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# Corrosion Inhibition Property of Plants, Seeds, Leaves, and Fruits: A Review

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**ABSTRACTS:** Plants, seeds, leaves, and fruits as a Natural inhibitors are investigated for mild steel corrosion in acidic media using weight loss, potentiodynymic electrochemical impendence spectroscopy, scanning electron microscopic study, and FTIR studies. While claiming natural material as a corrosion Inhibitor many researchers took synthetic organic compound into account as a inhibitor. Many researcher shown through the study the influence of compounds present in plants and their structure, concentration, method of application as well as media that inhibitor is used in on inhibition efficiency. Moreover, action mechanisms are studied. Corrosion inhibition mechanism was well supported by applying the Freundlich adsorption isotherm, Temkin and Frumkin adsorption isotherms.

For the corrosion inhibition of mild steel, the possible reaction centers are unshared electron pair of heteroatom's and π- electrons of aromatic/heterocyclic ring. In aqueous acidic solutions, main constituents exist either as neutral molecules or as protonated molecules (cations). The inhibitors may adsorb on the metal/acid solution interface by one and/or more of the following ways: (i) electrostatic interaction of protonated molecules with already adsorbed chloride ions, (ii) donor-acceptor interactions between the π-electrons of aromatic ring and vacant d orbital of surface iron atoms, (iii) interaction between unshared electron pairs of hetero atoms and vacant d-orbital of iron surface atoms.

The mechanism of physical adsorption is also supported from the values of some kinetic and thermodynamic parameters such as energy of activation.

**Keywords:** Mild steel, weight loss, heterocyclic ring, protonated molecules, inhibitor.

## I. INTRODUCTION

Corrosion is the destructive attack on a metal or metal alloy by chemical or electrochemical reaction with its environment [1]. Corrosion of metal is a major industrial problem that has attracted a lot of investigators in recent years[2-4]. Mild steel find a variety of application owing to its easy availability, ease of fabrication, excellent tensile strength, workability and low cost. It suffers from severe corrosion when it comes in contact with acid solutions during acid cleaning, transportation of acid, descalling, storage of acid and other chemical processes. The heavy loss of metal as a result of its contact with acids minimized to a great extent by use of inhibitors. Inhibitors are chemicals that often work by adsorbing themselves on metallic surface, protecting the metal surface by forming the film.

The scientific and corrosion literature has descriptions and list of numerous chemical compounds that exhibit inhibitive properties for steel in acidic solutions, e.g.azoles, amines, amino acids, alkenyl phenones, aromatic aldehydes, nitrogen-containing heterocyclic and their quaternary salts and condensation products of carbonyls and amines [4–11]. It is noticed that presence of heteroatom's such as nitrogen, sulphur, phosphorous in the organic compound molecule improves its action as a corrosion inhibitor in mild steel. It can be explained by the presence of vacant d orbital's in iron atom that form coordinative bonds with atoms able to donate electrons. Based on these facts more and more compounds containing numerous heteroatom's and functional groups are synthesized by many research workers as they are responsible for good properties regarding corrosion inhibition because they enable chemisorptions, also molecular weight is larger which facilitate physical adsorption[6-11]. Although synthetic organic compounds [12–13] have proved to be effective in inhibiting the corrosion of metals specially mild steel in acidic corrosive environment, the high cost and toxic nature of some of the compounds have been seen as a major setback. The need to develop economical, non-toxic, readily available as well as environmentally friendly processes to fill this gap has now made researchers to focus on the use of natural products and plant extracts as corrosion inhibitors.

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In the present paper comprehensive review has been carried out to understand the role of plants, seeds, leaves, and fruits as a Natural inhibitors in order to protect mild steel corrosion in acidic media using weight loss, potentiodynymic electrochemical impendence spectroscopy, scanning electron microscopic study, and FTIR studies. Study also reflect the need to make a review that would sum the results published by now and serve as a guidance for the future research.

**Ajwan Seeds extracts**

Asha M. Turkustani[14] investigated the effect of Ajwan Seeds as corrosion inhibitor on carbon steel in sulphuric acid medium. The inhibition mechanism is explained on the basis of weight loss, hydrogen evolution study. It has been mentioned that organic compound present in the Ajwan seeds such as Thymol,y-terpinene, p-cymene,b-pinene alpha- pinene and limonene can adsorbs on steel surface which protects the metal from the corrosion .Inhibition may be due to synergistic action of these compounds. The inhibition mechanism is also supported by Potentiodynamic polarization curves. The data revealed that Ajwan Seeds extract extracts retards both anodic and cathodic processes ( metal dissolving and hydrogen evolution).It has been also noted that presense of Ajwan seeds extract has pronounced effect on the corrosion current and shifts the potential by = 20mv to more negative potential value and remain approximetly constant by increasing the Ajwan extracts concentrations.

**Black pepper and piperine extract**

M.Dahamani and et al.[14] studied the comparative corrosion inhibition effect of Black pepper extract and piperine isolated from Black pepper on C38 carbon steel in 1 M HCl solution. Piperine isolated in ethanol from Black pepper and used for corrosion Inhibition study. They have reported 95% inhibition efficiency in Black pepper and 99% in piperine. Inhibition efficiency increases with the concentration of piperine. Adsorption enthalpy and activation energy was evaluated using Arrhenius equation and discussed with reference to corrosion inhibition efficiency .Effect of temperature on inhibition mechanism was studied and maximum efficiency Obtained at $60^{o}$c .The data revealed that this inhibitor may be useful for industrial descalling.

**Uncaria Gambir extract**

Mohd.Hazwan Hussain and Mohd.Jain Kassim[15] conducted the research of the effect of the Uncaria Gambir extract on the mild steel corrosion inhibition in aqueous solution having pH 5.The inhibition efficiency by ethyl acetate extract containing catachin has been studied by weight loss, Potentiodynymic polarization ,electrochemical impedance spectroscopy, scanning electron microscope technology with energy dispersive X-ray spectroscopy. Inhibition was found to be highest at 150 ppm inhibitor concentration. The overall mechanism shows that ethyl acetate extract of U.Gambir acts as mixed inhibitor.

**Pineapple leaves (Ananas Comosus L.) extract**

U. F. Ekanem et al.[16] Studied the effect of pineapple leaves (Ananas Comosus L.) extract on the corrosion Inhibition of mild steel in HCl using weight loss and hydrogen evolution methods at 30–$60^{0}$C. It was found that the pineapple leaves extract inhibited the acid induced corrosion of mild steel. The inhibition efficiency increases with increase in the extract concentration and with rise in temperature. Adsorption of the extract was found to obey Langmuir adsorption isotherm at all the concentrations and temperatures studied. The mechanism of chemical adsorption is proposed from the trend of inhibition efficiency with temperature. The proposed mechanism was also corroborated by kinetic and thermodynamic parameters obtained. Studies by some research groups have also shown that the ethanolic extract of pineapple leaves is composed of ananasate, 1-O-caffeoylglycerol, 1-O-p- coumaroylglycerol, caffeic acid, p-coumaric acid, b-sitosterol, and daucosterol [17,18]. It is, therefore, pertinent to say that the adsorption of these compounds onto mild steel surface is responsible for corrosion inhibition. It has been pointed out that the increase in inhibition efficiency with increase in extract concentration is an indication of an increase in the number of components of the extract adsorbed over the mild steel surface blocking the active sites, in which direct acid attacks proceed and protect the metal from corrosion, while the increase in inhibition efficiency with temperature rise is suggestive of strong adsorption of the phyto-constituents of the extract on the mild steel surface forming a protective layer and shielding the metal from corrosion [19,20].

The effect of temperature on corrosion rate was evaluated using Arrhenius equation: v=A [ exp (-Ea/RT)] .where v is the corrosion rate, Ea is the apparent activation energy of the mild steel dissolution, R is the molar gas constant, T is the absolute temperature, and A is the frequency factor. The calculated values of activation energy are listed in Table 3. It can be seen in the table that Ea

is lower in the presence of the inhibitor than in the absence of the inhibitor. This observation further supports the proposed chemisorption mechanism because unchanged or lower Ea in inhibited systems compared to blank is also reported by many research workers [21-24]. Increased Ea values revealed the physical adsorption mechanism. It has been found that Ea monotonously decreases with increase in extract concentration with the lowest value (52.5 kJ mol-1) being obtained at the highest extract concentration (0.5 g/L) .

**Rauvolfia serpentina extract**

Alkaloid extract of Rauvolfia serpentina was investigated by P. Bothi Raja and M.G. Sethuraman[25] as corrosion inhibitor for mild steel in 1 M HCl and $H_2SO_4$ using weight loss method at three different temperatures, viz., 303, 313, and 323 K, Potentiodynamic polarization, electrochemical impedance spectroscopy and scanning electron microscope (SEM) studies. It is evident from the results of this study that R. serpentina effectively inhibits the corrosion in both the acids through adsorption process following Tempkin adsorption isotherm. The protection efficiency increased with increase in inhibitor concentration and temperature. Free energy of adsorption calculated from the temperature studies also revealed the chemisorptions. The mixed mode of action exhibited by the inhibitor was confirmed by the polarization studies while SEM analysis substantiated the formation of protective layer over the mild steel surface.The impedance results show that corrosion inhibition takes place through charge transfer process.

**Bridelia retusa leaves extract**

Niketan Patel[26] investigated the extract of Bridelia retusa leaves as corrosion inhibitor of mild steel in 1N $H_2SO_4$ medium by weight loss, electrochemical polarization and electrochemical impedance spectroscopy and scanning electron microscopic studies. The weight loss result showed that extract of Bridelia retusa leaves is excellent corrosion inhibitor. Inhibition efficiencies found to be 91.6% at higher concentration of 200 ppm at 303K. Inhibition properties may be due to the adsorption of nitrogenous compounds in the extracts or tannin on the metals surface present in the extract [27].

Tannins are the complex astringents aromatic acidic glycosides found in various plants and there can be ruled out as they made up of polyphenols and their acidic and heterocyclic derivatives, because such constituents would not have extracted in acids. Polar organic compounds containing N, S, and O are good corrosion Inhibitors [28].These species are responsible for the formation of film oriented film layer by the adsorption of active constituents of the extract on the MS surface which essentially blocks the dissolution of metal ions.

The adsorption of the inhibitor is influenced by the nature of charge of the metal and its chemical structure of the inhibitor, distribution of charge in the molecule and type of electrolyte. The adsorption of the inhibitor follows the Langmuir adsorption isotherm.

**Fruit peels of mango, and orange extract**

Janaina Cardozo da and et al.[29] was investigated the inhibitive action of the aqueous extracts of fruit peels of mango, orange against corrosion of carbon steel in a 1 M HCl solution using electrochemical impedance spectroscopy, potentiodynamic polarization curves, weight loss measurements and surface analysis. Researcher analyzed aqueous extracts of mango, orange, passion fruit and cashew peels in different concentrations and found that the extracts act as good corrosion inhibitors for the tested system. The inhibition efficiency increases with increasing extract concentration and decreases with temperature. The adsorption of components of the fruit peel extracts on the surface of the carbon steel follows the Langmuir adsorption isotherm.

**Nyctanthes arbortristis extract**

R.Saratha and V.G.Vasudha[30] investigated the efficiency of acid extract of dry Nyctanthes arbortristis (Night Jasmine, Coral Jasmine) leaves as corrosion inhibitor for mild steel in 1N $H_2SO_4$ by weight loss and polarization studies. The results indicate Nyctanthes arbortristis leaves to be a good corrosion inhibitor of a mixed type and having efficiency as high as 90% at 1% inhibitor concentration. The mixed mode of inhibitor was explained on the basis of Tafel constant obtained through Potentiodynamic polarization studies. Tafel constant $b_a$ and $b_c$ markedly change in presence of the acid extract of the plant. The corrosion current values are also found to increase in presence of acid extract of the plant.From the Impedance study researcher claim that corrosion current decreases with inhibitor concentration. It has been stated that Phytoconstituents in the leaves of Nyctanthes arbortristis contain an alkaloidal principle named Nyctanthine. Leaves also contain mannitol, astringent principles, resinous substances, colouring matters, tannic acid, flavonoids and iridoid glucosides[31,32] . Due to the presence of these heterocyclic compounds

adsorption of the plant constituents on the metal surface is facilitated. Inhibition efficiency of NAL extract may be explained as due to the adsorption of these compounds on the metal surface thereby blocking the surface and protecting the metal from the aggressive atmosphere.

**Curry Leaves (Murraya Koenigii) extract**

The inhibitive action of extract of curry leaves (Murraya koenigii) on carbon steel in 1N HCl has been studied using weight loss, gasometric studies and electrochemical polarization and AC impedance measurements has been studied by **Sharmila** et al.[33] ·The effect of temperature on the corrosion behaviour of carbon steel in 1N HCl with optimum concentration of inhibitors was studied in the temperature ranging from 30 -80°C. The protective film formed on the surface of carbon steel by the adsorption of extracts in 1N HCl solution was confirmed by SEM studies. From weight loss data Inhibition efficiency was found to be 84.6% found at moderate concentration of inhibitor (4%v/v) and minimum inhibition efficiency was found to be at maximum concentration of inhibitor (10 %v/v). Inhibition efficiency is also supported by gasometric method. Researcher found that the results obtained from gasometric method are fall in line weight loss method.

**Bixin, Zenthoxlum almauta ,Echitamine, and Nyctanthin extract**

D.K. Gupta and et.al.[34] studied the effect of Bixin, Zenthoxlum almauta ,Echitamine, and Nyctanthin extract as corrosion inhibitor for mild steel and other metals in HCl and halide medium by weight loss method. The inhibition efficiency increases in the following order. Bixin < Zenthoxlum almauta < Echitamine < Nyctanthin this sequence reflects the effect of type of the unit present in the compound and their inhibitive action. The general trends of inhibitor performance of the inhibitor are similar as investigated by many research workers [27,28, 29].

**Hibiscus Syriacus Linn extract**

Prabavathi Nagarajan[35] studied the influence of the addition of the extract of naturally occuring Hibiscus Syriacus Linn and the flavonoid component Rutin on the corrosion of mild steel in 1M hydrochloric acid by weight loss measurement, gasometric and polarization study in the presence and absence of quaternary ammonium salt. It is observed that the extract of the plant and Rutin reduces the corrosion rate and the inhibition efficiency increases with increase in inhibitor concentration. It has been reported that the biological systems have the corrosion inhibition efficiency due to the functional groups present in aromatic and .heterocyclic rings along with electron rich elements like nitrogen, sulphur and oxygen. These substances are found to adsorb on the corroding metal surface and reduce the corrosion rate.

**Kalmegh (Andrographis paniculata) Leaves extract**

The role of Kalmegh (Andrographis paniculata) Leaves extract as Green Inhibitor was investigated for Mild Steel in Hydrochloric acid solution by using weight loss, electrochemical impedance spectroscopy, linear polarization, and potentiodynamic polarization techniques by Ambrish Singh, and et al [36] . Inhibition was found to increase with increasing concentration of the extract. The effect of temperature, immersion time, and acid concentration on the corrosion behavior of mild steel in 1M HCl with addition of extract was also studied. The inhibition was assumed to occur via adsorption of the inhibitor molecules on the metal surface. The adsorption of the molecules of the extract on the mild steel surface obeyed the Langmuir adsorption isotherm. The protective film formed on the metal surface was analyzed by FTIR spectroscopy. The inhibition property is due to main constituent of Kalmegh (Andrographis paniculata) leaves extract is Andrographolide having multiple bonds through which they get adsorbed on the mild steel surface. The high performance of Kalmegh (Andrographis paniculata) leaves extract could also be due to large size of constituent's molecule which covers wide areas on the metal surface and thus retarding the corrosion[37] Kalmegh (Andrographis paniculata) leaves extract is composed of numerous naturally occurring organic compounds. The inhibitive action of Kalmegh (Andrographis paniculata) leaves extract toward the acid corrosion of steel can be attributed to the adsorption of Kalmegh (Andrographis paniculata) leaves extract components onto the steel surface. FTIR showed that the leaves extract contains oxygen atoms in functional groups (O–H, C=C, C=O, C–H, C–O) and aromatic ring, which meets the general consideration of typical corrosion inhibitors. The no- bonded electrons of heteroatoms get protonated and thereby they get adsorbed on the negatively charged metal surface. Due to electrostatic interaction, the protonated constituent's molecules are adsorbed (physisorption) and high inhibition is expected. Kalmegh (Andrographis paniculata) leaves extract molecules can also adsorb on the

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metal surface on the basis of donor-acceptor interactions between π-electrons of aromatic ring and vacant d-orbitals of Fe. Similar study is also supported by studding the fruits extract of Shahjan (Moringa oleifera), Pipali (Piper longum) and Orange (Citrus aurantium).

**Eclipta Alba extract**

M. Shyamalay and A. Arulanantham[38] studied the Eclipta Alba as Corrosion Pickling Inhibitor on Mild Steel in Hydrochloric Acid medium. Corrosion inhibition effect of aqueous extract of Eclipta alba in 1 N hydrochloric acid has been investigated by weight loss, Potentiodynamic polarization and impedance methods and the extracts of Eclipta alba were found to be effective corrosion pickling inhibitor. The effect of immersion time and temperature revealed that the extracts of Eclipta alba with an optimum concentration of 8.0% v/v showed maximum inhibition efficiency of 99.6% at 3 hours immersion time and at 30±$^0$C. Arrhenius plots for mild steel immersed in 1 N HCl solution in the absence and presence of optimum concentration (8.0% in v/v) of Eclipta alba extract showed the effect of temperature. Polarization studies indicate that this plant extract acts as a mixed type inhibitor. The adsorption of Eclipta alba follows Langmuir adsorption isotherm. The inhibition action may be due to the presence of the Wedelactone and also the alkaloid Ecliptine present in the leaves of Eclipta Alba.

M. Shyamalay and A. Arulanantham also cliam that the transition of metal/solution interface from a state of active dissolution to the passive state is attributed to the adsorption of the inhibitor molecules at the metal/solution interface, forming a protective film. The rate of adsorption is usually rapid and hence, the reactive metal surface is shielded from the aggressive environment [39].Adsorption process can occur through the replacement of solvent molecules from metal surface by ions and molecules accumulated in the vicinity of metal/solution interface. Ions can accumulate at the metal/solution interface in excess of those required to balance the charge on the metal at the operating potential. These ions replace solvent molecules from the metal surface and their centers reside at the inner Helmholtz plane. This phenomenon is termed specific adsorption, contact adsorption. The exact nature of the interactions between a metal surface and an aromatic molecule depends on the relative coordinating strength towards the given metal of the particular groups present [40].

**Henna extract (Lawsonia inermis) extract**

The inhibitive action of henna extract (Lawsonia inermis) and its main constituents (lawsone, gallic acid, α-D-Glucose and tannic acid) on corrosion of mild steel in 1 M HCl solution was investigated by A. Ostovari and et. al.[41] through electrochemical techniques and surface analysis (SEM/EDS). Polarization measurements indicate that all the examined compounds act as a mixed inhibitor and inhibition efficiency increases with inhibitor concentration. Maximum inhibition efficiency (92.06%) is obtained at 1.2 g/l henna extract. Inhibition efficiency increases in the order: lawsone > henna extract > gallic acid > α-D-Glucose > tannic acid.

**Ocimum Basilicum and Cucurbita Pepo extracts**

Badiea A.M.and et.al[42] studied Inhibition efficiencies of Ocimum Basilicum and Cucurbita Pepo extracts on low carbon steel corrosion in industrial water have been investigated using mass loss, electrochemical measurements, and SEM. It was found that the plant extracts chosen revealed good performance as green inhibitors for low carbon steel in industrial water and their inhibitive performance was improved with increasing of concentration up to critical values of 2.96 and 5.25 g $L^{-1}$ for cucurbita and ocimum, respectively. Adsorption of these plant extracts obeyed Flory-Huggins's isotherm. Thermodynamic parameters were evaluated and discussed. SEM was carried out to characterize the film formed on the metal surface.

**Azadirachta indica extracts**

Azadirachta indica is composed of numerous naturally occurring organic compounds. Over 300 compounds have been isolated and characterized from the plant. Among these are: azadirachtin, azadirone, gedunin, nimbin, nimbandiol, nimbinene, nimbolide, nimonol, nimbolin, salannin,margolone, melianol, vilasanin, flavanoids and structurally related compounds [43-48]. Most of these compounds have complicated molecular structures, large molecular weights and significant number of oxygen, sulphur and nitrogen atoms incorporated in the structure. These compounds can absorb on the metal surface via the lone pairs of electrons present on their oxygen, sulphur and nitrogen atoms. The adsorption of such compounds on the metal surface creates a barrier for charge and mass transfer leading to a decrease in the interaction between the metal and the corrosive environment. As a result, the corrosion rate of the metal is decreased. According to Patel[49,50]. the inhibition properties of plant extracts

may be due to the presence of nitrogenous compounds in the extract[51] and tannins.Tannins [46] are complex astringent aromatic glycosides found in various plants. They are made up of polyphenols and their acidic and heterocyclic derivatives. Polar organic compounds containing N, S. O atoms are good corrosion inhibitors[51]. They may have been responsible for the formation of an oriented film layer which essentially blocks discharges of $H^+$ and dissolution of metal ions. Acid pickling inhibitors containing organic N, amine, S and OH groups behave similarly to inhibit corrosion. This complex composition of Azadirachta indica makes it difficult to assign the observed corrosion inhibitive effect to a particular constituent. However, one-third of the isolated compounds from Azadirachta indica are tetranortriterpenoids (limonoids). One of the limonoids is azadirachtin, the most potent, environmental friendly biodegradable pesticide, with growth-inhibiting properties at very low concentration[52]. Azadirachtin has been isolated from all parts of the Neem tree, but is present at highest concentration in the mature seeds[53]. From the trend in inhibition efficiencies (SD > RT > LV).

**Strychnos nux-vomica extract**

P.Bothi Raja and et.al [54] studied the inhibition efficiency of the extract of Strychnos nux-vomica for the corrosion of mild steel in 1 M sulfuric acid using weight loss test (carried out at 303–323 K), electrochemical measurement, and scanning electron microscope (SEM). The results of weight loss studies indicated that the inhibition efficiency increased with inhibitor concentration and the temperature of the system (following Temkin adsorption isotherm). Electrochemical studies proved that the inhibitor acts through mixed mode of inhibition and the inhibitor molecules adsorb on the metal–solution interface. SEM studies supported the adsorption of the inhibitor over the metal surface. The possible active ingredient responsible for the anticorrosion effect is identified as brucine which is isolated and screened for the anticorrosion effect using electrochemical studies and quantum chemical studies. The possible mode of corrosion inhibition of brucine is also derived using FT-IR studies.

## II. CONCLUSION:

A single adsorption mode between inhibitor and metal surface because of the complex nature of adsorption and inhibition of a given inhibitor. The adsorption of main constituents of leaves, seeds and fruit extract can be attributed to the presence of O-atoms, π- electrons and aromatic/heterocyclic rings. Presence of methoxy group also enhances the inhibition efficiency. Therefore, the possible reaction centers are unshared electron pair of heteroatom's and π-electrons of aromatic/heterocyclic ring. In aqueous acidic solutions, main constituents exist either as neutral molecules or as protonated molecules (cations). The inhibitors may adsorb on the metal/acid solution interface by one and/or more of the following ways: (i) electrostatic interaction of protonated molecules with already adsorbed chloride ions, (ii) donor-acceptor interactions between the π-electrons of aromatic ring and vacant d orbital of surface iron atoms, (iii) interaction between unshared electron pairs of hetero atoms and vacant d-orbital of iron surface atoms. Generally two modes of adsorption are considered on the metal surface in acid media. In one mode, the neutral molecules may be adsorbed on the surface of mild steel through the chemisorption mechanism, involving the displacement of water molecules from the mild steel surface and the sharing electrons between the hetero atoms and iron. The inhibitor molecules can also adsorb on the mild steel surface on the basis of donor–acceptor interactions between π-electrons of the aromatic / heterocyclic ring and vacant d-orbital's of surface iron atoms. In second mode, since it is well known that the mild steel surface bears positive charge in acid solution.

Based on various facts, it can be said that many natural compounds can be used as corrosion inhibitors for mild steel in acidic media. Media that inhibitor is used in is very important for selection. The presence of aggressive ions and pH are important parameters. Action mechanism is almost same for most of the inhibitors. These inhibitors form a protective layer by adsorption of physiochemical constituents present in plants. Higher inhibitor concentration and longer exposure of mild steel in inhibitor solution lead to inhibition efficiency increase. Molecular structure of the inhibitor, Hetero atoms N, S, and o with free electron pairs many aromatic compounds with delocalized π electrons, and high molecular weight of inhibitor fevours the inhibition efficiency.

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