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Adsorption and corrosion inhibition behaviour of *Brassica juncea* root extract on mild steel

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Abstract: *Brassica juncea* root extract (BJRE) was investigated as corrosion inhibitor on mild steel (MS) in 1 M HCl through weight loss and electrochemical methods. The results of root extract showed that inhibition efficiency (IE) increase with increase in concentration and decrease with increase in temperature. Polarization study indicated that *B. juncea* act as inhibitor of mixed type. Nyquist plot showed that with rising the root extract concentration, double layer capacitance decreased and the charge transfer resistance increased. Adsorption of *B. juncea* on MS followed the Langmuir adsorption isotherm.

Keywords: Mild steel, *Brassica juncea*, electrochemical.

1. Introduction

In industries acidic solutions is broadly used for numerous methods such as acid pickling, acid descaling, industrial acid cleaning and oil well acidizing[1], [2]. Degradation of metal occurs due to the chemical reaction between pure metal and alloy with corrosive medium to form a stable compound. Corrosion of metal is a major problem that must be resolved for safety, environment and economic reason. To minimize the corrosion of metal due to attack of acidic solution many techniques have been used during the past decade. The use of inhibitors among the several methods to control corrosion and its prevention is very widespread. However, many organic and inorganic compounds have been shown to be effective corrosion inhibitor for various metal but it was noted that many of these inhibitors are expensive and toxic for aquatic and animal life[3]. Most efficient inhibitors are organic compounds that contain oxides of nitrogen, oxygen and sulphur atoms in their structures[4], [5]. Naturally occurring inhibitors are often not toxic to the species in the environment compared to synthetic organic inhibitors. The research in the area of environmentally friendly corrosion inhibitor has centred on the study of synthetic natural or ecological corrosion

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inhibitors from numerous aromatic herbs, spices and medicinal plants. Corrosion inhibiting effect of extract and their constituents of various plants like Bitter leaf root extract (*Vernonia amygdalina*)[6], *Magnolia champaca*[7], Areca root extract[8], *Olea europea* L.[9], *Mangiferaindica* root extract[10], *Nardostachys jatamansi* root extract[11], *Veratrum* root extract[12], Gmelina arborea on mild steel, carbon steel has been reported with the prominent efficiency. Form the last few decades many efforts in this regard were made still not enough for practical examination. For a better future it is necessary to develop new green corrosion inhibitor for a safe environment and a healthy lifestyle. Regarding this, present research study was designed to find an inexpensive and environmentally natural substance which can be used as corrosion inhibitor on mild steel surface in acid media.

Fig. 1 *B. juncea* root

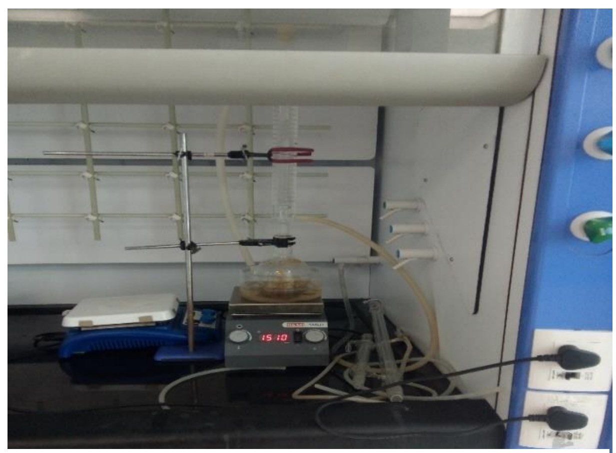

Fig. 2 *B. juncea* root extract preparation

In the present work we used *B. juncea* root which shown in Fig 1. *Brassica juncea* belongs to brassicaceae family. The plant has been distributed worldwide as a crop. It has been cultivated in India, Bangladesh, China, Japan, Nepal, Pakistan and many part of Eurasia. We have chosen root part of the plant which is inedible and usually discarded as waste. The methanolic extract of *B. juncea* root has been characterized through FT-IR and UV-Vis spectroscopy. The anti-corrosive

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effect of root extract on mild steel surface is investigated with the help of weight loss method as well as electrochemical techniques.

2. Experimental procedure

2.1 Materials and reagents

The hydrochloric acid, acetone, ethanol, methanol was bought from Sigma Aldrich. The 1 M electrolytic solution was prepared by dilution of 37% analytical hydrochloric acid with double distilled water. Commercially available mild steel was bought and its coupons with dimensions 3 cm × 2 cm × 0.25 mm were prepared.

Prior to weight loss experiment, the electrode has been abraded with emery paper up to 1000 grade, washed with double distilled water, cleaned with acetone, dried with hot air and stored in desiccator.

2.2 Extract preparation

Brassica juncea root were collected from the crop field at Haryana, India. The extra waste from the root were removed and washed under the tap water and dried at normal room temperature in shade area for several days. The dried root then cut into small pieces and convert into powdered form with mortar and pestle. 30 g of root powder was refluxed in methanol for 4 hours as shown in Fig 2, leave it for 1 hour to cool down the extract and then filtered. The methanol was evaporated through rotatory evaporator and extract were stored in glass vile for further use.

2.3 Weight loss experiment

MS coupons with size 3 cm × 2 cm × 0.25 mm were used for weight loss experiment. Prior to the immersion in acidic media the MS coupons were polished with various grade (100-1000 grade) emery paper starting from lower grade up to the mirror finishing. Firstly, the abraded MS pieces were weighed, dipped in the 200 ml blank 1 M HCl medium and in different concentration (200-1000 ppm) of inhibitor containing 1 M HCl medium at different temperature for 24 h. Subsequently, the samples were collected from the acid medium and the surface corrosion product of mild steel were cleaned, dried and re-weighed. Three parallel samples were used for accuracy of experiment. The weight loss parameters were calculated from following equation.

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$$Corrosion\ rate\ (C_r) = \frac{8.76\times10^4\ \Delta W}{ADT} \qquad \text{(i)}$$

Where ΔW is the weight loss in g, D is the density in gcm^{-3}, A is the area in cm^2 and T is time in hours and 8.76 $\times 10^{-4}$ is constant.

$$Inhibition\ Efficiecny\ (IE\%) = \frac{W_1 - W_2}{W_1} \times 100 \qquad \text{(ii)}$$

Where W_1 and W_2 are the weight loss of the mild steel specimen without and with inhibitor.

2.4 Electrochemical Study

Electrochemical studies were conducted with the help of Potentiostat/Galvanostat (PGSTAT204), Netherland, with a FRA32M module, which was software controlled named Nova 2.14 software and integrated into three electrode cell configurations. The working electrode was a 1 cm^2 mild steel piece, the counterelectrode was a graphite electrode and Ag/AgCl was the reference electrode. The Potentiodynamic polarization was studied for MS electrode when the *B. juncea* root extract was present within the concentration range of 200 ppm to 1000 ppm and temperature range at 303 K in 1 M HCl solution, potential range ± 250 mV with respect to OCP with scan rate of 1mV/s. Inhibition efficiency (η%) value for electrochemical polarization were calculated using the equation:

$$\eta\% = \frac{I^o_{corr} - I_{corr}}{I^o_{corr}} \times 100 \qquad \text{(iii)}$$

Where I^o_{corr} and I_{corr} are the corrosion current densities in without and with inhibitor for mild steel respectively.

Electrochemical impedance was measured over the frequency range of 100 KHz to 0.01 Hz frequency range with a peak-to-peak AC amplitude of 10 mV. The inhibition efficiency and double layer capacitance (C_{dl}) were computed using the equation:

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$$IE\% = \frac{R_{ct} - R_{ct}^{o}}{R_{ct}} \times 100 \quad \text{(iv)}$$

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad \text{(v)}$$

Where R_{ct} and R_{ct}^{o} are the charge transfer resistance in the presence and absence of extract, C_{dl} is the double layer capacitance and f_{max} is the frequency at which imaginary component of the impedance is maximum.

2.5 Surface Study

Surface morphology of corroded mild steel surface were studied under a metallurgical research microscopy. Metallurgical research images were recorded up to one micro (10^{-6}).

3. Result and Discussion

3.1 Weight loss measurement

Result of corrosion inhibition at various concentration of *B. juncea* root extract was analysed on mild steel using weight loss method due to its easy simplicity. Table 1 demonstrate the corrosion rate and inhibition efficiency of *B. juncea* root extract in 1 M HCl solution. The experimental results show that corrosion rate (C_R) is following decreasing order with increasing concentration of root extract which indicates an improved surface coverage by the extract. The C_R of mild steel coupons was observed as 4.94 mmy^{-1} with 1000 ppm at 293 K.

The decrease in inhibition efficiency may be explained that with the increase in temperature, electrochemical desorption of the adsorbed inhibitor and leads to the initiation of the dissolution of the metal[13]. In contrast to the effect of temperature, the concentration was found to be directly related to percentage inhibition efficiency as can be seen in the table 1. The inhibition efficiency observed for root extract was around 85% at 293 K temperature.

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Table 1 Weight loss results of MS in the absence and presence of *BJRE* in 1 M HCl at different temperature

C (ppm)	**C_R (mmy^{-1}) at 293 K**	**IE%**	**C_R (mmy^{-1}) at 303 K**	**IE%**	**C_R (mmy^{-1}) at 313 K**	**IE%**
0	33.57	-	41.15	-	48.51	-
200	12.43	62.97	16.46	60.00	25.23	47.99
400	10.08	69.97	13.58	66.90	19.41	58.28
600	7.52	77.59	10.87	73.58	17.08	64.89
800	5.71	82.99	9.06	77.98	14.56	69.98
1000	4.94	85.28	7.62	81.48	12.62	73.98

3.2 Electrochemical measurement

3.2.1 Electrochemical impedance study

Electrochemical impedance technique is extremely useful and advanced tool used for defining the electrodics, mechanism and adsorption of the inhibitor on the surface of metal in the corrosive medium to be precisely. The Nyquist plot obtained for MS in 1 M HCl with and without *BJRE* is illustrated in the Fig 3. Table 2 presents the EIS parameter such as R_{ct} and C_{dl} value for *B. juncea* root extract and shows that when the inhibitor concentration increases, the C_{dl} value decreases either by decreasing the local dielectric constant or by increasing the thickness of the double layer[14][15].

An increment in the root extract concentration also enhanced the diameter of impedance plots, which shows that adsorption of the inhibitor on the surface of MS forms a protecting layer[16]. Nyquist diagram have similar form for all tested concentration, indicating that no change in corrosion mechanism. Based on R_{ct} and C_{dl} values, extract molecules are observed to substitute

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water molecules by adsorption of inhibitory molecules at the interface of the metallic solution that results in a protective film being formed on MS surface[17][14]. The EIS results are consistent with Potentiodynamic polarization and weight loss values.

Table 2 Electrochemical impedance measurements for MS in 1 M HCl medium at various concentration of *BJRE* at 303 K

Temperature	**Conc. (ppm)**	**R_{ct} (Ωcm^2)**	**Cdl ($\mu F cm^{-2}$)**	**IE%**
30 °C	0	20.00	125.00	-
	200	51.00	48.30	60.78
	400	60.00	45.70	66.66
	600	80.00	38.40	75.00
	800	115.00	32.20	82.60
	1000	124.00	25.40	83.87

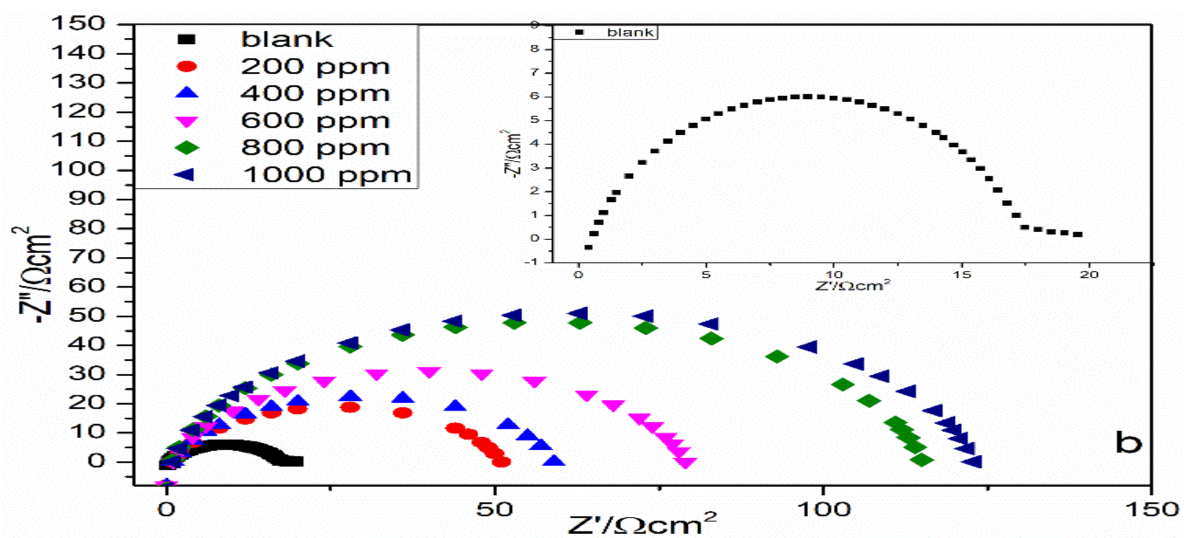

Fig. 3 Nyquist plot of MS with and without concentration of *BJRE* at 303 K in 1 M HCl

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3.2.2 Potentiodynamic polarization

Fig 4 represent the Potentiodynamic polarization curve of MS in 1 M HCl with and without *B. juncea* root extract. Polarization parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}) anode and cathode Tafel slope obtained from the Tafel curve are shown in Table 3. The addition of *B. juncea* root extract considerably reduces the metal dissolving rate of MS metal in 1 M HCl. The corrosion current density decreases by 14.3 to 2.12, yielding an inhibition efficiency of 85% at an inhibitor concentration of 1000 ppm. The anodic Tafel slope and cathodic Tafel slope are significantly reduced after addition of inhibitor, which revealed that *B. juncea* root extract can simultaneously control the cathodic and anodic reaction showing mixed type behaviour[18] [19]–[22].

Table 3 Polarization data of MS in 1 M HCl solution at various concentration of *BJRE* at 30 °C

Temperature (K)	Conc. (ppm)	I_{corr} (mAcm^{-2})	-E_{corr} vs Ag/AgCl	βa (mVd^{-1})	-βc (mVd^{-1})	η%
303 K	0	18.60	0.455	125	132	-
	200	7.78	0.459	92	110	58.21
	400	7.04	0.444	86	98	62.19
	600	4.97	0.442	73	83	73.32
	800	3.72	0.442	61	74	80.00
	1000	3.16	0.467	51	62	83.00

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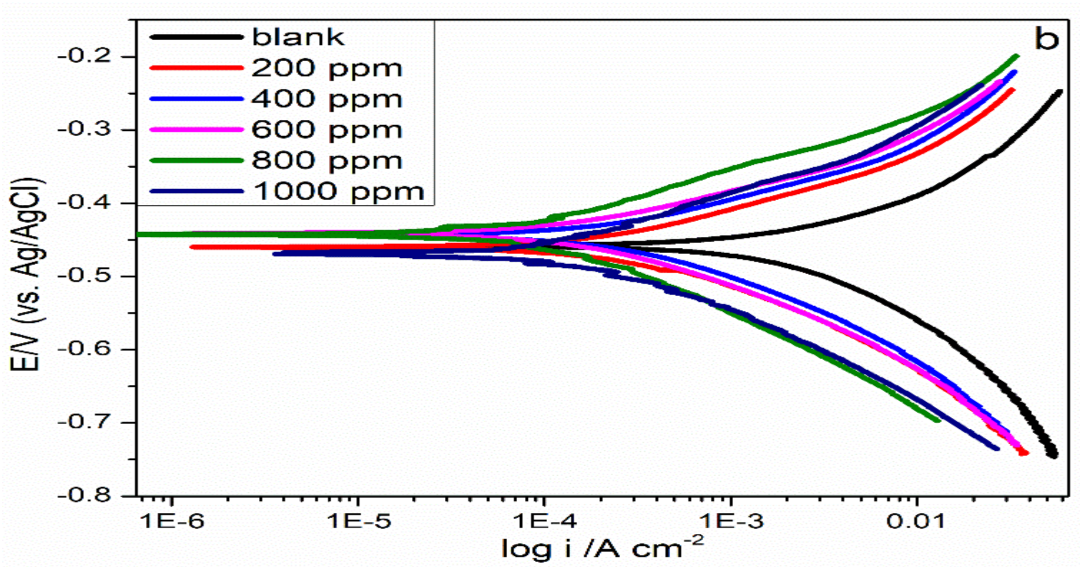

Fig. 4 Tafel curve of MS with *BJRE* in 1 M HCl at 303 K

3.3 Adsorption isotherm

There is physical and chemical adsorption of the corrosion inhibitor. Adsorption isotherm provides insight into the interaction among adsorbed molecule themselves and with the metal surface. The electrostatic interaction of the charged corrosion inhibitor with the metallic surface is part of the physisorption whereas the formation of coordinate bonds between lone pair of electron from heteroatom of organic component from extract an d unoccupied orbitals on the metallic surface is chemical adsorption. The linear regression coefficient R^2 is near 1 indicates that the adsorption isotherm is suitable for the Langmuir adsorption isotherm (Fig 6). Langmuir adsorption isotherm is obtained from the formula[23]–[25]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad \text{(vi)}$$

Where C as the inhibitor concentration, Kads is the equilibrium constant, θ surface coverage.

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The results of Langmuir adsorption isotherm presented in Table 4. As the temperature rises, the value of Kads decreases, showing that the interaction between the adsorbed molecule and metal's surface is weakened, thereby reducing inhibition efficiency with increase in temperature.

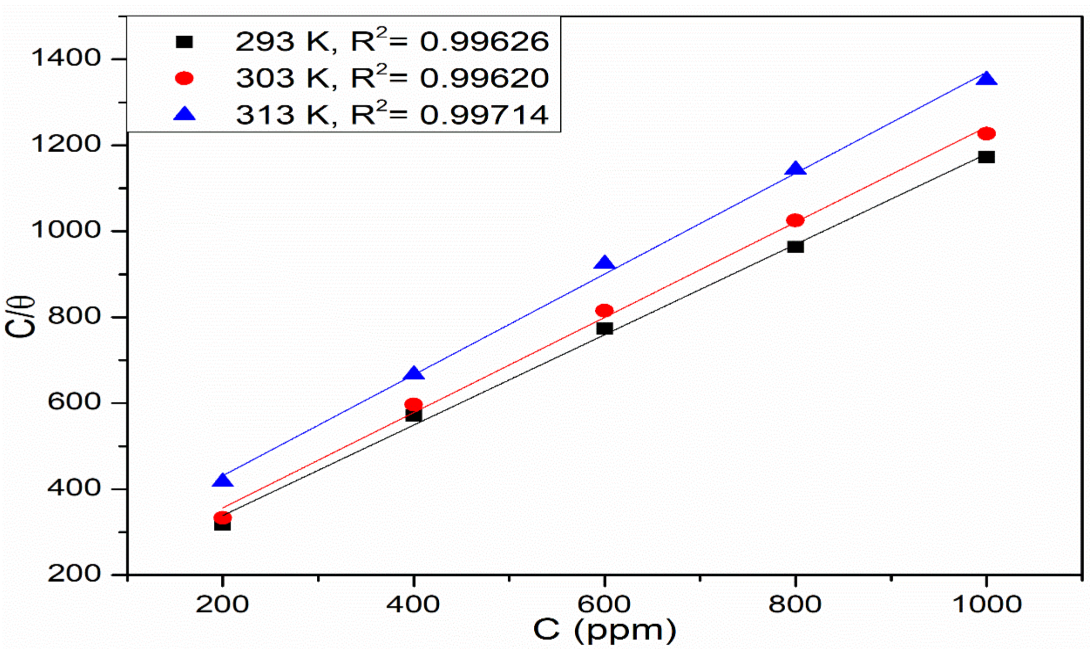

Fig. 4.3.16 Langmuir adsorption isotherm for MS in 1 M HCl at various temperature with Brassica juncea root extract

Table 4 Isotherm adsorption parameter of Langmuir model

Temperature (K)	**R^2**	**Slope**	K_{ads}	$-\Delta G^o_{ads}$ **(KJmol^{-1})**
293 K	0.99626	1.05	5.79	14.05
303 K	0.99620	1.10	4.39	13.37
313 K	0.99714	1.17	2.84	12.32

The result of study shows that the free energy value of adsorption lie below -20 KJmol^{-1} signifying spontaneous adsorption of the inhibitor via physisorption

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3.4 Surface study

Surface morphology of corroded mild steel sample were considered under metallurgical research microscope which was connected to a computer and micrograph were recorded. Microscopic image of corroded surface with and without inhibitor inform the effectiveness of corrosion inhibitor. Fig. 6 (a) shows rough surface and smooth surface is visible in Fig. 6 (b).

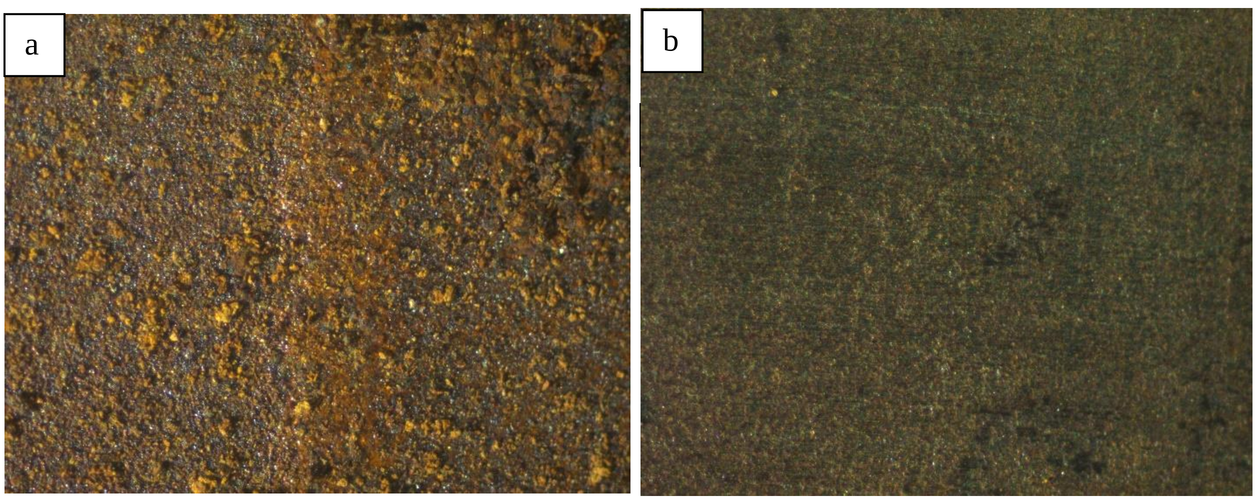

Fig. 6 Metallurgical Research micrograph of MS (a) without inhibitor, (b) with *B. juncea* root extract at 303 K

4. Conclusion

In this study, the inhibitory effect of corrosion of *Brassica juncea* root extract for mild steel in 1 M HCl was investigated through weight loss, electrochemical and surface morphological technique. Based on gravimetric and electrochemical studies, it is examined that the root extract efficiently controls the dissolution reaction of the metal and exhibits the maximum efficiency of 83% with 1000 ppm concentration at 303 K temperature. Tafel polarization showed that *B. juncea* root extract acts as a mixed type inhibitor for MS in 1 M HCl solution. The results from the EIS and the Tafel curve are well aligned. Adsorption of *B. juncea* root extract follows Langmuir's adsorption isotherm.

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Statement of interest

No conflict of interest.

CReDiT Roles

Sushmita's responsibilities include Conceptualization, Data curation, Funding acquisition, Investigation, Methodology, Resources, and Validation. Original draught of roles and writing.

Jyoti Sharma's responsibilities include Supervision, Formal analysis, Validation, Visualisation, and Writing - review and editing.

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