

Research Article

# Experimental investigation of anti-corrosive behaviour of *Beta vulgaris*: A green approach

<b>Shramila Yadav</b> Department of Chemistry, Rajdhani College, University of Delhi, New Delhi – 110015, India	Article Info https://doi.org/10.31018/
Shikha Kaushik Department of Chemistry, Raidhani College, University of Delhi,	Received: July 26, 2023
New Delhi – 110015, India	Accepted: September 18, 2023
Neelu Dneer Department of Chemistry, Acharya Narendra Dev College University of Delhi, New Delhi – 110019, India	
Sarita Kumar	
Inspect Pest and Vector Laboratory, Department of Zoology, Acharya Narendra Dev College University of Delhi, New Delhi – 110019, India	
Gurmeet Singh	
Vice Chancellor, Pondicherry University, Pondicherry, India Mansi Y. Chaudhary* 💿	
Department of Chemistry, Rajdhani College, University of Delhi, New Delhi – 110015, India <b>Meenakshi Gupta*</b> 🝺	
Department of Chemistry, Atma Ram Sanatan Dharam College, University of Delhi, New Delhi - 110010, India	
* Corresponding author. E-mail: meenaxi1978@gmail.com; corrosion.mansi@gmail.com	

# How to Cite

Yadav, S. *et al.* (2023). Experimental investigation of anti-corrosive behaviour of *Beta vulgaris*: A green approach. *Journal of Applied and Natural Science*, 15(3), 1315 - 1325. https://doi.org/10.31018/jans.v15i3.4969

# Abstract

The loss of metals due to corrosion can be prevented using green inhibitors. Using natural and eco-friendly plant products is futuristic, preventing the environment from toxic and harmful chemicals. The present study aimed to investigate whole beetroot (BR, *Beta vulgaris*) for its anti-corrosion behaviour by galvanostatic polarization and electrochemical impedance techniques at a temperature between 298 K- 328 K. The temperature study would help in proposing BR's adsorption mechanism on metal surfaces. The maximum inhibition efficiency of 94% at 298 K for 5% BR was observed, whereas a minimum of 75% was obtained for 1% BR at 328 K. It was found to be a mixed-type inhibitor that followed Langmuir isotherm. From thermodynamic studies,  $\Delta G^{o}_{ads}$  was found to be -13.64 kJ/mol, which revealed that BR adsorbed physically on the surface of mild steel. R<sub>ct</sub> values increased while C<sub>dl</sub> values decreased on exposure of metal surface with BR extract. The scanning electron micrographs (SEM) and atomic force micrographs (AFM) witnessed the formation of a protective layer on the mild steel surface, which served as a barrier between the metal and corrosive medium. The present study provides a remedy for the financial and structural losses due to metal corrosion in an acidic medium.

Keywords: Corrosion, Electrochemical Impedance Spectroscopy, Mild Steel, Langmuir isotherm, Physical adsorption

# INTRODUCTION

Mild steel deterioration is one of the major concerns as it is widely used in various industries including processing, water pipes, cooling water systems, boilers, refining and mining of gas, oil industries, and skyscrapers (Habeeb *et al.*, 2018; Alibakhshi *et al.*, 2019; Badr *et al.*, 2018 and Medupin et al., 2013). It is low cost, affordability, high mechanical power, and ease of processing encouraged its widespread usage as an industrial input (Punitha *et al.*, 2022 and Muthamma *et al.*, 2021). The main problem associated with using mild steel (MS) in industry is its resistance against corrosion, especially in acidic solutions (Habeeb *et al.*,

This work is licensed under Attribution-Non Commercial 4.0 International (CC BY-NC 4.0). © : Author (s). Publishing rights @ ANSF.

2018). Corrosion is described as the physicochemical reaction between a metal and its environment that significantly changes the properties of the metal, environment and its technical system. (Umeozokwere et al., 2016; Chaouiki et al., 2020 and Chugh et al., 2020). Corrosion results in the formation of many useless products, which reduces the structural stability and durability of metal system. It is a major concern in sectors where acids are being used for many purposes. Many inorganic and organic corrosion inhibitors are being investigated and used as inhibitors to prevent various metals from being eaten away due to corrosion (Abdallah et al., 2006; Yohai et al., 2013; Durowaye et al., 2014; Zou et al., 2014; Goyal et al., 2018 and Caldona et al., 2021). Numerous researchers have studied the suitability of various organic compounds as inhibitors, particularly those containing chromate, other heavy metals, and heterocyclic compounds, which are gradually being restricted as they have toxic effects on the environment. In the present time, awareness of the toxic effects of these chemicals has resulted in shifting towards the green revolution in industries too. Therefore, using natural and eco-friendly plant products is futuristic, and they have several advantages such as availability, biodegradability, efficiency, and they are environmentally friendly and renewable. Origanum vulgare has been investigated as a corrosion inhibitor on aluminium and mild steel in an acidic medium, resulting in 97.7% and 91.4% efficiency, respectively (Bashir et al., 2018; Dhaundiyal et al., 2019). The extract of Asparagus racemosus proved to be a good corrosion inhibitor, and it follows Langmuir adsorption isotherm (Bashir et al., 2017). In a study by Rodríguez et al. (2018), inhibition efficiency of 97% was reported for Prunus persica leaves extract in the presence of sulphuric acid. Prunus persica extract retards both cathodic and anodic reactions but with cathodic predominance. The same trend of inhibition efficiency was reported for rhizome extracts of Acorus calamus on mild steel corrosion (Kumar et al., 2013). Numerous plant extracts from plant leaves, barks, seeds, fruits, and roots have shown promising behaviour to inhibit the corrosion of metals in different aggressive media (Ambrish et al., 2012; Sangeetha et al., 2012; Prabakaran et al., 2017; Al Otaibi et al., 2021 and Sajadi et al., 2022). The plant extracts are rich in nitrogen, sulphur and oxygen-containing functional groups, which have free electrons that can bind to partially dissolved metal ions, retarding further dissolution and exhibiting good corrosion inhibition (Victoria et al., 2015; Aribo et al., 2017 and Verma et al., 2018).

Beetroot is an edible plant of the *Amaranthaceae* family (Nikan *et al.*, 2019) and is distributed throughout Asia Minor, the Mediterranean, and Europe. BR benefits the human body's ionic balance, which is associated with low sodium concentrations and significant potassium

and magnesium content. The high content of red colour content (betacyanins), high vitamins (B and C), minerals, and fibre present in BR are responsible for its beneficial dietary and medicinal effects.

Betacyanins reduce oxidative stress and the harmful effects of free radicals as well as exhibit antibacterial and antiviral properties, which inhibit the proliferation of cancer cells and are involved in the prevention of cardiovascular diseases (Nikan *et al.*, 2019 and Chhikara *et al.*, 2019). The processing of beets and the consumption of products made from them has increased rapidly since it was recognized as an extremely rich source of antioxidants (Balázs, 1994; Székely & Máté, 2022). A significant amount of essential and non-essential amino acids is also present in BR (Nemzer *et al.*, 2011). The present study aims to investigate the extract of whole beetroot (BR) in sulphuric acid medium as an inhibitor of corrosion of mild steel.

The corrosion inhibition of mild steel in well water (Selvi *et al.*, 2009), in simulated oil well water (Joycee *et al.*, 2022) and in HCI medium (Nagiub *et al.*, 2016) by the extract of beetroot has been studied and reported. The corrosion inhibition by beet extract has also been reported on aluminium metal in aqueous medium (Nithya *et al.*, 2015) and all these studies have shown promising results. The present study aimed to investigate the corrosion inhibition of mild steel in 0.5 M  $H_2SO_4$  using the extract of *Beta vulgaris* (BR) by electrochemical studies, temperature kinetics, electrochemical impedance studies (EIS) and surface morphology using Scanning electron microscopy (SEM) and Atomic force microscopy (AFM).

## MATERIALS AND METHODS

### Preparation of beetroot extract

Beta vulgaris, commonly known as beetroot, subfamily Betoideae of the family Amaranthaceae, was purchased from the local market of North Delhi, India. It was then washed and cleaned. 150 g of the whole root was taken in a round bottom flask and was refluxed with 250 ml of 0.5 M H<sub>2</sub>SO<sub>4</sub> for 8 hours. It was kept overnight to extract the basic components. After extraction, the resultant acidic solution of BR was filtered off and used as a stock solution for all the studies. Various concentrations (v/v %) 1%, 3%, 4% and 5% of the extract were prepared by dissolving the desired volume in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

#### Mild steel specimen

The present study used a mild steel specimen with a chemical composition of 0.15% carbon, 1.02% manganese, 0.8% silicon, 0.025% sulphur, 0.025% phosphorous, and the rest iron. The specimens of dimensions 3.0 cm×1.0 cm×1.0 cm soldered on one end with an insulated Cu (copper) wire embedded in epoxy resin,

leaving a working area of  $1 \text{ cm}^2$ , were used for electrochemical studies. Coupons of  $1 \text{ cm} \times 0.4$  cm were used for SEM and AFM studies. The surface preparation of the mechanically abraded specimens was carried out using different grades of emery paper (up to 1200 grit), followed by cleaning with acetone and rinsing with double-distilled water to obtain polished coupons for all the studies (Kanojia *et al.*, 2005).

#### **Electrochemical techniques**

A conventional three electrodes cell assembly was used for Galvanostatic Polarization Studies (GPS) and Electrochemical Impedance Studies (EIS), having mild steel (MS) as the working electrode, platinum as the counter electrode, and Saturated calomel electrode (SCE) fixed in luggin capillary as the reference electrode. A constant distance of approximately 1-2 mm was maintained throughout the experiment between the tip of luggin capillary and working electrode surface. The measurements were carried out in aerated nonstirred 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions without and with various concentrations of 1%, 3%, 4% and 5% of the BR extract at temperatures 298 K, 308 K, 318 K and 328 K. The cell assembly was kept for 4 hours to achieve open circuit potential (OCP) before each run. The potential of the metal electrode vs. SCE was measured with the help of an electrochemical workstation CHI760C (CH Instruments, Inc, USA). Tafel plots were performed at a scan rate of 0.010 V/s. Kinetic and activation parameters for adsorption and dissolution processes were then calculated. Impedance measurements were carried out using AC signals of amplitude 5 mV peak to peak at the open circuit potential in the frequency range 100 kHz to 10 mHz.

### Surface characterization

Polished and pit-free mild steel coupons were subjected to corrosion exposure using  $0.5 \text{ M H}_2\text{SO}_4$ , the highest 5% and lowest 1% concentration of BR extract to observe the extent of inhibition for 24 hours. They were removed from the solutions without touching the surface, dried in desiccators for 24 hours and then (LEO 435 VP) SEM was used to study 2-D surface morphology. A Scanning probe microscope VEECO CP II AFM was used to study 3D surface morphology (Verma *et al.*, 2018).

# **RESULTS AND DISCUSSION**

## Galvanostatic polarization studies

The cathodic and anodic polarization curves for different concentrations 5%, 4%, 3%, 1% of BR extract at four different temperatures 208 K-328 K are displayed in Fig. 1 (a-d), on which acid plots were overlaid.

The corrosion kinetic parameters such as corrosion potential ( $E_{corr}$ ), corrosion current density ( $I_{corr}$ ), anodic

and cathodic Tafel slopes ( $\beta_a$  and  $\beta_c$ ) and Inhibition efficiency (IE%) were derived from tafel plots and tabulated in Table 1. The polarization curves were extrapolated back to OCP to get the corrosion current (Kanojia *et al.*, 2005). The Inhibition efficiency (IE) is then calculated using equation (1)

$$IE (\%) = \left[\frac{Icorr_{Acid} - Icorr_{BR}}{Icorr_{Acid}}\right] \times 100$$
(1)

No remarkable change in the OCP values was observed in the absence and presence of BR at all temperatures, indicating that BR behaved as a mixed-type inhibitor. Recent studies have shown that if the Ecorr displacement is greater than 85 mV, an inhibitor may be classified as cathodic or anodic; otherwise, it may be classified as mixed type (Gao et al., 2014; Vu *et al.*, 2020 and Badreah et al., 2023). The present study indicated that the examined inhibitor was a mixed -type inhibitor because the maximum displacement in  $E_{corr}$  varied from 5 to 30 mV.  $\beta_a$  and  $\beta_c$  varied with the addition of different concentrations of BR, implying controlled reactions (Sharma et al., 2023). The BR extract not only hindered cathodic hydrogen evolution reaction, but also retarded MS anodic dissolution. The values of anodic slopes were influenced significantly by the inhibitor, which showed that BR inhibits the corrosion process mainly by inhibiting the anodic metal dissolution reaction. A prominent decreasing trend in Icorr values was observed with BR in H<sub>2</sub>SO<sub>4</sub>. It was observed that Icorr values decreased with higher concentration of BR and increased with a temperature rise. This indicates that BR extract shows promising results at 5% concentration for MS corrosion in H<sub>2</sub>SO<sub>4</sub>, at lower temperatures. Interestingly, IE of BR at highest c (5%) was 94% and at lowest c (1%) was 84%. This could be due to the better  $\theta$  accomplished by BR molecules on the MS surface (Shukla et al., 2011). The corrosion rate in the presence of BR increased with an increase in the solution temperature from 298 K to 328 K. From Table 1, it is obvious that the highest IE was observed at 298 K while the lowest was at 328 K. The IE % in BR showed a decreasing trend as reported earlier (Sharma et al., 2023; Shukla et al., 2011; Al-Baghdadi et al., 2021), with an increase in temperature from 298 K to 328 K. This can be explained based on Le-Chatelier's principle; the adsorption exothermic reaction started to move in the backward direction, leading to the desorption of extract molecules from the MS surface, as the system temperature increased. These results suggested that BR retarded the dissolution of MS, by adhering to the MS surface, which hindered the contact of corrosive medium, even at high temperatures.

#### **Temperature kinetics**

The nature of the adsorption of the protective layer on

Yadav, S. et al. / J. Appl. & Nat. Sci. 15(3), 1315 - 1325 (2023)

Temp.	Concentration of BR	$-E_{corr}$ $I_{corr}^{2}$ $Q_{corr}^{2}$ $Q_{corr}^{2}$					
(K)	in 0.5 M H <sub>2</sub> SO <sub>4</sub> (v/v) %	(mV)	I <sub>corr</sub> (mA/cm)	β <sub>c</sub> (V/dec)	β <sub>a</sub> (V/dec)	IE (%)	A
298	5	474	0.0842	9.158	21.944	94.09	0.9409
	4	481	0.1216	9.036	13.368	91.46	0.9146
	3	514	0.1911	8.045	10.113	86.59	0.8659
	1	487	0.2256	9.085	25.921	84.17	0.8417
	0	509	1.425	7.203	8.721	-	-
308	5	487	0.1512	9.298	12.694	90.59	0.9059
	4	474	0.1473	9.121	24.309	90.85	0.9085
	3	473	0.1864	8.956	20.865	88.46	0.8846
	1	474	0.3685	8.728	21.558	77.11	0.7711
	0	500	1.616	7.361	9.880	-	-
318	5	482	0.2824	8.725	24.230	89.58	0.8958
	4	483	0.3035	8.579	21.683	88.83	0.8883
	3	481	0.4743	8.229	26.583	82.47	0.8247
	1	490	0.6371	8.032	24.043	76.49	0.7649
	0	473	2.706	7.184	13.384	-	-
328	5	501	0.6820	7.934	9.578	89.03	0.8903
	4	490	0.8973	7.589	20.986	85.57	0.8557
	3	480	1.207	7.536	19.204	80.59	0.8059
	1	503	1.533	8.878	2.610	75.35	0.7535
	0	475	6.219	6.033	9.199	-	-

Table 1. Parameters of MS in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the presence of BR extract

MS: Mild steel, BR: Beetroot

the MS surface can be determined by studying the temperature kinetics. In chemisorption, adsorbed molecules are bonded to the surface through valence bonds, which may be endothermic or exothermic. In physisorption, adsorbed molecules are held to the MS surface through physical attraction, which does not involve a significant change in the electronic orbital patterns. The type of adsorption involved between MS surface and inhibitor molecules depends on adsorption isotherms. In this study, different adsorption isotherms like Langmuir, Temkin, Frumkin, Freundlich, El-Awady and Flory- Huggins were tried and the best-fitted adsorption isotherm (where R<sup>2</sup>≈ 1) for adsorption of BR on mild steel was obtained. Corrosion and surface coverage,  $\theta$  of mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the presence of various concentrations of BR at different temperatures are tabulated in Table 1.  $c/\theta$  vs c produces a straight line with  $R \approx 0.99$  at all temperatures as shown in Fig. 2 and Table 2. This elucidates that the adsorption of the BR obeys the Langmuir adsorption isotherm (Al-Baghdadi et al., 2021), which follows equation (2):

$$\frac{c}{\theta} = \frac{l}{K_{ads}} + c \tag{2}$$

where  $K_{ads}$  is the equilibrium constant for the process of adsorption.

The intercept of the plot (Table 2) was used to calculate the adsorption equilibrium constant ( $K_{ads}$ ) which in turn

was used to calculate the Gibb's free energy change (Mobin *et al.*, 2019) for the adsorption process using equation (3).

$$\Delta G_{ads}^{\circ} = -2.303 \, RT log \, (55.5 \, K_{ads}) \tag{3}$$

The determined thermodynamic parameters are summarized in Table 3. According to the literature,  $\Delta G_{ads}^{\circ} > -20 \, kJ/mol$  is considered as physisorption,  $\Delta G_{ads}^{\circ} < -40 \, kJ/mol$  is chemisorption while  $-20 \, kJ/mol < \Delta G_{ads}^{\circ} < -40 \, kJ/mol$  is considered as comprehensive adsorption (Sin *et al.*, 2017; Loto and Tobilola, 2018 and Chen *et al.*, 2022). The negative values of  $\Delta G_{ads}^{\circ}$  reveal the spontaneity of the adsorption process and the calculated values of  $\Delta G_{ads}^{\circ} > -20 \, kJ/mol$  indicating that the adsorption mechanism of BR on mild steel surface in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions was typical of physisorption.

Fig. 3 depicts the graph log K vs. 1/T, used to calculate  $\Delta H_{ads}^{\circ}$  and  $\Delta S_{ads}^{\circ}$  and parameters (Akinbulumo *et al.*, 2020) which are given in Table 3. The negative value of  $\Delta H_{ads}^{\circ}$  (-11.68 kJ/mol) indicated the exothermic and spontaneous nature of adsorption of BR on MS surface, which concurs with the decrease in IE % with a rise in temperature. The positive  $\Delta S_{ads}^{\circ}$  (6.81 × 10<sup>-3</sup>)



**Fig. 1.** Galvanostatic polarization curves for mild steel in the presence of various concentrations of BR at (a) 298K, (b) 308K, (c) 318K and (d) 328K.

(4)

kJ K<sup>-1</sup> mol<sup>-1</sup>) also supplements the spontaneity of physisorption BR extract on MS surface.

The plot of log  $I_{corr}$  against 1/T in equation (4) gives a slope from which the activation energy, E<sub>a</sub> was calculated. The Arrhenius equation described the relationship (Akinbulumo *et al.*, 2020) between the corrosion rate ( $I_{corr}$ ) and temperature (T) as

$$log I_{corr} = log A - \frac{E_a}{2.303 RT}$$

where A is the Arrhenius factor and R is the universal gas constant.

The increased  $E_a$  in the presence of BR than that of free acid indicates that the extract considerably increased the activation energy of the metal dissolution process, which can be explained based on the adsorption of BR on the metal surface, thereby creating a barrier between the metal surface and the corrosive media. Literature has revealed that the higher activation energy value in the presence of the inhibitor is attributed to its physisorption, while the lower value is associated with its chemisorption (Larabi *et al.*, 2005; Negm *et al.*, 2008; Rahiman *et al.*, 2017). As shown in Table 4, the  $E_a$  decreased with the decrease in BR concentration; however, it was still greater than that of the uninhibited solution.

## **Electrochemical impedance studies**

Electrochemical impedance studies (EIS) are an additional tool to study the effect of BR on the MS surface immersed in acidic corrosive medium. Charge transfer resistance ( $R_{ct}$ ) and double layer capacitance ( $C_{dl}$ ) of the system were determined in order to understand the adsorption behaviour and are represented in the form of Nyquist plot in Fig. 5, in the presence and absence of BR at 298 K at different concentrations. The experimentally determined parameters, such as  $R_{ct}$ ,  $C_{dl}$ , phase angle ( $\alpha^{\circ}$ ) are presented in Table 5. It could be seen from the table that with the increase in BR concentration,  $R_{ct}$  values increased while  $C_{dl}$  values decreased.  $R_{ct}$  value was reported as maximum for 5% BR and the value of  $C_{dl}$  is minimum for it. The decrease

 Table 2. Linear regression parameters for Langmuir isotherm of BR

Temp (K)	Slope	Intercent(1/K)	<b>R</b> <sup>2</sup>	
Temp. (IX)	olope	intercept( int)	N	
298	1.0330	0.2269	0.9967	
308	1.0506	0.2372	0.9998	
318	1.0622	0.3050	0.9971	
328 1.0767 0.3354 0.9957				
R <sup>2</sup> : Regression coefficient				

Yadav, S. et al. / J. Appl. & Nat. Sci. 15(3), 1315 - 1325 (2023)

Table 3. Thermodynamic parameters for BR calculated from Langmun sotherm				
Temp. (K)	К	ΔG <sup>°</sup> <sub>ads</sub> (kJ/mol)	ΔH <sup>o</sup> <sub>ads</sub> (kJ/mol)	ΔS <sup>o</sup> <sub>ads</sub> (kJ/K/ mol)
298	4.4072	-13.64		
308	4.2158	-13.78		
318	3.2786	-13.57	-11.68	6.8077 × 10 <sup>-3</sup>
328	2.9815	-13.74		

Table 3. Thermodynamic parameters for BR calculated from Langmuir isotherm

in  $C_{dl}$  values is related to the decline in local dielectric constant and/or an increase in the thickness of the protective layer (Mathew *et al.*, 2020).

This decline in dielectric constant was due to the replacement of water molecules by BR extract, which is responsible for the thickening of double electric layer (Fu *et al.*, 2023) and in turn, decreases the extent of metal dissolution. A single capacitive loop was observed in all Nyquist curves (Fig. 5(a)). The arc radius increased with increased BR concentration, indicating that adding BR strengthens the corrosion-inhibitive film

**Table 4.**  $E_a$  for the corrosion of mild steel in absence and presence of BR

c (v/v %)	E <sub>a</sub> (kJ/mol)
5	56.59
4	55.11
3	53.01
1	51.64
0	40.51



Fig. 2. Langmuir adsorption isotherm of beet root



Fig. 3. Plot of variation of log K vs 1/T

on MS surface. The smallest arc was observed in the presence of acid. The low-frequency impedance value (*f*) and the maximum phase angle ( $\alpha^{\circ}$ ) both increased with the addition of BR, suggesting the formation of a more stable protective layer on MS surface to prevent corrosive ions from eroding carbon steel (Fu *et al.*, 2023).

Fig. 5 (b) shows the Bode plot; there was an increase in the absolute impedance value |Z|, at low frequencies, after MS treatment with BR. As the concentration of BR increased from 1% to 5%, the inhibitive layer strengthened as adsorption became more effective Fig. 5(c) shows a continuous well-pronounced phase angle shift at higher frequencies. Addition of BR to the acid, changes the phase angle to more negative values, indicating the adsorption of the inhibitor (Mathew *et al.*, 2020). IE% was calculated using equation 5 (Sharma *et al.*, 2023)

$$IE \% = \frac{R_{ct(BR)} - R_{ct(acid)}}{R_{ct(BR)}} \times 100$$
(5)

## **Morphological studies**

Surface morphology of MS surface with and without inhibitor has been examined using SEM images which complimented the results obtained from electrochemical techniques. Fig. 6 (a) shows the polished MS surface without any treatment at ×1000 magnification, while Fig. 6 (b) and (c) show the MS surface after immersion in 0.5 M  $H_2SO_4$  for 24 hours at two different magnifications viz. ×1000 and ×3000, respectively. The effect of the corrosive medium is seen in these figures. SEM images of MS surface after dipping in 5% and 1% BR extract solution for 24 hours are shown in Fig. 6 (d)



Fig. 4. Plot of log I<sub>corr</sub> vs 1/T

Yadav, S. et al. / J. Appl. & Nat. Sci. 15(3), 1315 - 1325 (2023)

Acid on MS

1 % BF 3 % BR 4 % BR

Table 5. Impedance parameters for the corrosion of MS in absence and presence of BR						
Inhibitor c (v/v %)	R <sub>ct</sub> (Ωcm²)	F (Hz)	۵°	C <sub>dl</sub> (μF/cm²)	IE (%)	θ
5	303.164	9.766	66.4	53.78	91.18	0.9118
4	231.649	9.766	65.5	70.38	88.45	0.8845
3	170.422	17.44	66.5	53.57	84.30	0.8430
1	145.862	5.486	60.1	198.99	81.66	0.8166
0	26.750	25.70	52.2	231.62	-	





Fig. 5. (a) Nyquist plot, (b) Bode Plot and (c) Phase angle of MS in absence and presence of BR at 5%, 4%, 3%, 1% at 298 K.



Fig. 6 (a). Polished Mild steel (b) Mild Steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 1000 magnification

-6 (g) at magnifications ×1000 and ×3000. The metal surface was fully covered with the inhibitor molecules, giving it a high degree of protection against corrosion in the presence of 5% solution of BR. The extent of corrosion as visible from micrographs was much less at higher concentrations (5%) than specimens exposed to lower (1%) concentration of BR. This is in direct agree-



Fig. 6 (c). Mild steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 3000 magnification

ment with the results obtained from other techniques, i.e. the extent of corrosion inhibition increases with an increase in BR concentration.

AFM is a powerful technique to investigate the surface morphology at nano- to micro-scale. The threedimensional (3D) AFM morphologies in the presence of corrosive  $H_2SO_4$ , 5% and 1% BR are shown in Fig. 7



**Fig. 6 (d).** Mild steel in the presence of 5% BR at 1000 magnification (e) Mild steel in  $0.5 \text{ M H}_2\text{SO}_4$  in the presence of 5% BR at 3000 magnification



**Fig. 6 (f).** Mild steel in the presence of 1% BR at 1000 magnification (g) Mild steel in 0.5 M  $H_2SO_4$  in the presence of 1% BR at 3000 magnification



Fig. 7. (a). Mild steel in the presence Fig. 7 (b). Mild steel in presence of 5% Fig. 7 (c). Mild steel in presence of

Table 6. AFM roughness data for the MS surface in 0.5 M  $\rm H_2SO_4$  without and with BR

Extracts	Average area RMS (nm)
Acid	141.3
5% BR	32.7
1% BR	73.9

MS: Mild steel, BR: Beetroot

(a) - (c). AFM images qualitatively characterized topographical changes. The metal surface could be quantitatively evaluated by measuring the difference in the surface roughness and is given in Table 6. The average area analysis method is employed to calculate the roughness of the metal surface. In this, the whole area of one side of the metal surface was considered.

Fig. 7(a) clearly shows the extent of corrosion in the presence of sulphuric acid. Deep pits and cracks were seen clearly, which shows the degree of surface damage. The roughness of metal surface (RMS) value of MS in acid was 141.3 nm, signifying the extent of corrosion as the higher the RMS, the greater the corrosion extent as reported by Peimani *et al.* (2018). MS exposed in the presence of 5% BR formed a coherent layer on the surface of carbon steel, and after that, small, spherical particles deposited on the top of the film. In this case, the RMS value was 32.7 nm, which

showed the inhibiting nature of the film formed. The surface topography of MS in the presence of 1% BR showed that the BR molecules formed a barrier film, which protect the mild steel surface from corrosion but to a lesser extent. This can be seen by its RMS value (73.9 nm).

## Conclusion

Electrochemical measurements in the present study showed that the inhibition efficiency decreases slightly with the decrease in B. vulgaris (BR) extract concentration from 5% to 1%. IE % decreased as the temperature increased. BR is a mixed type of inhibitor as indicated by E<sub>corr</sub> but predominantly anodic as the anodic Tafel slope ( $\beta_a$ ) was found to be higher than cathodic Tafel slope ( $\beta_c$ ), therefore retarded corrosion mainly by anodic metal dissolution reaction. The adsorption of BR followed Langmuir's isotherm. The calculated value of Gibb's free energy values signified the physical adsorption of BR on MS surface. EIS measurements were in good agreement with results obtained from galvanostatic studies. SEM and AFM micrographs witnessed the formation of a protective layer on MS. Thus, it was concluded that B. vulgaris could be an effective, ecofriendly, and economic inhibitor to retard the corrosion of mild steel in corrosive acidic media.

## ACKNOWLEDGEMENTS

Authors thank Department of Physics, University of Delhi, for the instrumentation facility and All India Institute of Medical Sciences, Delhi, for obtaining SEM images.

### **Conflict of interest**

The authors declare that they have no conflict of interest.

# REFERENCES

- Abdallah, M., EI □Etre, A. Y., Soliman, M. G. & Mabrouk, E. M. (2006). Some organic and inorganic compounds as inhibitors for carbon steel corrosion in 3.5 percent NaCl solution, *Anti-corrosion Methods and Materials*. 53, 118-123. https://doi.org/10.1108/00035590610650820
- Akinbulumo, O. A., Odejobi, O. J. & Odekanle, E. L. (2020). Thermodynamics and adsorption study of the corrosion inhibition of mild steel by Euphorbia heterophylla L. extract in 1.5 M HCl. *Results in Materials,* 5, 100074. https://doi.org/10.1016/j.rinma.2020.100074
- Al-Baghdadi,S., Gaaz, T.S., Al-Adili, A., Al-Amiery, A. &Takriff, M. S. (2021). Experimental studies on corrosion inhibition performance of acetylthiophene thiosemicarbazone for mild steel in HCl complemented with DFT investigation, *International Journal of Low-Carbon Technologies*, 16 (1), 181–188. https://doi.org/10.1093/ijlct/ ctaa050
- Al Otaibi, N., & Hammud, H. H. (2021). Corrosion inhibition using harmal leaf extract as an eco-friendly corrosion inhibitor. *Molecules*, 26(22), 7024. https://doi.org/ 10.3390/molecules26227024
- Alibakhshi, E., Ramezanzadeh, M., Haddadi, S. A., Bahlakeh, G., Ramezanzadeh, B. & Mahdavian, M. (2019). Persian Liquorice extract as a highly efficient sustainable corrosion inhibitor for mild steel in sodium chloride solution. *Journal of Cleaner Production*, 210, 660-672. https://doi.org/10.1016/j.jclepro.2018.11.053
- Ambrish, S. & Quraishi, M. A. (2012). Azwain (Trachyspermum copticum) seed extract as an efficient corrosion inhibitor for aluminium in NaOH solution. *Research Journal of Recent Sciences* ISSN, 2277, 2502.
- Aribo, S., Olusegun, S. J., Ibhadiyi, L. J., Oyetunji, A. & Folorunso, D. O. (2017). Green inhibitors for corrosion protection in acidizing oilfield environment. *Journal of the Association of Arab Universities for Basic and Applied Sciences*, 24, 34-38. https://doi.org/10.1016/j.jaub as.2016.08.001
- Badreah A. Al Jahdaly, (2023). Rosmarinus officinalis extract as eco-friendly corrosion inhibitor for copper in 1 M nitric acid solution: Experimental and theoretical studies, *Arabian Journal of Chemistry*, 16 (1), 104411, ISSN 1878-5352, https://doi.org/10.1016/ j.arabjc.2022.104411.
- Badr, E. A., Bedair, M. A. & Shaban, S. M. (2018). Adsorption and performance assessment of some imine derivatives as mild steel corrosion inhibitors in 1.0 M HCI solution by chemical, electrochemical and computational methods. *Materials Chemistry and Physics*,

219, 444-460.https://doi.org/10.1016/j.matchemphys.2 018.08.041

- 10. Balázs, S. (1994). Zöldségtermesztők kézikönyve. Mezőgazda Kiadó, Budapest, 631-639.
- Bashir, S., Singh, G. & Kumar, A. (2017). Shatavari (Asparagus Racemosus) as green corrosion inhibitor of aluminium in acidic medium. *J Mater. Environ. Sci.*, 8(12), 4284-4291.https://doi.org/10.26872/jmes.2017.8.12.451
- Bashir, S., Singh, G., & Kumar, A. (2018). An investigation on mitigation of corrosion of aluminium by Origanum vulgare in acidic medium. *Protection of Metals and Physical Chemistry of Surfaces*, 54, 148-152. https:// doi.org/10.1134/s2070205118010185
- Caldona, E. B., Zhang, M., Liang, G., Hollis, T. K., Webster, C. E., Smith Jr, D. W. & Wipf, D. O. (2021). Corrosion inhibition of mild steel in acidic medium by simple azole-based aromatic compounds. *Journal of Electroanalytical Chemistry*, 880, 114858.https://doi.org/10.1016/j.jelechem.2020.114858.
- Chaouiki, A., Chafiq, M., Lgaz, H., Al-Hadeethi, M. R., Ali, I. H., Masroor, S. & Chung, I. M. (2020). Green corrosion inhibition of mild steel by hydrazone derivatives in 1.0 M HCI. *Coatings*, 10(7), 640. https://doi.org/10.3390/ coatings10070640
- Chen, M. F., Chen, Y., Lim, Z. J. & Wong, M. W. (2022). Adsorption of imidazolium-based ionic liquids on the Fe (1 0 0) surface for corrosion inhibition: Physisorption or chemisorption?. *Journal of Molecular Liquids*, 367, 120489. https://doi.org/10.1016/j.molliq.2022.120489
- Chhikara, N., Kushwaha, K., Sharma, P., Gat, Y., & Panghal, A. (2019). Bioactive compounds of beetroot and utilization in food processing industry: A critical review. *Food chemistry*, 272, 192-200.https://doi.org/10.1016/ j.foodchem.2018.08.022
- Chugh, B., Singh, A. K., Thakur, S., Pani, B., Lgaz, H., Chung, I. M., ... & Ebenso, E. E. (2020). Comparative investigation of corrosion-mitigating behavior of thiadiazole-derived bis-schiff bases for mild steel in acid medium: experimental, theoretical, and surface study. *ACS omega*, 5(23), 13503. https://doi.org/10.1021/acsomega.9b04274
- Dhaundiyal, P., Bashir, S., Sharma, V. & Kumar, A. (2019). An investigation on mitigation of corrosion of mildsteel by Origanum vulgare in acidic medium. *Bulletin* of the Chemical Society of Ethiopia, 33(1), 159-168. https://doi.org/10.4314/bcse.v33i1.16
- Durowaye, S. I., Durowaye, V. O. & Begusa, B. M. (2014). Corrosion Inhibition of Mild Steel in Acidic Medium by Methyl Red (2, 4-Dimethylamino-2'-carboxylazobenzene). *Int. J. Eng. Technol*, 4(8), 469-475.
- Fu, S., Yang, X., Peng, Y., Wang, Q., Sun, Q., Zhang, J., ... & Li, J. (2023). Corrosion Behaviors of Tetrasodium Iminodisuccinate (IDS) as an Environmentally Friendly Inhibitor: Experimental and Theoretical Studies. *Coatings*, 13(3), 613. https://doi.org/10.3390/coatings13030613
- Gao, X., Zhao, C., Lu, H., Gao, F. & Ma, H. (2014). Influence of phytic acid on the corrosion behavior of iron under acidic and neutral conditions. *Electrochimica Acta*, 150, 188-196.https://doi.org/10.1016/j.electacta.2014.09.160
- Goyal, M., Kumar, S., Bahadur, I., Verma, C. & Ebenso, E. E. (2018). Organic corrosion inhibitors for industrial cleaning of ferrous and non-ferrous metals in acidic solutions: A review. *Journal of Molecular Liquids*, 256, 565-

573. https://doi.org/10.1016/j.molliq.2018.02.045

- Habeeb, H. J., Luaibi, H. M., Dakhil, R. M., Kadhum, A. A. H., Al-Amiery, A. A., & Gaaz, T. S. (2018). Development of new corrosion inhibitor tested on mild steel supported by electrochemical study. *Results in physics*, 8, 1260-1267. https://doi.org/10.1016/j.rinp.2018.02.015
- Joycee, S. C., Raja, A. S., Amalraj, A. S. & Rajendran, S. (2022). Corrosion mitigation by an eco-friendly inhibitor: Beta vulgaris (beetroot) extract on mild steel in simulated oil well water medium. *Int. J. Corros. Scale Inhib*, 11(1), 82-101. https://doi.org/10.17675/2305-6894-2022-11-1-4
- Kanojia, R. & Singh, G. (2005). An interesting and efficient organic corrosion inhibitor for mild steel in acidic medium. *Surface engineering*, 21(3), 180- 186.https:// doi.org/10.1179/174329405x49985
- Kumar, S. A., Sankar, A., Kumaravel, M., & Rameshkumar, S. (2013). The Inhibition of Mild Steel Corrosion in Sulphuric Acid Media by Acorus Calamus Extract. *International Journal of Engineering Innovations and Research*, 2(2), 167.
- Larabi, L., Harek, Y., Benali, O. & Ghalem, S. (2005). Hydrazide derivatives as corrosion inhibitors for mild steel in 1 M HCI. *Progress in Organic Coatings*, 54(3), 256-262.https://doi.org/10.1016/j.porgcoat.2005.06.015
- Loto, R. T. & Tobilola, O. (2018). Corrosion inhibition properties of the synergistic effect of 4-hydroxy-3methoxybenzaldehyde and hexadecyltrimethylammoniumbromide on mild steel in dilute acid solutions. *Journal* of King Saud University-Engineering Sciences, 30(4), 384 -390. https://doi.org/10.1016/j.jksues.2016.10.001
- Mathew, Z. P., Rajan, K., Augustine, C., Joseph, B. & John, S. (2020). Corrosion inhibition of mild steel using poly (2-ethyl-2-oxazoline) in 0.1 M HCl solution. *Heliyon*, 6(11), e05560. https://doi.org/10.1016/j.heliyon.2020.e05560

30. Medupin, R. O., Ukoba, K., Yoro, K. O. & Jen, T. C.

- (2023). Sustainable approach for corrosion control in mild steel using plant-based inhibitors: A review. *Materials Today Sustainability*, 100373. https://doi.org/10.1016/ j.mtsust.2023.100373
- Mobin, M., Basik, M. & El Aoufir, Y. (2019). Corrosion mitigation of mild steel in acidic medium using Lagerstroemia speciosa leaf extract: A combined experimental and theoretical approach. *Journal of Molecular Liquids*, 286, 110890. https://doi.org/10.1016/j.molliq.2019.110890
- Muthamma, K., Kumari, P., Lavanya, M., & Rao, S. A. (2021). Corrosion inhibition of mild steel in acidic media by N- [(3, 4-Dimethoxyphenyl) Methyleneamino]-4-Hydroxy-Benzamide. *Journal of Bio-and Tribo-Corrosion*, 7, 1-19. https://doi.org/10.1007/s40735-020-00439-7
- Nagiub, A. M., Khalil, H. F. Y., Mahross, M. H., Mahran, B. N. A. & El-Sabbah, M. M. B. (2016). Beet Root Extract as a Corrosion Inhibitor for Mild Steel in 1.0 M HCl Solution. *Int. J. Scient. Engg. Research*, 7, 656-663.
- Negm, N. A. & Zaki, M. F. (2008). Corrosion inhibition efficiency of nonionic Schiff base amphiphiles of paminobenzoic acid for aluminum in 4N HCL. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 322(1-3), 97-102. https://doi.org/10.1016/ j.colsurfa.2008.02.027
- Nemzer, B., Pietrzkowski, Z., Spórna, A., Stalica, P., Thresher, W., Michałowski, T. & Wybraniec, S. (2011).

Betalainic and nutritional profiles of pigment-enriched red beet root (Beta vulgaris L.) dried extracts. *Food Chemistry*, 127(1), 42-53.https://doi.org/10.1016/j.foodchem.20 10.12.081

- Nikan, M., & Manayi, A. (2019). Beta vulgaris L. In Nonvitamin and Nonmineral Nutritional Supplements (pp. 153-158). Academic Press. https://doi.org/10.1016/b978-0-12-812491-8.00021-7
- Nithya, A., Shanthy, P., Vijaya, N., Rathish, R. J., Prabha, S. S., Joany, R. M. & Rajendran, S. (2015). Inhibition of Corrosion of Aluminium by an aqueous extract of beetroot (Betanin). *Int. J. Nano Corr. Sci. Eng*, 2(1), 1-11.
- Peimani, A. & Nasr-Esfahani, M. (2018). Application of anise extract for corrosion inhibition of carbon steel in CO 2 saturated 3.0% NaCl solution. *Protection of Metals and Physical Chemistry of Surfaces*, 54, 122-134. https:// doi.org/10.1134/s2070205118010240
- Prabakaran, M., Kim, S. H., Mugila, N., Hemapriya, V., Parameswari, K., Chitra, S. & Chung, I. M. (2017). Aster koraiensis as nontoxic corrosion inhibitor for mild steel in sulfuric acid. *Journal of Industrial and Engineering Chemistry*, 52, 235-242. https://doi.org/10.1016/ j.jiec.2017.03.052
- Punitha, N., Sundaram, R. G., Vijayalakshmi, K., Rengasamy, R. & Elangovan, J. (2022). Interactions and corrosion mitigation prospective of pyrazole derivative on mild steel in HCl environment. *Journal of the Indian Chemical Society*, 99(9), 100667. https://doi.org/10.1016/ j.jics.2022.100667
- Rahiman, A. F. S. A. & Sethumanickam, S. (2017). Corrosion inhibition, adsorption and thermodynamic properties of poly (vinyl alcohol-cysteine) in molar HCI. *Arabian Journal of Chemistry*, 10, S3358-S3366. https://doi.org/10.1016/j.arabjc.2014.01.016
- Rodríguez-Torres, A., Olivares-Xometl, O., Valladares-Cisneros, M. G. & González-Rodríguez, J. G. (2018). effect of green corrosion inhibition by prunuspersica on AISI 1018 carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub>. *International Journal of Electrochemical Science*, 13, 3023-3049. https://doi.org/10.20964/2018.03.40
- Sajadi, G. S., Naghizade, R., Zeidabadinejad, L., Golshani, Z., Amiri, M. & Hosseini, S. M. A. (2022). Experimental and theoretical investigation of mild steel corrosion control in acidic solution by Ranunculus arvensis and Glycine max extracts as novel green inhibitors. *Heliyon*, 8 (10), e10983. https://doi.org/10.1016/j.heliyon.20 22.e10983
- Sangeetha, M., Rajendran, S., Sathiyabama, J. & Prabhakar, P. (2012). Asafoetida extract (ASF) as green corrosion inhibitor for mild steel in sea water. *Int. Res. J. Environment Sci*, 1(5), 14-21.
- Selvi, J. A., Rajendran, S., Sri, V. G., Amalraj, A. J., & Narayanasamy, B. (2009). Corrosion inhibition by beet root extract. *Portugaliae Electrochimica Acta*, 27(1), 1-11. https://doi.org/10.4152/pea.200901001
- 46. Sharma, S., Sharma, M., Dheer, N., Ujjain, S. K., Ahuja, P., Singh, G. & Kanojia, R. (2023) A Novel Leaf Extract of Sorghum Vulgare as an Eco-friendly Corrosion Inhibitor for Mild Steel Corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub>. *Portugaliae Electrochimica Acta*, 41, 273-287. https://doi.org/10.4152/ pea.2023410402
- 47. Shukla, S. K., & Ebenso, E. E. (2011). Corrosion inhibi-

tion, adsorption behavior and thermodynamic properties of streptomycin on mild steel in hydrochloric acid medium. *Int. J. Electrochem. Sci,* 6(8), 3277-3291.

- Sin, H. L. Y., Rahim, A. A., Gan, C. Y., Saad, B., Salleh, M. I. & Umeda, M. (2017). Aquilaria subintergra leaves extracts as sustainable mild steel corrosion inhibitors in HCI. *Measurement*, 109, 334-345. https://doi.org/10.1016/ j.measurement.2017.05.045
- Székely, D. & Máté, M. (2022). Red Beetroot (Beta Vulgaris L.). In Advances in Root Vegetables *Research*. *Intech Open*. https://doi.org/10.5772/intechopen.106692
- Umeozokwere, A. O., Mbabuike, I. U., Oreko, B. U. & Ezemuo, D. T. (2016). Corrosion rates and its impact on mild steel in some selected environments. *Journal of Scientific and Engineering Research*, 3(1), 34-43.
- Verma, C., Ebenso, E. E., Bahadur, I. & Quraishi, M. A. (2018). An overview on plant extracts as environmental sustainable and green corrosion inhibitors for metals and alloys in aggressive corrosive media. *Journal of MolecularLliquids*, 266, 577-590. https://doi.org/10.1016/ j.molliq.2018.06.110

- Victoria, S. N., Prasad, R. & Manivannan, R. (2015). Psidium guajava leaf extract as green corrosion inhibitor for mild steel in phosphoric acid. *Int. J. Electrochem. Sci*, 10 (3), 2220-2238.
- 53. Vu, N. S. H., Binh, P. M. Q., Dao, V. A., Thu, V. T. H., Van Hien, P., Panaitescu, C. & Nam, N. D. (2020). Combined experimental and computational studies on corrosion inhibition of *Houttuynia cordata* leaf extract for steel in HCI medium. *Journal of Molecular Liquids*, 315, 113787.https://doi.org/10.1016/j.molliq.2020.113787
- Yohai del Cerro, L., Vazquez, M. V. & Valcarce, M. B. (2013). Phosphate ions as corrosion inhibitors for reinforcement steel in chloride-rich environments. *Electrochimica acta*, 88–96, https://doi.org/10.1016/j.electacta.20 13.03.180
- 55. Zou, C., Yan, X., Qin, Y., Wang, M. & Liu, Y. (2014). Inhibiting evaluation of β-Cyclodextrin-modified acrylamide polymer on alloy steel in sulfuric solution. *Corrosion Science*, 85, 445-454. https://doi.org/10.1016/j.corsci.20 14.04.046