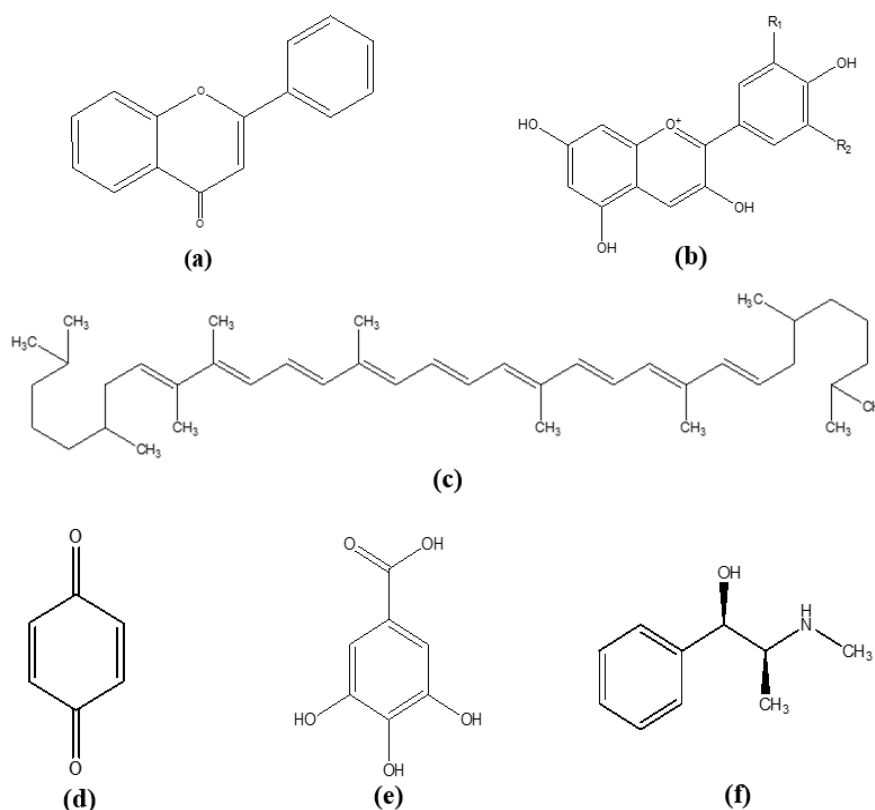


Figure 1. Chemical structure of a photochemical present in natural dyes (a)Flavonoids [22], (b)Anthocyanin[23], (c)Carotenoid[24], (d)Quinine [25], (e)Tannin [26] and (f)Alkaloid [27]

**Flavonoids** feature a 15- carbon skeleton with two phenyl rings linked by a heterocyclic pyrone ring, typically with a hydroxyl group. The  $-OH$  groups and  $\pi$ -electrons from aromatic rings chelate metal ions ( $Fe^{2+}$ ) and adsorb via physisorption/chemisorption, forming a hydrophobic barrier that blocks  $HCl/H_2O$  access to the metal surface. Multiple  $-OH$  enhance H-bonding with oxide layers, boosting inhibition efficiency[22]. **Anthocyanins** are flavylium cations ( $C_{15}H_{11}O_5^+$ ) with a positively charged oxonium ring and conjugated glycosides. The cationic centre electrostatically adsorbs onto a negatively charged surface via  $Cl^-$  adsorption, while extensive conjugation delocalizes electrons from parallel adsorption. Forming barrier films blocking anodic/cathodic sites [28, 29]. **Carotenoids** possess a polyene chain (9-11 conjugated double bonds) with  $\beta$ -ionone rings at both ends. Long hydrophobic chains lie flat on metal, creating thick water-repellent films via the Van der Waals force. Conjugated  $\pi$ - system donates electrons to metal d-orbitals, passivating the active site [24, 27]. **Quinones** contain two carbonyl groups ( $C=O$ ) in a

six-membered ring with extended conjugation. Carbonyl oxygen atoms coordinate directly with Fe atoms, while quinone redox activity scavenges radicals and stabilizes passive films, forms chelate complexes, preventing Fe dissolution [28]. **Tannins** are polyphenolic oligomers, multiple  $-OH$  forms polynuclear Fe- tannate complexes via multidentate chelation, creating crosslinked 3D protective films. Exceptional at high  $Cl^-$  due to iron-tannin precipitate sealing micro-defects [26]. **Alkaloids** feature nitrogen heterocycles with lone pair electrons on N. The N atom donates electrons to the metal surface empty d-orbitals forming coordinate bonds, while aromatic rings enable  $\pi$ -interactions and compact monolayer block charge transfer.

Furthermore, numerous natural dye molecules possess  $\pi$ -electron systems, exemplified by conjugated aromatic rings, which facilitate  $\pi$ -d orbital overlap with transition metal surfaces, thereby augmenting their inhibition efficacy. This structural intricacy is not solely responsible for the

vivid hues of these dyes but also for their capacity to function as mixed-type corrosion inhibitors, mitigating both anodic metal dissolution and cathodic hydrogen evolution reactions.

#### *Classification of Natural Dyes*

Natural dyes employed as corrosion inhibitors can be systematically classified according to their chemical composition and phytochemistry, with each category demonstrating distinct functional groups that promote interaction with metallic surfaces. Anthocyanins, which are predominantly located in *Hibiscus sabdariffa*, various berries, and red cabbage, are classified as water-soluble flavonoid pigments characterized by a C6–C3–C6 structural framework. The molecular configurations of these compounds are abundant in hydroxyl and keto functional groups, facilitating effective coordination with metallic ions. This inherent characteristic significantly enhances surface adsorption and effectively mitigates corrosion, as evidenced by research indicating that hibiscus extract conferred 89–92% protection for mild steel immersed in 1 M HCl [30]. Flavonoids, which are found in tea (*Camellia sinensis*), are defined by the presence of two aromatic rings linked by a three-carbon bridge that culminates in a pyran ring. Their phenolic hydroxyl and ketone functional groups promote robust chelation and adsorption through  $\pi$ -electron donation and hydrogen bonding mechanisms [31]. Another influential category comprises the indigoids, which are derived from the *Indigofera tinctoria* plant. Indigo, the principal constituent, is characterized as a bis-indole compound exhibiting extensive conjugation alongside carbonyl functionalities. Its planar conformation facilitates  $\pi$ - $\pi$  stacking interactions with metallic substrates, thereby engendering a uniform and adherent protective layer. Indigo extracts have demonstrated inhibition rates reaching as high as 85% against copper and mild steel in nitric acid environments. Carotenoids, which are sourced from turmeric (*Curcuma longa*), saffron (*Crocus sativus*), and carrot peels, are characterized by elongated conjugated hydrocarbon chains with terminal oxygen-containing moieties. Curcumin [11], a prominent carotenoid present in turmeric, possesses diketone and hydroxyl functionalities that permit robust chemisorptive binding to metallic surfaces. It has exhibited inhibition efficiencies as high as 92% in both acidic and neutral chloride environments. Finally, tannins, which are high-molecular-weight polyphenolic compounds extracted from sources such as oak bark, acacia, and pomegranate peels, exhibit remarkable

inhibition efficacy. Their structural composition includes gallic acid units and sugar residues, which provide numerous phenolic sites for interaction with the metallic substrate. This interaction leads to the formation of dense, adherent films that function as effective barriers against corrosive agents. Tannic acid, in particular, has been shown to inhibit corrosion of mild steel in hydrochloric acid by as much as 95%, a finding corroborated by electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) analyses. Collectively, these classes of dyes underscore the versatility and efficacy of natural compounds in environmentally sustainable corrosion mitigation strategies [32].

#### *Advantages of natural dyes as corrosion inhibitors*

Natural dyes present a multitude of advantages that render them exceptionally appropriate as eco-friendly corrosion inhibitors. Their inherent eco-friendliness and biodegradability allow for natural decomposition without the generation of persistent or toxic byproducts, which is particularly advantageous for applications within environmentally sensitive domains such as marine coatings and potable water systems. The non-toxic and safe characteristics of these dyes—frequently derived from consumable or medicinal flora—significantly mitigate health risks during both their application and disposal, thereby rendering them optimal for utilization in food-processing apparatus, pharmaceutical equipment, and other hygiene-sensitive contexts. From an economic perspective, natural dyes are both cost-effective and readily accessible, frequently extracted from agricultural byproducts like onion peels or pomegranate rinds. This not only diminishes the costs associated with raw materials but also bolsters circular economy frameworks by converting waste into valuable functional substances. Furthermore, these dyes are procured from rapidly renewable biomass, providing a sustainable alternative to petroleum-derived synthetic inhibitors and decreasing reliance on finite fossil fuel resources. Chemically, natural dyes encompass various active functional groups—such as hydroxyl, carboxyl, and amino groups—as well as  $\pi$ -electron systems, which promote robust adsorption onto metallic surfaces, culminating in effective and long-lasting corrosion protection. Moreover, natural dyes demonstrate a high degree of compatibility with other eco-friendly additives, including plant-derived oils and biodegradable polymers, often yielding synergistic effects that further amplify their inhibition efficacy [21].

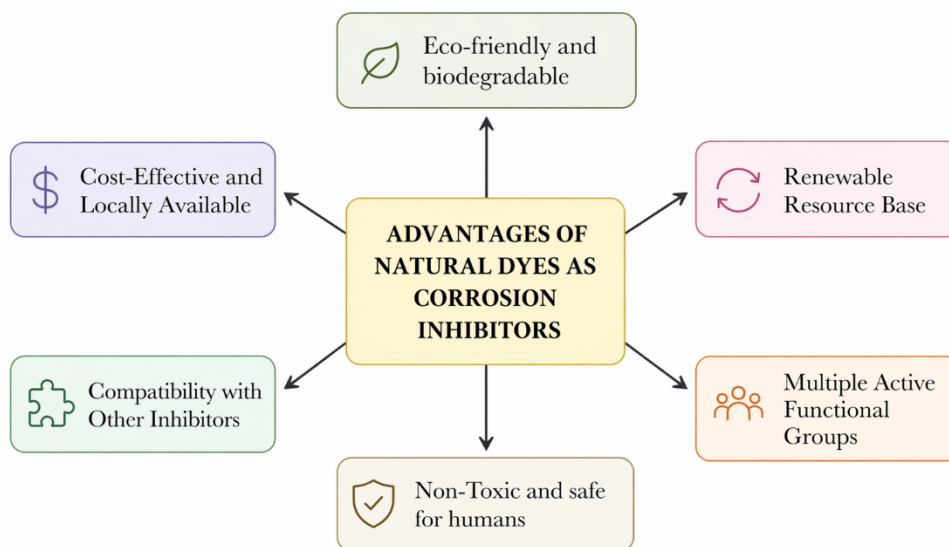


Figure 2. Advantages of natural dyes as corrosion inhibitors [1, 27]

### 3. MECHANISM OF INHIBITION BY NATURAL DYES

Natural dyes serve to mitigate corrosion predominantly by adhering to the metallic substrate and establishing a dense, protective layer that obstructs both anodic and cathodic processes. This adherence is promoted by the existence of electron-donating functional moieties such as hydroxyl ( $-OH$ ), carbonyl ( $C=O$ ), carboxyl ( $-COOH$ ), amino ( $-NH_2$ ), and methoxy ( $-OCH_3$ ), in conjunction with conjugated  $\pi$ -electron frameworks. These functional groups interact with the unoccupied d-orbitals of metallic atoms, thereby facilitating chemisorption via covalent or coordinate bonding mechanisms. Concurrently,  $\pi$ -electron interactions alongside van der Waals forces play a significant role in physisorption, culminating in a dual adsorption mechanism that fortifies film stability and enhances corrosion resistance. The adsorption phenomenon typically adheres to established isotherms such as Langmuir or Temkin, signifying the potential for either monolayer or multilayer deposition on the metallic surface.

In the examination of *Lawsonia inermis* (henna) [10], the bioactive compound lawsone (2-hydroxy-1,4-naphthoquinone) is characterized by the presence of both hydroxyl and carbonyl functional groups that exhibit significant interactions with metal ions, particularly  $Fe^{2+}$ , on the surfaces of mild steel. The inherent quinonoid structure, in conjunction with the aromatic ring, facilitates  $\pi$ -d interactions, thereby enhancing the adsorption efficacy of lawsone and leading to the formation of

a protective corrosion-inhibiting layer that displays resistance against acidic degradation. Empirical studies substantiate that lawsone functions as a mixed-type inhibitor, thereby diminishing both the anodic dissolution of iron as well as the cathodic evolution of hydrogen reactions. Comparably, *Curcuma longa* (turmeric) possesses curcumin, which is notable for its keto-enol tautomerism, permitting the establishment of robust coordination bonds via both  $-OH$  and  $C=O$  moieties. The extensive conjugated system inherent to curcumin further augments  $\pi$ -electron adsorption, culminating in the development of a dense and adherent film on metallic surfaces. Experimental evidence has demonstrated that curcumin significantly impedes corrosion in acidic chloride environments through the formation of stable  $Fe$ -curcumin complexes [11].

Kermes dye, originating from insect sources, encompasses a sophisticated composition of polyphenolic compounds characterized by an abundance of hydroxyl and aromatic groups. These functional groups promote both physisorption and chemisorption on the surfaces of mild steel, thereby resulting in the development of a protective film that effectively obstructs active sites of corrosion. The efficacy of kermes as an inhibitor exhibits an increasing trend with rising concentrations; however, it demonstrates a declining tendency with elevated temperatures, suggesting that both physical and chemical adsorption mechanisms are concurrently operative. Another noteworthy natural dye source is *Musa paradisiaca* (banana peel), which is abundant in phytochemicals, including flavonoids, phenolic acids, and alkaloids. These phytochemical

constituents possess numerous donor atoms that facilitate spontaneous adsorption onto the metallic surface, typically conforming to Langmuir or Frumkin isotherms. The resultant barrier layer proficiently segregates the metal from corrosive ions, particularly in acidic environments[33].

In all instances examined, the efficacy of natural dyes as corrosion inhibitors is fundamentally rooted in their structural complexity and the presence of numerous active sites that are capable of engaging with the metal substrate. Such interactions effectively diminish the metal's vulnerability to corrosive entities, including  $H^+$  and  $Cl^-$  ions, thereby disrupting the electrochemical mechanisms that underpin corrosion. The propensity of natural dyes to generate robust, adherent, and environmentally benign protective films—alongside their non-toxic and biodegradable characteristics—renders them a highly viable alternative to traditional synthetic inhibitors. Consequently, natural dyes not only provide substantial corrosion resistance but also coincide with the principles of sustainable development and the objectives of green chemistry.

Lawsone from heena represents quinones, in which its naphthoquinone carbonyls ( $C=O$ ) chelate  $Fe^{2+}$  ions, forming insoluble complexes superior to those of flavonoids in turmeric and *Tagetes erecta*, which rely on multiple hydroxyl ( $-OH$ ) groups for H-bonding and  $\pi$ -stacking but require higher doses. Carotenoids like crocin in saffron and bixin in annatto create extended hydrophobic polyene barriers via van der Waal forces, outperforming anthocyanins in hibiscus and red cabbage at long term protection, but need high concentration to achieve 90 % efficiency. Tannins dominate in arecanut, black tea and *Camellia sinensis*, forming crosslinked Fe-tannate precipitates through multidentate chelation, most effective in aggressive  $Cl^-$  medium. Alkaloids provide compact cathodic protection, berberine and senecio show N-lone pair donation to the steel d-orbital at lower concentration than flavonoids, while betalains in *Beta vulgaris* offer  $N^+$  chelation similar to eosin Y. *Solanum torvum*, fenugreek, *Catharanthus roseus*, *chromolaena odorata* and *Piper longum* contain alkaloids and flavonoids for synergistic effects[31,34–45].

The corrosion inhibition potential of natural dyes is predominantly ascribed to their capacity to adsorb onto the metal interface, thereby establishing a protective barrier that obstructs the interaction between the metal and corrosive species such as  $H^+$ ,  $Cl^-$ , or  $O_2$ . This protective film mitigates both anodic metal dissolution and the cathodic generation of hydrogen or oxygen. The underlying mechanism encompasses physical

adsorption (physisorption), chemical adsorption (chemisorption), or a synergistic combination of both, contingent upon the molecular architecture of the dye, the specific metal in question, the corrosive milieu, and environmental variables such as pH and temperature[46,47].

#### Adsorption Theories and Isotherms

The interaction of dye molecules with metal surfaces follows well-established adsorption isotherms that model how they accumulate on the surface.

Natural dye-based corrosion inhibitors demonstrate their efficiency largely through adsorption mechanisms, which can be modelled using isotherm equations. The **Langmuir isotherm** [47] assumes monolayer adsorption on a homogeneous metal surface with uniform binding sites and energies. It is represented by equation 1,

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (1)$$

where C is the dye inhibitor concentration,  $\theta$  is the surface coverage, and  $K_{ads}$  is the equilibrium adsorption constant[47].

Research involving dyes such as curcumin and tannic acid demonstrates a pronounced linearity in the Langmuir plots, thereby suggesting the presence of robust and stable monolayer chemisorption. Conversely, the Temkin isotherm accounts for interactions between adsorbates and posits that the enthalpy of adsorption diminishes linearly as surface coverage escalates. This consideration is particularly pertinent for dye molecules characterized by multiple functional groups, which may incite steric or electrostatic repulsion. In parallel, the Freundlich isotherm, an empirical framework appropriate for heterogeneous surfaces, endorses the phenomenon of multilayer adsorption. This is frequently evident in natural dye extracts that encompass a plethora of compounds such as tannins and polyphenols, which adhere at disparate energy levels owing to their structural heterogeneity[48].

The interaction between dye molecules and metallic substrates may be broadly classified as either electrostatic or covalent bonding. Electrostatic interactions, which are emblematic of physisorption, predominate at reduced temperatures where protonated dye molecules exhibit an attraction to negatively charged metallic surfaces. Conversely, chemisorption entails the establishment of covalent bonds through the sharing of electrons. In this context, lone pairs located on heteroatoms (such as oxygen or nitrogen) alongside  $\pi$ -electrons from aromatic rings integrated within the dye structure contribute electron density to the unoccupied d-orbitals of the

metallic atoms[49]. This interplay culminates in the formation of a robust and adherent protective layer that obstructs corrosive agents from accessing the metal substrate. Numerous natural dyes, including quercetin and lawsone, are abundant in electron-donating moieties (for instance,  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $=\text{O}$ ) and feature delocalized  $\pi$ -systems. These characteristics facilitate substantial  $\pi$ -d orbital overlap with the metallic surface, thereby augmenting both the strength of adsorption and the efficacy of the inhibitor. Computational investigations employing Density Functional Theory (DFT) have substantiated this notion by revealing considerable HOMO-LUMO interactions and elevated adsorption energies, thereby validating their potential as efficacious corrosion inhibitors. Furthermore, the existence of additional phytochemicals within natural dye extracts frequently engenders synergistic interactions. Compounds such as alkaloids, terpenoids, essential oils, and polysaccharides enhance surface coverage, increase viscosity, and augment the overall compactness of the inhibitor film [9]. For example, the conjunction of curcumin with neem oil extract has exhibited enhanced corrosion resistance attributable to improved adhesion and cohesive film development. Tannins are particularly noteworthy for their capacity to form complexes with metallic ions, thereby functioning as chelating agents that stabilize the dye-metal interface. The efficacy of natural dyes is also contingent upon a variety of environmental variables. The pH of the medium exerts a substantial influence on dye behaviour; in acidic environments, excessive protonation may diminish adsorption efficiency, although certain dyes may exhibit superior performance in neutral or mildly acidic conditions where competition with  $\text{H}^+$  ions is less pronounced. Temperature is also a pivotal factor—elevated temperatures generally favour chemisorption, as evidenced by positive adsorption enthalpy values ( $\Delta\text{H}^\circ$ ), which imply endothermic adsorption processes. Furthermore, the specific type of metal being safeguarded influences inhibitor performance. Dyes such as lawsone have demonstrated enhanced efficacy on mild steel at increased temperatures, thereby supporting the chemisorption hypothesis, whereas dyes like indigo exhibit superior performance at lower temperatures where physisorption predominates. Consequently, the interaction among adsorption behaviour, dye chemistry, and environmental conditions collectively dictates the inhibitory effectiveness of natural dye-based corrosion inhibitors[50,51].

### 3. TYPE OF NATURAL DYE USED AS A CORROSION INHIBITOR-CASE STUDIES WITH EFFICIENCY TABLE

One of the most extensively documented systems pertains to the extract of henna leaves (*Lawsonia inermis*), which is characterized by a high concentration of the active compound lawsone (2-hydroxy-1,4-naphthoquinone). When applied to mild steel in 1 M HCl, the extract demonstrated an impressive inhibition efficiency of up to 94% at a concentration of 1.2 g/L. Both electrochemical assessments and weight-loss measurements indicated a substantial reduction in the rate of corrosion. The underlying mechanism was ascribed to chemisorption, which was corroborated by the enhanced efficiency observed at elevated temperatures and the formation of surface films, as evidenced by scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyses[10].

Another notably potent inhibitor is curcumin; the bioactive compound derived from turmeric (*Curcuma longa*). A Schiff base synthesized from curcumin and evaluated in 0.5 M  $\text{H}_2\text{SO}_4$  on mild steel exhibited inhibition efficiencies reaching up to 90% at a concentration of 250 ppm. The inhibitor molecules adhered to the metal surface through interactions involving their diketone and phenolic functional groups, thereby establishing a protective barrier. Thermodynamic analyses indicated the presence of robust chemical adsorption[11].

The extract of *Barleriaglabra* petals was subjected to evaluation in a 1 M  $\text{H}_2\text{SO}_4$  environment, resulting in an inhibition rate of 88% at a concentration of 250 ppm. The constituents of the dye were observed to adhere to the steel substrate via physisorption, thereby establishing a protective barrier that mitigated both anodic and cathodic electrochemical reactions. The manifestation of the inhibitory effect was corroborated through surface morphology analyses conducted via Scanning Electron Microscopy (SEM) and validated through electrochemical impedance spectroscopy measurements. Indigo dye, which is sourced from *Indigofera tinctoria*, exhibited an efficacy exceeding 85% for mild steel in sulfuric acid when utilized in conjunction with halide ions. These supplementary agents contributed to enhanced adhesion of the protective film and improved interactions at the surface level. The adsorption process was categorized as chemisorption, as determined by both kinetic and thermodynamic evaluations. In instances where indigo carmine, a synthetic derivative of natural indigo, was employed in isolation, the inhibition efficiency was notably suboptimal (~27% at low concentration). Nonetheless, its performance demonstrated considerable enhancement with elevated dosages and in combination with surfactants, indicating a promising avenue for formulation optimization[52].

Crocin, the principal carotenoid pigment derived from *Crocus sativus* (saffron), has demonstrated significant corrosion inhibition across various systems. When applied to aluminium alloys, including A1050, AA5083, AA5754, and AA6082 within a 0.01 M NaCl solution, Crocin achieved an inhibition efficiency of approximately 95% at a concentration of 1.25 mM. In this scenario, the adsorption process was primarily characterized as chemisorption, wherein the sugar moieties and conjugated polyene chain within the Crocin molecular structure exhibited robust interactions with the aluminium oxide layer. Conversely, upon evaluation on a tinplate surface in a 0.5 M oxalic acid medium, Crocin manifested an efficiency of 87.3%, which was primarily influenced by physisorption. This dualistic behaviour underscores the capacity of the same natural compound to demonstrate varying

adsorption mechanisms contingent upon the metal substrate and the corrosive environment [50].

Kermes dye, derived from the desiccated bodies of Kermes scale insects, has been subjected to investigation concerning its effects on mild steel in a 1.0 M hydrochloric acid solution. The dye demonstrated a remarkable corrosion inhibition efficiency of 96%, which can be ascribed to its extensive aromatic framework and the presence of functional groups, such as carbonyls and hydroxyls. The mechanism of adsorption was characterized by chemisorption, indicating a robust interaction between the dye molecules and the metallic surface via  $\pi$ -electron donation and complexation. The combination of this exceptional efficiency and the environmentally benign characteristics renders Kermes an appealing candidate for application in industrial acid pickling processes [33]

Table 1. Efficiency table of different natural dyes and their adsorption type

Natural Dye/ Extract	Metal	Medium	Conc. (ppm)	Inhibition Efficiency (%)	Adsorption Type	Ref.
Lawsone (Henna)	Mild Steel	1 M HCl	1200	~94	Chemisorption	[10]
Curcumin dye	Carbon Steel	Sea water	250	~93	Chemisorption	[11]
Cationic dye	7075 Al alloy	3.5% NaCl	1000	~95	Physisorption	[53]
Berberine	P110SS Steel	3.5 % NaCl	1500	~97	Physisorption	(32)
Crocin	A1050, AA5083, AA5754 and AA6082 aluminium alloys	0.01 M NaCl	1220	95	Chemisorption	[50]
Crocin	tinplate surface	0.5M H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	3000	87.3	Physisorption	[51]
Kermes	Mild Steel	1.0 M HCl	1450	96	Chemisorption	[33]
Solanumtorvum	Mild Steel	1 M H <sub>2</sub> SO <sub>4</sub>	900	91	Physisorption	[54]
Arecanut	Copper	0.5 M HCl and 0.5 M NaOH	4500	80	Physisorption	[39]
Black tea	Mild steel	1.0 M HCl and 1.0 M H <sub>2</sub> SO <sub>4</sub>	900	~ 88.5	Physisorption	[40]
VermoniaAnygdalina	Mild Steel	1.0 M H <sub>2</sub> SO <sub>4</sub>	5	~ 80	Chemisorption	[55]
Senesio	Copper	1.0 M HNO <sub>3</sub>	3	91	Physisorption	[42]
Fenugreek	Steel	10 ppm and 35 ppm Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	600	75	Physisorption	[56]
Catharanthus Roseus	Aluminium	1M and 2 M HCl	7000	99.3	Chemisorption	[57]
Eosin Y dye	Carbon Steel	1 M HClO <sub>4</sub>	3,450	96	Physisorption	[44]
Turmeric	Copper	0.5 N HCl	600	98.5	Physisorption	[35]
Red cabbage dye	Mild Steel	1 N HCl and H <sub>3</sub> PO <sub>4</sub>	50,000	83.4	Physisorption	[38]
Tageteserecta	Mild Steel	0.5M H <sub>2</sub> SO <sub>4</sub>	1000	98.07	Physisorption	[36]
Camellia sinensis	Mild Steel	1.0 M HCL	800	90.58	Chemisorption	[58]
Beta vulgaris	Mild Steel	0.5M H <sub>2</sub> SO <sub>4</sub>	50,000	94.05	Physisorption	[29]
Hibiscus rosa	Mild Steel	Simulated oil well water	100,000	82	Physisorption	[59]
Damask Rosa	Mild Steel	Simulated oil well water	1000	96	Mixed type	[60]
ChromolaenaOdorata	Carbon Steel	H <sub>2</sub> CO <sub>3</sub>	500	80.95	Physisorption	[61]
Betalain pigments	Aluminium	1.0 M HCl	1200	98.4	Physisorption	[43]

Piper longum	MS	1.0 M HCl	600	96.3	Physisorption	[62]
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Natural dyes constitute a highly promising category of bio-based corrosion inhibitors, owing to their distinctive chemical structures, adsorption properties, and minimal environmental ramifications. This section delves into the characteristics and efficacy of several of the most rigorously investigated natural dyes employed in corrosion inhibition. Each dye is scrutinised for its chemical functionality, corrosion inhibition effectiveness, and environmental compatibility.

As the aggregated data in Table 1 reveal, that quinone based dyes like lawsone derived from henna exhibit an inhibition efficiency of 94% on mild steel in a 1 M HCl solution through a chemisorption process. Polyphenolic compounds, found in black tea [40], *Camellia sinensis* [58], *Areca nut* [39], *Fenugreek*, *Hibiscus rosa* [30], *Damask rosa* [60] and *Chromolaena odorata*, demonstrate inhibition efficiencies ranging from about 75% to 96%, predominantly through physisorption. The adsorption characteristics of dyes onto metal surfaces are described by Langmuir or Temkin isotherms due to interaction involving  $\pi$ - electrons and hydrogen bonding. Alkaloid-rich extracts like berberine, *Catharanthus roseus* and *Piper longum* achieve inhibition rates of up to 99.3 % with adsorption processes mainly due to nitrogen heteroatoms and conjugated systems following Langmuir adsorption behaviour. Carotenoid and apocarotenoid pigments, such as crocin and annatto dye, show efficiency ranging from 80- 95%, showing Chemisorption and physisorption based on their structural nature and isotherm behaviour, mainly showing the Langmuir and the Freundlich model. Dyes are rich in flavonoid and anthocyanin efficiency range from 83- 98%, like red cabbage, *Beta vulgaris* and *Tagetes erecta*, primarily due to physisorption mechanism involving electrostatic and  $\pi$ - $\pi$  interactions. Dyes showing metal electrolyte interaction preferable results in high efficiency till 98.5 % at low dosage; on the other hand, *Solanum torvum* necessitate higher concentration arrangements from 50,000 to 250,000 ppm to achieve comparable inhibition levels, indicating weaker adsorption and solubility limit. In general, the adsorption behaviour is commonly represented by the Langmuir isotherm with sporadic deviations to the Temkin or the Freundlich models, indicating a monolayer adsorption process with potential lateral interaction. The variation in inhibition efficiencies stems from distinctions in donor atoms, aromaticity, planarity, solubility properties and nature of the metal and corrosive medium [26,29,34,36–38,42,43,55–59, 61– 64]

*Comparative Performance of Lawsone, Curcumin and Tannin-based Dyes.*

Lawsone, Curcumin and tannin- based dye represent three structurally distinct classes of plant-derived corrosion inhibitors. A detailed comparison across their molecular structure, functional groups, adsorption mechanism, effective concentration ranges, typical inhibition efficiencies and behaviour under acidic or neutral conditions.

In terms of molecular structure, Lawsone is a compact, mononuclear quinone whose small, rigid framework facilitates efficient diffusion toward the metal surface. Curcumin, by contrast, features a larger diketone backbone with phenolic and enol groups arranged along an extended conjugated system, giving it greater molecular flexibility but also greater susceptibility to environmental degradation. Tannins are structurally the most complex of the three, existing as oligomeric or polymeric polyphenols rather than discrete small molecules with molecular architecture that varies depending on source and extraction methods. Lawsone represents carbonyl and hydroxyl groups as its primary donor site, interacts with metal surfaces predominantly through chelation and chemisorption mediated by its quinone oxygen, with adsorption typically conforming to Langmuir monolayer behaviour. Curcumin carries multiple carbonyl and hydroxyl groups, along with its  $\beta$ -diketone tautomeric form, offering a greater number of potential coordination sites. It engages in a combination of physisorption and partial chemisorption through its multiple oxygen donor groups. Tannins contain a high density of catechol and galloyl hydroxyl groups distributed across their polymeric framework, making them structurally the richest in electron-donating capacity among the three. They tend towards multilayer physisorption and are particularly noted for their ability to form a continuous protective film across the metal surface. Lawsone's optimal performance lies between 50 to 400mg/L, with peak efficiency attained at 200mg/L achieving efficiency in the range of 70 to 90% under acidic conditions, where its structure supports stable adsorption and molecular integrity is well preserved. Its efficiency may change due to concentration range and pre-treatment conditions of metal surface, hence require careful optimization of both parameters to achieve consistent results.

Curcumin require higher concentration due to its lower aqueous solubility, also limits the amount of active inhibitor available at the metal interface. Hence its efficiency range lies between 60- 85% though the lower end of this range is frequently encountered when acid instability becomes a limiting factor. Curcumin being pH sensitive

undergo degradation which also reduces its reproducibility in practical applications.

Tannins are effective across a low concentration range as well showing the efficiency ranging from 78-88%. In an acidic medium its film formation efficiency reduces but still shows prominent inhibition performance. Long-term limitation lies in the natural variability of their source material and the inconsistencies introduced during extraction and purification, which produce batches of differing composition and hydroxyl content, complicating systematic evaluation and scale-up [26,27,34,65].

#### *Reliability of reported efficiency (Electrochemical v/s weight loss methods)*

Weight loss methods provide a straightforward, long-term measure of average corrosion rate by quantifying mass loss of metal coupons exposed to corrosive medium over an extended period, mainly days to weeks. This approach yields the corrosion rate in units like mpy (miles per year) or mmpy, calculated by the equation 2 [59,66]:

$$CR = \frac{87.6 \times W}{D \times A \times T} \quad (2)$$

Where W is weight loss (mg), D is metal density (g/cm<sup>3</sup>), A is exposed area (cm<sup>2</sup>) and t is exposed time (h). This method is simple, cost-effective and robust for ranking inhibition efficiencies under static conditions, reflecting real world bulk corrosion behaviour. On the other hand, electrochemical methods, including PDP (potentiodynamic polarization) and EIS (electrochemical impedance spectroscopy) provide insight into corrosion kinetics and mechanisms. PDP scans potential vs current to derive parameters like Corrosion current density and Tafel slopes from the Butler-Volmer equation, enabling inhibition efficiency to be calculated via equation 3.

$$\eta = \frac{i_{blank} - i_{inhibitor}}{i_{blank}} \times 100 \quad (3)$$

EIS models Nyquist/ Bode plots with equivalent circuits to quantify charge transfer resistance and double layer capacitance, collectively revealing adsorption mechanisms. These techniques are sensitive to detect <1% changes and provide mechanistic data in a short time [66].

Comparing both, weight loss methods reflect average corrosion over time and are less prone to artifacts making them highly reproducible for overall performance ranking. However, electrochemical methods like PDP and EIS are rapid and mechanistically rich and more susceptible to variability from instrumental settings, fitting assumptions, and test stability. This can lead to overly optimistic efficiencies if not controlled. The

total reliable studies combine weight loss for validation and electrochemical testing for mechanisms, followed by surface study. This multimethod approach mitigates limitations and strengthens claims.

#### *AI/ML in corrosion inhibition design. Nano-formulation of natural dye. Hybrid inhibitors: Industrial performance*

The field of natural dye-based corrosion inhibition is undergoing a strategic shift from empirical, single compound experimentation towards a rational, design-oriented framework. Nano-formulation techniques utilizing polymeric nanoparticles, mesoporous silica, or cyclodextrins emerged as a better way to stabilize dyes like curcumin. These systems offer controlled release capabilities that enhance surface coverage and extend the lifespan of the inhibitor. Alongside, hybrid inhibitors are gaining attention due to their better efficiency and durability provided by the synergistic interactions. By incorporating additives such as iodide ion, the metal surface charge can be modified to facilitate strong cooperative adsorption. More complex formulations integrate natural dye with polymers or inorganic salts like Zn<sup>2+</sup> to combine molecular adsorption with physical barrier effects. The transition towards "inhibitor by design" is being driven by computational advancements in density functional theory (DFT) and Machine learning (ML). These tools allow researchers to predict performance using molecular descriptors such as HOMO-LUMO energy gaps, dipole moments and adsorption energies. Despite this potential, the reliability of these models is currently hindered by small, inconsistent datasets. Advancing this front will require the development of curated, high-quality data libraries to bridge the gap between virtual molecular modelling and practical experimental validation [67,68].

#### 4. COMPARATIVE ANALYSIS: NATURAL DYES V/S TRADITIONAL INHIBITORS

One of the most salient differentiations resides in their respective toxicological profiles. Conventional inhibitors—exemplified by chromates, nitrites, and phosphates—are recognized as deleterious, frequently linked to carcinogenic and mutagenic properties, and present considerable hazards to both aquatic ecosystems and human health. Conversely, natural dyes are predominantly non-toxic, derived from consumable or therapeutic flora such as turmeric and henna, and entail negligible health or ecological hazards. In the realm of evaluating ecological ramifications, natural dyes exhibit a markedly superior efficacy in comparison to synthetic inhibitors. These dyes are derived from

renewable biomass resources, encompassing agricultural residues and plant extracts, thus contributing insignificantly to environmental pollution and requiring minimal processing efforts. In contrast, conventional inhibitors, being derived from petroleum, intensify carbon emissions and promote ecological degradation throughout their comprehensive lifecycle. About biodegradability,

natural dyes once more possess a distinct advantage. Their organic composition facilitates their natural decomposition within the environment, resulting in the generation of non-toxic residues. Conversely, synthetic inhibitors frequently demonstrate persistence in aquatic ecosystems and terrestrial soils, leading to enduring contamination issues.

Table 2. Natural Dyes versus Traditional Corrosion Inhibitors –Key Parameters

Parameter	Natural Dyes	Traditional Inhibitors	Ref.
Toxicity	Non-toxic, safe for humans and the environment	Often toxic (e.g., chromates, nitrites); hazardous to health and ecosystems	[8,9, 23,24]
Environmental Footprint	Minimal, derived from renewable plant sources	High, petroleum-derived and non-renewable	
Biodegradability	Easily biodegradable; decomposes into harmless by-products	Poorly biodegradable; persistent in the environment	
Cost-effectiveness	Low cost, sourced from agricultural waste and local biomass	High cost due to complex synthesis and raw materials	
Rural Applicability	High-quality raw materials are locally available, and extraction methods are simple	Limited; requires industrial-grade synthesis and controlled logistics	
Industrial Scalability	Moderate; requires standardization, consistent yield, and formulation support	High, well-established manufacturing and supply chains	
Inhibition Efficiency	85–95% in lab studies; varies with conditions	90–98% in both lab and field conditions	
Performance in Real Conditions	Variable; may degrade or desorb under extreme pH or temperature	Stable under a wide range of operational conditions	
Examples	Lawsone, Curcumin, Quercetin, Tannic Acid, Indigo	Amines, Chromates, Phosphates, Benzotriazoles	
Regulatory Pressure	None; eco-safe and REACH-compliant	High; many restricted under environmental and health regulations	

Cost-effectiveness represents a domain in which natural dyes demonstrate significant superiority. Derived from abundant and often discarded biomass, these dyes are relatively inexpensive and readily available, particularly in rural or developing areas. This characteristic renders them particularly suitable for community-level or small-scale corrosion prevention initiatives, in contrast to synthetic inhibitors, which incur higher costs due to the requirements of chemical synthesis, purification, and transportation logistics. Nonetheless, the challenge of industrial scalability persists for natural dyes. While synthetic inhibitors have reaped the benefits of decades of optimization, established supply chains, and advanced formulation technologies, natural dyes continue to face issues such as batch-to-batch variability, low extraction yields, and a deficiency in standardization. Tackling these problems is crucial for facilitating the large-scale industrial implementation of bio-based corrosion inhibitors.

In the realm of performance assessment, numerous natural dyes demonstrate inhibition efficiencies ranging from 85% to 95% within meticulously controlled laboratory settings, frequently exhibiting comparability to conventional

inhibitors. Nevertheless, in practical applications—characterized by temperature variances, fluid dynamics, and potential contamination—natural dyes may exhibit diminished performance attributed to factors such as desorption, degradation, or compromised surface adhesion. Conversely, synthetic inhibitors tend to sustain a consistent level of efficiency even in the face of severe and fluctuating industrial conditions [8,9,23,28].

## 5. SUSTAINABILITY AND ENVIRONMENTAL ASPECTS

The application of natural dyes as corrosion inhibitors is gaining increasing recognition due to its alignment with global sustainability objectives, particularly those outlined in the United Nations Sustainable Development Goals (SDGs) 12 and 13, which advocate for responsible consumption and production practices, as well as proactive climate action. Primarily sourced from renewable materials such as agricultural by-products and plant biomass, natural dyes embody the foundational concepts of zero-waste chemistry. Typical sources encompass onion skins, pomegranate peels, henna foliage, turmeric rhizomes, and various agro-waste products that

would otherwise exacerbate environmental degradation. The transformation of these materials into high-value corrosion inhibitors signifies a waste-to-wealth initiative that effectively reduces waste generation and mitigates the environmental impact associated with the production of synthetic chemicals [69-71].

Natural dyes represent environmentally benign alternatives to traditional petrochemical-derived corrosion inhibitors, many of which exhibit non-biodegradable characteristics, pose toxicity risks to aquatic organisms, and demonstrate environmental persistence. Conversely, natural dyes such as lawsone (extracted from henna), curcumin (derived from turmeric), and anthocyanins (sourced from red cabbage or hibiscus) possess biodegradable and non-toxic attributes, featuring a variety of functional groups including hydroxyl ( $-OH$ ), carboxyl ( $-COOH$ ), and amino ( $-NH_2$ ) that enhance the adsorption efficacy on metal surfaces. The presence of these functional groups facilitates the formation of stable complexes with metal ions, thereby fostering the development of protective films and ensuring effective corrosion inhibition in corrosive environments [1,49].

In the realm of industrial applicability, natural dyes have exhibited considerable potential in domains such as pipeline safeguarding, automotive parts manufacturing, and infrastructure subjected to acidic, saline, or marine environments. Their implementation in closed-loop cooling and recirculating systems is particularly beneficial, as it diminishes both the frequency and concentration of inhibitor dosing, thereby enhancing cost-effectiveness and operational sustainability. Preliminary life-cycle assessment (LCA) investigations have indicated that the overall carbon footprint, energy utilization, and environmental ramifications of natural dye-based inhibitors are markedly lower than those associated with synthetic inhibitors—particularly when dyes are derived directly from waste without extensive purification or chemical treatment. Regulatory developments further facilitate the implementation of natural dyes. In contrast to numerous synthetic inhibitors that are subjected to rigorous regulatory frameworks such as REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals), natural dyes typically circumvent such constraints owing to their low toxicity, renewability, and minimal ecological persistence [12]. Ecotoxicological evaluations of natural dyes, including henna and indigo, have indicated diminished aquatic toxicity and insignificant bioaccumulation, rendering them appropriate for application in environmentally sensitive domains such as water treatment facilities and marine coatings. Notwithstanding their merits, the extensive

industrial adoption of natural dyes as corrosion inhibitors continues to encounter obstacles. The standardization of extraction methodologies is imperative to guarantee reproducibility and quality across production batches. Variability in the characteristics of plant-derived raw materials can influence the uniformity of inhibitor efficacy. Moreover, the advancement of environmentally-friendly, solvent-free, or microwave-assisted extraction techniques is crucial for enhancing sustainability throughout the production continuum. The optimization of formulation strategies and long-term field performance assessments will be vital for transitioning natural dyes from laboratory-scale validation to comprehensive industrial implementation [23,24].

## 6. LIMITATIONS, REPRODUCIBILITY AND INDUSTRIAL FEASIBILITY

One prominent challenge resides in the inherent variability of natural sources. The chemical composition of dyes derived from botanical sources can exhibit considerable variation contingent upon factors such as edaphic conditions, temporal aspects of harvesting, and methodologies of extraction. This lack of consistency may result in oscillating inhibition efficacy and complications in standardization, which are pivotal for industrial applications that necessitate reliable performance [72].

Another constraint pertains to the limited solubility and stability of various natural dyes in corrosive environments, including acidic or saline media. For instance, compounds such as curcumin are characterized by their inadequate water solubility and susceptibility to variations in pH, light exposure, and temperature, which may diminish their efficacy over extended periods. Moreover, elevated concentrations are frequently necessitated to attain inhibition efficiencies that are comparable to those of synthetic inhibitors, thereby raising concerns regarding both cost-effectiveness and compatibility with materials [73].

A critical reproducibility barrier emerges from heterogeneous extraction procedures, as *Piper longum* [62] was extracted by 5 hours of reflux in 500 mL distilled water, while *Lawsoniainermis* used methanolic extraction, and *Tagetes erecta* employed aqueous grinding and filtration. No systematic study comparing extraction methods for the same plant source exists. This methodological inconsistency ensures that "*Piper longum* extract" studied in one laboratory is chemically distinct from that in another; a fundamental impediment to reproducibility. Also, extract quality degradation over time was universally ignored. *Beta vulgaris* (beetroot) extract was kept overnight before

use, yet oxidation of betacyanins and other polyphenols that occurred during storage would alter their concentration and structure. Red Cabbage Dye extracts were preserved in a dark refrigerator, but no time dependent stability data were provided. On the other side, for *Catharanthus roseus* and *Murraya koenigii*, freshly prepared solutions were employed, but the extract stability durations were unstated. Without standardized extraction, storage and stability protocols, cross study comparisons become fundamentally unreliable [29,38,43,57].

The processes involved in extraction and purification represent an additional area of concern. Although natural dyes are typically sourced from agro-waste, the extraction processes may entail substantial volumes of water, the use of organic solvents, or energy-intensive methodologies. In the absence of optimization, these procedures could potentially negate the environmental advantages and economic viability, particularly on a larger scale. Like, industrial pickling operations use acid inhibitors at 1- 10 % w/v concentration, used for synthetic inhibitors, but problematic for dye or extracts. For *Tagetes erecta*, the optimum concentration at laboratory scale was 1.0 g/L, scaling to a 10,000-litre pickling tank would require 10 kg of extract daily. Cost considerations are unstable but critical; marigold flower extract preparation incurs labour and energy costs potentially exceeding cost savings from avoiding synthetic inhibitors. Moreover, the extract variability directly impacts the required dosing; if seasonal variation or plant source variation alters bioactive alkaloid content, the inhibitor concentration would require adjustment to maintain target efficiency. Dye/ extract-based inhibitor lack standardization and necessitates frequent efficacy testing, increasing operational costs and complicating adoption in resources in constrained industrial settings. From a regulatory and industrial perspective, the deficiency of thorough studies addressing toxicity, degradation, and long-term environmental impacts constrains the approval and confidence in natural dyes for critical applications such as pipelines or automotive systems. Furthermore, their performance in multi-metal systems or under dynamic conditions (for instance, varying temperatures or flow rates) remains inadequately investigated [13,27].

## 7. CONCLUSION

Natural dye/ extracts represent promising environmentally sustainable alternatives to conventional corrosion inhibitors, with demonstrated laboratory efficiency consistently exceeding 80 to 95% inhibition efficiency across validated electrochemical and gravimetric methodologies. The effectiveness of these bioactive inhibitors fundamentally derives from their rich phytochemical

composition, particularly heteroatoms containing alkaloids, flavonoids, tannins and phenolic compounds that form protective adsorption layers on metal surfaces through both physisorption and chemisorption mechanisms. Alkaloids containing dyes show maximum efficiency even at low dosage due to the  $\pi$ - electron donors showing physisorption (96-99 % efficiency). While alkaloids and quinones provide moderate protection through lone-pair donation, the multidentate binding and planar orientation of flavonoids provide the most robust steric hindrance against aggressive electrolytic ions, making them more efficient green inhibitors at elevated concentration. Some significant scientific and practical barriers prevent straightforward translation of laboratory successes to industrial scale applications. Primary concerns include: (i) Reproducibility deficiencies stemming from inherent biological variability in plant materials independent of extraction conditions; (ii) Methodological inconsistencies with individual extracts showing less than 15 % efficiency variations between weight-loss methods and electrochemical methods, complicating performance specification; (iii) Temperature sensitivity with efficiency degradation of 10-30 % above 50°C for most extracts, limiting applicability in thermal or elevated temperature environment; (iv) Indefinite long term stability or storage data particularly regarding oxidation, microbial contamination and phytochemical degradation during extended storage or continuous exposure. Hence, while natural dyes hold clear promise as components of sustainable corrosion protection strategies, their real impact will depend on shifting the research focus from isolated efficiency reports to reproducible, mechanism driven findings.

## 8. FUTURE PROSPECTS

The future scope of this research lies mainly in bridging the gap between laboratory scale synthesis and large-scale industrial application. The main highlight is the evolution of standardised extraction and testing protocols through reproducible, high-yield synthesis methods; researchers should ensure the chemical consistency required for industrial quality control. Also, the transition to long term immersion and field scale studies is critical. As current laboratory data provides a snapshot of performance, real world assets require protection over extended periods. Hence, researchers should include pilot scale testing in harsh, fluctuating environments to evaluate the efficiency and feasibility in unpredictable conditions. As nano-based materials are ruling most industries, likewise, nano formulations and hybrid systems should be considered to enhance the performance of inhibitors and their adsorption properties. These formulations can be further optimized through the integration of computational and AI-guided screening methods like Density

Functional Theory (DFT) and Molecular Dynamics (MD) simulations, which will allow for the precise prediction of adsorption energy and electronic interactions at the metal inhibition interface. Eventually, if coupled with machine learning algorithms, these digital tools can rapidly filter a vast library, identifying the most potent molecular structures, which will eventually reduce the “trial and error” time in the lab and direct the research more towards data driven and sustainable approach to industrial corrosion protection.

#### 9. ABBREVIATIONS

- VOCs - Volatile Organic Compounds
- EIS – Electrochemical Impedance Spectroscopy
- SEM – Scanning Electron Microscopy
- Kads – Equilibrium Adsorption Constant
- DFT – Density Functional Theory
- HOMO – Highest Occupied Molecular Orbitals
- LUMO – Lowest Unoccupied Molecular Orbitals
- $\Delta H^\circ$  - Adsorption Enthalpy
- AFM – Atomic Force Microscopy
- LCA – Life Cycle Assessment
- REACH- Registration, Evaluation, Authorisation and Restriction of Chemicals

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## IZVOD

### PRIRODNE BOJE KAO EKOLOŠKI PRIHVATLJIVI INHIBITORI KOROZIJE: ODRŽIVI PRISTUP ZAŠTITI METALA

*Prirodne boje, istorijski slavljene zbog svoje sposobnosti da poboljšaju vizuelnu privlačnost tekstila, hrane i artefakata, sada dobijaju sve veće priznanje za svoje funkcionalne primene, najznačajnije kao ekološki prihvatljivi inhibitori korozije. Korozija u agresivnim industrijskim okruženjima zahteva formulaciju ekološki kompatibilnog inhibitora koji bi zamenio konvencionalne toksične sisteme. Prirodne boje, ekstrahovane iz botaničkog porekla, pojavljuju se kao održiva alternativa zbog svojih obilnih fitohemijskih sastojaka i biorazgradivosti. Njihova efikasnost u inhibiciji je prvenstveno pod uticajem prisustva heteroatoma, p-elektronske gustine i molekularne planarnosti, koji poboljšavaju adsorpciju i naknadno formiranje zaštitnih filmova na metalnim površinama. Pokazuju različito ponašanje adsorpcije poput hemisorpcije, fizisorpcije ili mešovitog tipa inhibicije. Uporedni pregled otkriva da boje izvedene iz tanina, flavonoida i hinona pokazuju superiornu efikasnost, postižući svoju najveću stabilnost iako je njihova efikasnost zasnovana na medijumu, temperaturi i korišćenom supstratu. Nekoliko prepreka, poput ograničene mehanističke validacije i nedostatka standardizacije, ograničavaju njihovu praktičnu primenu. Stoga, buduća istraživanja moraju da se naglase na korelacijama strukture i aktivnosti, naprednoj analizi površina i hibridnim ili modifikovanim sistemima kako bi se potvrdila uloga prirodnih boja kao pouzdane alternative za toksične inhibitore.*

**Ključne reči:** *Prirodna boja, inhibitor korozije, zaštita metala, održivo, površinska adsorpcija*

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