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A SYSTEMATIC EXFOLIATION OF PRIOR ARTS ABOUT THE USE OF NATURAL AND SYNTHESIZED 1,4-NAPHTHOQUINONES TOWARDS CORROSION INHIBITION-AN EXHAUSTIVE REVIEW

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Abstract

In this review segment, use of natural and synthesized 1,4-naphthoquinones for corrosion inhibition was comprehensively covered based on the past research disclosures. The prior arts were gathered from various research article repositories by the use of search terms like 'Quinonoids as corrosion inhibitors' and '1,4-Napthoquinones as corrosion inhibitors' as a part of direct referencing. Additionally, back and cross referencing were also done to ensure the complete collection of prior arts. This work will help the researchers to understand the credibility of 1,4 naphthoquinones as corrosion inhibitors in the global platform. Interestingly, the henna leaf extract (aqueous or solvent mediated) having 2-hydroxy 1,4-naphthoquinone (Lawsone, $NO-12$) was the most explored phytochemical under natural or green corrosion inhibitor category. More importantly, a few natural extracts having 1,4-naphthoquinones were widely used as corrosion inhibitors in different mediums. With regard to phytochemical extracts, the collective inhibition ability of many phytochemicals will add to corrosion inhibition process. But in recent years, we can observe the use of specific compounds (synthesized/isolated derivatives of 1,4-naphthoquinone) as alone for the intended corrosion inhibition. Under the context of immediate scope, we have disclosed around 23-26 new molecules having 1,4-naphthoquinone framework for experimental ventures towards corrosion inhibition. This work would favor the use of some new 1,4 naphthoquinones in its pure form towards retarding corrosion with the assistance of supportive molecular framework.

Keywords: 1,4-Naphthoquinones, Corrosion inhibition, Adsorption, Green inhibitors, Synergism, Impermeable film.

Introduction

1,4-Napthoquinones are renowned to have numerous pharmacological applications and hence, they are popular as active pharmaceutical ingredients in various medicines to treat variety of diseases. The

pharmaceutical significance of synthetic or natural 1,4-naphthoquinone centric moieties were well explored by the global researchers [Batiha et al., 2024a; Batiha et al., 2024b; Angulo-Elizari et al., 2024; Khan et al., 2023; Navarro-Tovar et al., 2023; Aminin

et al., 2020; Mostert et al., 2016]. The structure driven molecular actions of 1,4 naphthoquinone derivatives were also well documented [Widhalm and Rhodes, 2016]. With regard to technological aspects, more particularly towards corrosion inhibition capabilities of these moieties were under moderate scope from long back. Interestingly, we could able to notice the gradual increase in intend by the researchers around the world in recent years to utilize these moieties as potential corrosion inhibitors. Under the context, this review initiative was focussed towards the collection of prior art disclosures about the corrosion inhibition capabilities of 1,4 naphthoquinone derivatives. In support to this, the quinonoids (organic molecules) under the scope are rich in polar atoms $(0, N, \mathcal{C})$ and S) and hence would contribute to better complexation and surface adsorption. This eventually would lead to the formation of a firm protective film over the metal surface to retard corrosion effectively [Zhao et al., 2023].

Numerous methods were adopted to estimate the inhibition efficiency of inhibitors over different metals in varied environments. A few such common methods adopted in the past disclosures are weight loss, potentio-dynamic polarization, electrochemical impedance spectroscopy, electrochemical frequency modulation, open circuit potential etc. Similarly, the protective film formed on the metal/alloy surface to retard corrosion was examined by various techniques like scanning electron microscopy, fourier-transform infrared spectroscopy, ultraviolet-visible spectroscopy, energy dispersive X-ray spectroscopy etc. By these strategies, corrosion inhibition impact of the used molecule or the mixture of molecules (in extracts) can be estimated [Sharma et al., 2023].

In this review segment, we aim to disclose a till date collective information about natural and synthesized 1,4 naphthoquinones as corrosion inhibitors. Numerous collective review articles were published on corrosion inhibition of metals

or alloys by organic molecules but specific to present article scope was not attempted.

Sourcing of specific publications

The prior arts were collected from the global pool of publications by the assistance of various search tools/repositories like "Google Scholar", "ResearchGate", "Google Patents", "Scopus database" etc. Some specific search terms like 'Quinonoids as corrosion inhibitors' and '1,4-Napthoquinones as corrosion inhibitors' were used to gather vast number of publications. Every publication displayed was critically examined to collect close resemblance and exact matching publications.

Exfoliation of prior arts

The corrosion inhibitory action of walnut green husk extract (WGHE) and $Nd(NO₃)₃$ on aluminum in HCl solution. The combination of WGHE and $Nd(NO₃)₃$ gave good inhibition efficiency than their use individually. It was established by various renowned techniques like mass loss method, polarization curve measurement, electrochemical impedance spectroscopy, scanning electron microscope and atomic force microscope. The vital components of WGHE are naphthoquinones (including NQ-1) and flavonoids (quercetin and rutin) [Miao et al., 2022].

Synthesis, characterization and anticorrosive capability of three derivatives of 1,4-naphthoquinone (NQ-2 to NQ-4) and a derivative of hydroxy-naphthalene was reported. The corrosion inhibition estimation was done by weight loss determination and density functional theory based estimations. These corrosion inhibition tests were done at different temperatures (303K, 333K and 363K) to estimate the weight decline in the test sample (mild-steel in HCl solution). Under the context, NQ-4 had exhibited highest corrosion inhibition efficiency (89.39%) [Wodi et al., 2022].

The corrosion inhibition capability of six amino acid derivatives of 1,4 naphthoquinone (NQ-5 to NQ-10) were disclosed based on density functional theory studies. The charge distribution study had revealed that, the derivatives which can donate and receive electrons through back donation can effectively inhibit the corrosion process. More importantly, low energy band gap, high molecular softness and the existence of electron donating groups on the derivatives can impart corrosion inhibition features. Under the context, NQ-6 and NQ-8 had displayed very good inhibition ability than other compounds [Esan et al., 2022]. The synthesis, isolation, characterization, biological activities and toxicities of these compounds were reported earlier [Buchkevych et al., 2021]. How that, the derivatives which can
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Figure 3. NQ-5 and NQ-6

Figure 4. NQ-7; NQ-8; NQ-9; and NQ-10

The corrosion inhibition capability of NQ-11 was illustrated towards mild-steel in 1.0M HCl solution. The presence (adsorption) of NQ-11 over mild-steel imparts more smoothness to the surface than that in the absence of $NQ-11$, thus protects the surface from corrosion [Odozi et al., 2022].

 \circ \overline{H} \circ \overline{H} \circ \overline{H} tabulated the use of numerous inhibitors like $\frac{1}{2}$ $\frac{1}{2}$ $\frac{1}{2}$ organic molecules and plant extracts NQ-6 o o complete including henna extract having 2-hydroxy A review article on eco-friendly corrosion inhibitors on mild steel in acidic solution was presented. The work had 1,4-naphthoquinone (Lawsone, NQ-12) [Shashirekha et al., 2022].

A review article was published regarding NQ-12 centric transition metal complexes. The initiative was focused primarily on the synthesis and biological applications of some transition metal complexes associated with NQ-12 and its derivatives. Moreover, it had covered the use of NQ-12 for corrosion under different mediums. Thus, the initiative had covered the extended applications of NQ-12 and its metal complexes [Selvaraj et al.. 2022]. A broad spectrum review article was reported regarding the use of plant extracts as green corrosion inhibitors to safeguard carbonsteel in acidic medium. The work had emphasized the effectiveness of henna extract having NQ-12 in various past disclosures towards corrosion inhibition [Salim et al., 2022]. A review article was presented on the applicability of a few organic molecules as corrosion inhibitors. Those molecules are 1,4-naphthoquinone (NQ-13), 1,5-naphthalene-diol, 3-amino-1,2,4-triazole-5-thiol, ammonium tetrathiotungstate, clotrimazole, amoxicillin, antimicrobial and antifungal drugs. This review disclosure had specifically covered aluminum and aluminum-composite corrosion inhibitors in chloride-containing solutions [Kumar et al., 2022].

The application of henna leaf extract having NQ-12 was illustrated as corrosion inhibitor in the simulated environment (synthetic seawater) for mild-steel. The high inhibition impact is due to better adsorption of the extract over steel surface. Moreover, low toxicity and easy biodegradability of the

NQ-12 demonstrated over copper in 0.5M HCl $NQ-12$ (in 6-10% concentration) was O henna extract was also explored in the OH disclosure [Siddekha, 2022]. The highest inhibition efficiency of henna extract having solution [Diab and Abd El-Haleem, 2022].

A review article was reported with an emphasis on green eco-friendly corrosion inhibitors to protect metals used in oil and gas industries. The work covers the use of various inhibitors like organic molecules, plant extracts including henna leaf extract having NQ-12 and polymeric molecules to prevent corrosion. Meanwhile, the green remedies are highlighted to prevent corrosion issues in industries [Panchal et al., 2021]. A review article was disclosed regarding the role of green corrosion inhibitors to protect zinc. It had covered the use of plant materials, leaf extracts including NQ-12 and some additives as inhibitors [Vashi and Zele, 2021]. A review article was reported regarding the corrosion inhibitive actions of henna leaf extract (Lawsonia inermis, having NQ-12) on mild-steel in various acidic solutions. It was observed that, the corrosion inhibition efficiency of the extract had increased with an increase in the concentration and decreased with an increase in medium acidity [Serbout et al., 2021].

NQ-13 in 0.1M HCl solution using Tapinanthus O were executed over mild-steel and aluminum O played a vital role in retarding the bio-The crude methanolic extract of Lawsonia inermis having NQ-12 was used effectively as an anti-biofilm on mild-steel 1010. The introduced coating on the metal had prevented the bio-corrosion process in a re-circulating waste-water system. The antibacterial potential of the extract had corrosion process [Narenkumar et al., 2021]. The computational and experimental studies bangwensis leaf extract in ethanol as corrosion inhibitor. It was estimated by weight loss method and potentio-dynamic polarization tests. The leaf extract was examined (by GCMS) and its major constituents are 1,6,10-dodecatriene, 3 chlorophenol, pentadecanoic acid, 2,3 diphenyl-1,4-naphthoquinone (NQ-14), 1 monolinoleoyl glycerol trimethyl-silyl ether and stigmasterol. In support to higher inhibition efficiency of the extract, the adsorption mechanism had favored physisorption pathway [Eddy and Okon, 2021].

The effectiveness of henna leaf extract having NQ-12 and gallic acid as inhibitors was illustrated on steel in simulated concrete pore solution (SCPS) having 0.5M NaCl solution. It was estimated by an open circuit potential, potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The henna leaf extract and gallic acid had behaved as a anodic corrosion inhibitor and NQ-12 as a mixed type through chemisorption pathway. Meanwhile, henna extract had exhibited high corrosion inhibition efficiency than its major constituents like NQ-12 and gallic acid [Brixi et al., 2021]. A review article was presented on the use of numerous plant extracts including henna extract having NQ-12 as green corrosion inhibitors. This initiative had explored the simple methods to achieve extracts and their economical use as inhibitors. Under the context. NO-12. coumarin and gallic acid were notified for their contribution to corrosion inhibition [Badawi and Fahim, 2021].

A review article was reported regarding the use of plant extracts as corrosion inhibitors for mild-steel in acidic solutions. The plant extracts contain numerous bioorganic molecules (includes $NQ-12$) having polar atoms such as *O*, *P*, *S* and N. Hence, these polar centric molecules would get adsorbed on the metal surface to create an impermeable film to retard corrosion [Bilgic, 2021]. Three large organic molecules containing morpholine, 1,4 naphthoquinone (NQ-15), 7-chloroquinoline and 1,3,5-triazine cores were synthesized and used for corrosion inhibition studies.

The corrosion prevention capabilities of these moieties were established on the surface of stainless steel AISI 316 in NaCl and Na2S medium by potentio-dynamic polarization and electrochemical impedance studies [Westphal et al., 2020]. *A Systematic Exfoliation* ...
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Some quinone derivatives like xanthone, xanthene, thioxanthone, acridone and 1,4-naphthoquinone (NQ-13) were used as inhibitors of copper corrosion inhibition in acetonitrile medium. Interestingly, NQ-13 had exhibited lower inhibition rate due to the absence N atom in its molecular framework. In this regard, the study was extended to compounds like thiourea, diphenylthiourea, phenylthiourea and ethylenethiourea. The presence of sulphur group in thiourea derivatives had empowered them to display higher inhibition behavior than the quinone derivatives [Chooto et al., 2020]. The inhibition behavior of walnut green husk extract (WGHE) and sodium lignosulfonate (SLS) was studied on the corrosion of cold rolled steel in phosphoric acid solution. The moderate inhibition efficiency of WGHE can be attributed to the presence of two organic molecules like NQ-13 and 2 phenylchromone (PC). Furthermore, individual WGHE or SLS had behaved as cathodic inhibitors. But the mixture (WGHE/SLS) had exhibited mixed-type inhibition behavior with high inhibition efficiency. This behavior was due to the formation of collective complexation and enhanced adsorption features of them on the metal surface.

Interestingly, NQ-13 and PC with SLS had displayed less inhibition capability compared to WGHE/SLS [Li et al., 2020]. A review article was presented regarding the use of green corrosion inhibitors for steel in acidic medium. The work had covered the use of numerous components as inhibitors like plant extracts including henna extract having NQ-12, ionic liquids, drug molecules, amino acids, polymers and inorganic materials [Wei et al., 2020]. The role of henna extract having NQ-12 as potential corrosion inhibitor for steel API5LGr-B in $H₂S$ -containing solution at 25^oC was illustrated. As the extract concentration was increased, the corrosion current density had decreased and the inhibition efficiency had considerably enhanced. As per the study, the extract driven inhibition process was based on physisorption pathway [Hamrahi et al., 2020].

The aqueous Lawsonia inermis extract having NQ-12 was used as a bioorigin corrosion inhibitor for steel alloy 4130 in NaCl (3.5% by weight) solutions. The extract had shown promising results in the entire inhibition establishment tests, which was truly based on the extract concentration, temperature of the medium and rotation speed [El-Shamy et al., 2020]. Some extensive studies were conducted to safeguard lead in a lead-acid battery from corrosion by the impact of sulphuric acid. It was achieved by the use of henna extract having NQ-12 and more importantly the inhibition efficiency had increased substantially with the rise in temperature [Bouabdallah and Bounoughaz, 2020]. The corrosion inhibition properties of henna leaf extract was established on tin in acidic and alkaline phases. The work had established the optimum concentration (0.5%) for an effective corrosion inhibition. More importantly, the use of extract on tin was established to be more effective in alkaline medium than in acidic medium [Ibrahim, 2020]. A review article was disclosed with an emphasis on corrosion inhibition actions of henna leaf extract having NQ-12. The work had highlighted generation of protective film on the metal surface due to the formation of complex between iron and NQ-12 [Devi et al., 2020].

The use of henna (Lawsonia inermis, having NQ-12) leaf extract was illustrated as a green corrosion inhibitor for carbon-steel in 1.0M HCl solution. The inhibition impact was established through weight loss, potentio-dynamic polarization, AC impedance spectra and electrochemical frequency modulation methods. The efficiency of inhibition had increased exponentially with an increase in concentration of the extract and decreased with the rise in temperature [Fouda et al., 2019]. The extraction, characterization and corrosion inhibition capability of seven aromatic molecules like caffeic acid, thymol, gallic acid, tannic acid, NQ-12, wedelolactone and ellagic acid was demonstrated. These molecules were obtained from plants and hence can be termed as green alternatives for the intended corrosion inhibition of iron. All the seven bio-origin compounds had exhibited similar type of electrochemical behavior, it is due to the existence of intrinsic aromaticity [Fang et al., 2019].

The corrosion inhibition behaviors of NQ-12 and some of its derivatives (NQ-16 to NQ-25) were reported on the basis of extensive DFT studies. This initiative had explored the relationship between the inhibition features and the molecular framework of the organic molecules in contact with steel or iron. This work had established the correlation between electronic properties of NQ-12 and the ten di-chlorinated derivatives in neutral, cationic and anionic states and the corrosion inhibition efficiency in contact with an iron atom. The inhibition efficiency of other molecules are better than NQ-12, due to low energy gap, better charge transfer, and relative position of HOMO energy in remaining ten derivatives [Belkada et al., 2019].

A book chapter was published highlighting the use of plant parts (as extracts) as corrosion inhibitors in numerous aqueous phases. The disclosed chapter had covered the use of henna extract having NQ-12 for corrosion inhibition studies [Nasab et al., 2019]. The corrosion inhibition ability of henna leaf extract having NQ-12 was established on tin in 1.0M HCl solution and 1.0M NaOH solution. It was established based on weight-loss method performed at 25-500C. The henna leaf extract was found to be an excellent inhibitor for tin in alkaline condition [Bashir et al., 2019]. A review article was reported with a focus on the use of green corrosion inhibitors. The role of those inhibitors can be to prevent/control/retard the process of corrosion. The green inhibitors are biodegradable, ecologically acceptable and renewable [Marzorati et al., 2019].

0 0 minutes for two carbon seed in O O The combinational use of stem OH \sim OH extracts of brahmi and henna having NQ-12 O OH for an efficient inhibition was established [Al NQ-17 solution. During the context, optimum was demonstrated as an effective corrosion inhibitor for low carbon-steel in 0.5M NaOH inhibition concentration of the mixed extract Hasan et al., 2019].

NQ-21 The density functional theory study ຕ່ ບໍ່ ບໍ່ O coating was reported to achieve NQ-18 NQ-19 corrosion inhibition. The microencapsulated $\frac{1}{\alpha}$ $\frac{1}{\alpha}$ $\frac{1}{\alpha}$ $\frac{1}{\alpha}$ salt water solution [Odarczenko et al., 2018]. $\begin{array}{ccc}\n0 & 0 \\
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adsorbed onto steel surface. Thereafter, NQ-O O NQ-12 embedded in an epoxy coating OH (polyurethane shell) facilitates the anti- \circ c \circ c \circ thiol, NQ-26) were conducted on Au (111) O O of the adsorption consequences OH $_\sim$ $_\sim$ $_\sim$ OH $_\sim$ (physisorption and chem NQ-23 12 structure interacts with metal ion and $NQ-25$ surface. The study revealed that, the The use of NQ-12 and a water-based corrosive agent to remain dormant until it gets released by the damage and gets corrosion inhibition efficiency in a neutral and chemisorption) and dissociation possibilities of 5-hydroxy-3 butanedithiol-1,4-naphthaquinone (Jug-C4 adsorption process involves a dissociation path in which a hydrogen atom moves to the immediate neighboring site and a hydrogen atom migrates to its most stable site. More importantly, the effect of naphthoquinone function was found to be negligible in the adsorption process [Lassoued et al., 2018].

The corrosion inhibition effect of henna leaf extract having NQ-12 was demonstrated on carbon-steel ST37 empowered with hybrid coating of TMSM-PMMA (a fusion of 3 methacryloxypropyltrimethoxysilane and poly-methylmethacrylate) in HCl solution. The polarization tests had disclosed that henna extract had behaved as a mixed type of inhibitor and high inhibition efficiency was observed for 3% of henna extract concentration in TMSM-PMMA coating [Khoshkhou et al., 2018]. A review article was reported on the application of plant extracts as corrosion inhibitors for metals or alloys in an aggressive corrosive medium. Numerous plant parts as extracts and diverse metals or alloys being covered for the disclosure of their inhibition action. The work had even covered the use of henna extract having NQ-12 for the inhibition of corrosion [Verma et al., 2018]. Density functional theory based studies were disclosed regarding the application of henna extract (having NQ-12) for the corrosion prevention of iron in acidic medium.

The components of henna extract (NQ-12, gallic acid and D-glucose) had contributed to inhibit the corrosion process through efficient adsorption over iron surface. As per the study, NQ-12 and gallic acid had exhibited strong adsorption features on the metal than D-glucose. Among the three major constituents of henna extract, NQ-12 can have better corrosion inhibition efficiency than other molecules due to its favorable structural features [Kumar et al., 2018]. Some of the natural products like plant extracts, amino acids, proteins and biopolymers were used as anticorrosion agents for mild steel in acidic medium. Under the context, aloe-vera, banana sap and the henna extract having NQ-12 were found to exhibit higher inhibition capability than other green inhibitors. More importantly, the henna extract was more effective towards inhibition than the other extract samples [Pandian et al., 2018].

The spectral characterization and the use of Lawsonia inermis extract having NQ-12 was reported to retard the corrosion of aluminum alloy in seawater. The aluminum alloy 5083 was immersed in seawater in the absence and presence of henna extract and it was subjected to electrochemical impedance spectroscopy and potentio-dynamic polarization. As per the results, the corrosion inhibition was achieved by the effective adsorption of inhibitor (extract) on the aluminum surface [Zulkifli et al., 2017]. A

review article was disclosed with an emphasis on corrosion inhibitors for ferrousmetals, non-ferrous metals and alloys in NaCl solution. The work had disclosed the use of numerous sectors of inhibitors like inorganic salts, plant extracts, organic molecules including NQ-13 and a few dual mixtures [Verma, et al., 2017]. A comprehensive review article was reported on the corrosion inhibition of off-shore oil and gas production utilities using organic molecules (including NQ-12) as good corrosion inhibitors. The renowned inhibitors commonly used in oil and gas industry are multi-component synthetic organic molecules and phytochemicals of green inhibitors with S, N and O atoms in their molecular structure [Olajire, 2017].

A review article was published with an emphasis on the types of corrosion, corrosion process and the use of natural plant extracts as corrosion inhibitors for mild-steel. During the context, use of Lawsonia extract having NQ-12, resin, tannin, coumarin, gallic acid and sterols was highlighted as an effective natural corrosion inhibitor [Chigondo and Chigondo, 2016].

The corrosion inhibition properties of Lawsonia inermis leaf extract having NQ-12 was established on mild steel in acetic acid solution. The mixed-type inhibition efficiency of the leaf extract was estimated by weight-loss method, AC impedance and potentio-dynamic polarization measurements [Chaudhari and Vashi, 2016]. Lawsonia inermis extract having NQ-12 was used on aluminum alloy 5083 as an effective corrosion inhibitor in marine environment. The corrosion inhibition efficiency had increased as the concentration of henna extract was increased [Hajar et al., 2016]. Henna extract having NQ-12 was used for the corrosion inhibition of carbon-steel with the use of an acid in a well. This work was primarily focused on safeguarding the metals used in oil or gas fields from subterranean formations [Shankar and Patil, 2015].

The corrosion inhibitive action of extract mixture (henna and rosemary) was illustrated on stainless steel 304L in NaCl (3.5% by weight) solution. The inhibitive efficiency was established through

electrochemical tests and surface analysis for adsorption consequences. The work concludes by confirming that, these extract mixtures are very good adsorptive inhibitors in saline medium [Pourriahi et al., 2014]. A green methodology to prevent corrosion of mild-steel in 1.0M NaOH solution was reported. It was established by the use of an innovative mixture (henna extract and zeolite powder). The inhibition efficiency was established at various temperatures by weight-loss method. Meanwhile, the adsorption, activation and statistical studies were also covered in the initiative [Jayakumar et al., 2014].

An investigative study was conducted to explore the side effects (acid core flooding and surface wettability) of henna extract on reservoir rock grains. Meanwhile, the henna extract had shown very high corrosion inhibition efficiency on N80 steel in acidic medium. The same team [Abdollahi and Shadizadeh, 2012] had worked on the impact studies of acid additives on anti-corrosive behavior of henna extract having NQ-12 in regular mud acid. The inhibition impact was studied on steel API N80. The henna extract as alone inhibitor had displayed high inhibition efficiency than in the presence of additives [Abdollahi and Shadizadeh, 2013]. A review article was reported on the use of natural products to safeguard aluminum and its alloys in various conditions and their corrosion inhibition efficiencies. Meanwhile, supportive details like adsorption isotherms and protective film formation to retard corrosion was also discussed [Sangeetha et al., 2013].

A review article was disclosed regarding corrosion inhibition through greener approach. This initiative had highlighted the abilities of bio-origin compounds like tannins, organic amino acids, alkaloids, organic dyes as good corrosion inhibitors. The organic molecules in plant extracts (including henna extract) are made up of polar atoms such as O, P, S and N. These organic molecules adsorb on the metal surface through the polar atoms to form the firm impermeable barrier to inhibit corrosion [Patni et al., 2013]. The corrosion inhibition in carbon-steel was achieved by

the use of henna extract having NQ-12 in acidic medium. Based on the results, henna extract had behaved as mixed type inhibitor with good inhibition efficiency. Moreover, the work had explored the associated thermodynamics aspects, adsorption features and electrochemical studies [Hamdy and El-Gendy, 2013].

The aqueous extract of henna leaves having NQ-12 was used for the corrosion inhibition of carbon-steel in seawater conditions. The inhibition behavior was established by weight-loss method, polarization tests and AC impedance spectral studies. As per the outcome, henna extract had exhibited high inhibition efficiency by behaving as mixed type inhibitor [Johnsirani et al., 2012]. The extraction of NQ-12 from Lawsonia inermis plant and its application as a potential corrosion inhibitor on mild-steel in 1.0M HCl solution was disclosed. It was established through weight-loss method and the inhibition efficiency had increased with an increase in concentration of NQ-12 [Dananjaya et al., 2012]. A thin film coating preparation using henna extract having NQ-12 was illustrated to prevent the corrosion of stainless steel 316L. Polymerized vinyltrimethoxysilane (PVTMS) in ethanol was mixed with aqueous henna extract and refluxed to obtain the homogeneous sols. From these sols, nanostructure hybrid PVTMS/henna thin films were carefully deposited (via spin-coating technology) on stainless steel 316L.

These film coated metals had exhibited improved resistance to corrosion even in an aggressive environment. Thus, such a coated metal can be employed for various biomedical applications. The PVTMS coating embedded with 0.05% henna extract having NQ-12 gave the maximum corrosion inhibition efficiency [Motalebi et al., 2012]. Lawsonia inermis extract having NQ-12 was used as the natural corrosion inhibitor for aluminum alloy (5083) in seawater. The inhibition study was established based on the studies like weight-loss, fourier transform infrared, electrochemical impedance spectroscopy and adsorption isotherm. Highest inhibition efficiency (88%) was achieved by the use of henna extract

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(500ppm) in 60 days. The study had also hinted that, the adsorption of the extract was not permanent on the surface of aluminum alloy (5083) and hence precipitation had occurred as the duration extended [Nik et al., 2012]. A review article was reported on the use of plant origin materials over metal or alloys as green corrosion inhibitors. Under the context, numerous plant origin components were reported for their corrosion inhibition behaviors including henna extract having NQ-12 [Rani and Basu, 2012].

An extensive study was conducted on the molecular structure of seven quinone derivatives (including NQ-13) as corrosion inhibitors of mild-steel in neutral aqueous medium. It was stated that, the decrease in ionization potential and increase in dipole moment of quinone derivatives would make them better inhibitors. Furthermore, the variation in the geometric and electronic structure of ortho- and para- oriented molecules can also lead to varied inhibition efficiency and action mechanism [Stoyanova and Slavcheva, 2011].

Henna extract having NQ-12 was used as green corrosion inhibitor over aluminum alloy (AA5083) in seawater. The inhibition impact was established by weightloss estimation, fourier transform infrared, electrochemical impedance spectroscopy and potendio-dynamic polarization studies. The work had explored the extraction of henna extract in ethyl acetate and methanol. Interestingly, ethyl acetate extract had exhibited better corrosion inhibition features [Nik et al., 2011]. Anogessus leocarpus gum (AL gum) was used as an adsorption inhibitor for the corrosion of mild-steel in HCl solution. The composition study of AL gum by GCMS had revealed the presence of sucrose (10.03%), phthalic acid (2.53%), n-hexadecanoic acid (11.73%), oleic acid (30.49%), pentacenequinone (4.41%), and NQ-14 (21.43 %). The combination of these constituents will lead to the formation of multi-molecular layer of adsorption and inhibitor-metal complex, thus metal surface gets protection [Eddy et al., 2011].

The corrosion inhibition studies were conducted by the use of henna extract (Lawsonia inermis) and its main constituents like NQ-12, gallic acid, D-glucose and tannic acid on mild-steel in 1.0M HCl solution. The inhibition capability of the extract was established through electrochemical techniques and surface analysis (SEM/EDS). As per the study outcome, inhibition efficiency had enhanced with the rise in mixed inhibitor (extract) concentration and it had acted as a mixed type corrosion inhibitor to safeguard the metal [Ostovari et al., 2009]. A review article was published on the use of phytochemicals as corrosion inhibitors in various solution phases. The work disclosed the use of many plant origin components as inhibitors including henna extract having NQ-12 [Buchweishaija, 2009]. Aqueous henna extract having NQ-12 was used as corrosion inhibitor for carbon-steel in an aqueous solution containing 60 ppm of chloride ions. Inhibition efficiency was established by weight-loss method, in the absence and presence of zinc ions. The inhibition efficiency was found to be excellent in the presence of zinc ions, due to the formation of impermeable film comprising (Fe²⁺ with $NQ-12$) complex and zinc hydroxide [Rajendran et al., 2009].

A review article was reported on the use of natural products as corrosion inhibitors, which included henna extract having NQ-12. It had covered the insights on the rich sources of components which have very high corrosion prevention efficiency towards various metal and alloys in an aggressive medium [Raja and Sethuraman, 2008].

An extensive study was conducted to disclose the effective concentration of NQ-13 required for the corrosion inhibition of aluminum in aerated and de-aerated solutions of 0.5M NaCl. Numerous supportive tests were conducted and the result outcomes suggested that, the adsorption of NQ-13 on aluminum surface had significantly lowered the severity of pitting corrosion [Sherif and Park, 2006].

The aqueous extract of henna leaves having NQ-12 was demonstrated as corrosion inhibitor of carbon-steel, nickel

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and zinc in acidic, neutral and alkaline medium. The inhibition efficiency had enhanced as the concentration of extract was increased. Moreover, the complex formation between metal ions and NQ-12 was also explored to support the inhibition pathway [El-Etre et al., 2005].

The water soluble extracts of economic plants (date palm, corn and henna) were used as corrosion inhibitors for steel, aluminum, copper and brass in acidic and alkaline medium. Under the context, leaf extracts of date palm and henna (having NQ-12) were proved to be very effective in corrosion inhibition [Rehan, 2003].

The chemisorption of the active species in henna extract and its corrosion inhibition properties were investigated. The major active species in the extract are gallic acid, NQ-12, and dextrose. This eco-friendly extract was proved to be an effective inhibitor for steel and commercial grade aluminum in acidic and alkaline medium. But the same inhibition impact was not observed in saline conditions [Al-Sehaibani, 2000].

The role of seven organic molecules having quinonoid moiety (including NO-13) were investigated to retard corrosion in carbon-steel in neutral aqueous solutions (sodium sulphate, sodium chloride, sodium hydroxide and simulated cooling water medium). It was established based on electrochemical studies of those compounds which exhibited varied oxidizing and adsorption properties in different solutions [Slavcheva et al., 1993a].

The corrosion inhibition features of another nine organic molecules having quinonoid moiety (including NQ-13) were also disclosed. These compounds were examined for their inhibition behaviors on mild-steel corrosion in model cooling water. The inhibition efficiency depends on key factors like temperature, concentration and the type of the substance. Furthermore, the increase in molar mass, area, adsorption, number of complex bonds and conjugated benzene rings in the molecule had contributed to the increase in corrosion inhibition efficiency [Slavcheva et al., 1993b). The corrosion prevention in metals was achieved by the use of aqueous alkanolamine

solutions used in acid gas removal (industrial gas treating systems). In this scenario, the corrosion prevention was achieved by the use of combination of specific vanadium compounds and an organic compound having nitro-substituted aromatic acids, nitro-substituted acid salts, and 1,4-naphthoguinone (NQ-13) [McCullough and Kenneth, 1985].

A water dissociable and soluble salt of hydrazine catalyzed by the presence of various quinones (including NQ-13) was used as an effective corrosion inhibitor in aqueous systems. This inhibitor package was prepared for its application in boilers, hot water heating systems, water cooling systems etc [Sexsmith and Bruce, 1983].

Some organic amine compositions which are free from nitrosamine contaminants were used to retard corrosion. The composition had an organic amine and an inhibitor additive was chosen from the group consisting of NQ-13, 1,4 naphthohydroquinone, alkyl-derivatives of quinones and mixtures of the same [Gum and Nancye, 1981].

An innovative corrosion inhibiting composition was reported having a hydrazine compound, an organo-metallic complex and some quinones (including NQ-13). The work had explored the use of such compositions as oxygen scavengers in corrosive mediums [Noack. 1977].

A process was disclosed for distilling the corrosive carboxylic acids, which are free from olefinic unsaturation in a distillation apparatus constructed of metal. The major steps involved are introducing a crude dilute solution of corrosive acid into the distillation zone, distilling in the presence of an optimum quantity of para-benzoquinone or NQ-13 and recovering the concentrated corrosive acid from the distillation unit. The introduced additives would inhibit the corrosion of metals in the unit even under severe acidity [Clovis and Jerome, 1976].

An aqueous corrosion protection composition was reported comprising the mixture of aqueous hydrazine (having hydrazine hydrate and a water soluble ortho or para-quinone or naphthoquinone or anthraquinone). This corrosion protection initiative was concerned to metal surfaces in sealed vessels and pipe systems containing water [Herbert, 1970].

Numerous organic compounds were used as corrosion inhibitors of iron in sodium chloride solution. Certain classes of organic compounds, either alone or in combination were established experimentally as very good corrosion inhibitors. The compounds used for the studies include benzoquinones. napthoquinones, hydroquinones etc [Ardagh et al., 1933].

Furthermore, recently a review article was reported on the corrosion inhibition behavior of henna extract having NQ-12 to safeguard metals and alloys in various aqueous mediums [Vashi, 2024]. A gap filling study was conducted to establish the importance of henna extract (varied concentration) having NQ-12 as corrosion inhibitor for mild-steel in HCl medium. Supportive measurements had established that, the extract was able to alter both cathodic and anodic reactions [Okore et al., 2024]. A review article was published regarding the efficiency of plant extract/s in protecting steel in an acidic environment. The work had covered the importance of henna extract and its prime constituents including NQ-12 towards corrosion inhibition [Sharma et al., 2024].

Some novel substituted amino derivatives of 1,4-naphthoquinone were synthesized to estimate their activity against malaria and cancer. Under the context, these O , N , and S atom rich 1,4-naphthoquinones (NQ-27 series and NQ-28 series) can be taken up for corrosion inhibition studies in the near future to establish their importance towards safeguarding metals and associated alloys [Sanjay et al., 2022].

Summary

Table 2 will provide the collective data regarding the prior art disclosed natural or synthesized 1,4-naphthoquinones as potential corrosion inhibitors for different metals or alloys in varied environments. Under the context, eighty two publications were collected having the specific details of intended molecules as corrosion inhibitors. Among them, twenty four publications are exclusive review articles, book chapters and the remaining fifty eighty publications are original articles (published in academic journals, patent and trade mark office repositories).

Table 2: Summary of disclosed molecule/s in the literature towards corrosion inhibition of various metals and alloys

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Corrosion inhibition fundamentals

During corrosion inhibition, molecules/ions of the inhibitor will adsorb on the metal or alloy surface to form a firm protective barrier to restrict or retard the entry of H⁺ or dissolved oxygen. The determination of adsorption parameters like equilibrium constant and free enthalpy was possible only when one type of a molecule with known molecular weight was used as the inhibitor. If two or more molecules (phytochemicals in plant extracts) are used, then synergistic intermolecular actions would lead to corrosion prevention [Lrhoul et al., 2023; Verma et al., 2024].

 In the present collection of prior arts, there are numerous disclosures which are driven by plant extracts or mixture of biomolecules (phytochemicals) towards corrosion

inhibition. In that context, synergy of several molecules would contribute to adsorption phenomenon and hence the reported values of adsorption parameters will have no meaning in actual context.

The quinonoid structure has its own impact on the corrosion inhibition of metals or alloys. Some of the properties of these molecules like presence of θ atoms with unpaired electrons, π bonds and conjugated benzene rings would contribute to enhanced absorbability on the substrate surface. Additionally, an increase in the molar mass of the molecule also would assist the inhibition. For a few molecules it was established that, they decrease the rate of corrosion in neutral aqueous solutions. More importantly, the protective effect was attributed to their oxidizing properties. In some other cases, molecule would adsorb on the metal surface to form a impermeable

film and block the corrosion process [Slavcheva et al., 1993b].

Future scope

Use of biomolecules or phytochemicals rich plant extracts as natural corrosion inhibitors would be a good idea but the specific major molecule in the extract has to be identified and extracted in its pure form. Some simple and feasible chemical synthesis can be tried to manufacture such specific inhibitor molecules to commercialize the methodology. Moreover, still only a few synthesized 1,4 naphthoquinone derivatives are used for corrosion inhibition trials. A few popular 1,4-naphthoquinone drugs like Parvaquone (NQ-29), Buparvaquone (NQ-30), Atovaquone (NO-31) etc [Khan et al., 2023] could be tested as the potential corrosion inhibitors. In line to this, some of the expired drugs are used previously as efficient corrosion inhibitors to safeguard metals or alloys [Vaszilcsin et al., 2023].

Figure 13. NQ-29; NQ-30; and NQ-31

Conclusion

It was observed that, NQ-12 and NQ-13 are the major but structurally simple natural 1,4-napththoquinones used as corrosion inhibitors as alone or as extracts until 2018. In later years, a numerous 1,4 naphthoquinones were used by the researchers around the globe to establish the importance of these moieties towards corrosion inhibition. This review article

would contribute to uplift the technological significance to 1,4-naphthoquinones towards safeguarding metals or alloys. Meanwhile, some of the drug molecules (regular/expired) having naphthoquinone chromophore can also be tested for corrosion inhibition behavior under drug repurposing initiatives. This initiative becomes a selective attempt to collect all the research and review disclosures related to corrosion inhibition by natural and synthesized 1,4-napthoquinones in different forms. During the process, many academic journal articles and a few filed patents were traced, examined and its salient features were extracted to have a systematic flow of information about the corrosion prevention feasibility. This review venture would facilitate the emergence of new 1,4 naphthoquinones as potential corrosion inhibitors. This can happen through the use of various phytochemical extracts or alone derivatives having 1,4-naphthoquinone ring in their molecular structure.

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