

# Exploration of *Crotalaria spectabilis* Stem Alkaloids as Green and Environmentally Benign Corrosion Inhibitor Against Mild Steel in 1 M H<sub>2</sub>SO<sub>4</sub> Medium

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## Highlights

- Alkaloids extracted from *Crotalaria spectabilis* stem were used as a green inhibitor
- Corrosion inhibition was studied in terms of weight loss & electrochemical method
- Weight loss method shows 90.3% inhibition efficiency in 1000 ppm inhibitor solution
- The alkaloids showed 92.86% inhibition efficacy via potentiodynamic polarization

## Abstract

The study of corrosion inhibition using plant extracts as environmentally friendly inhibitors is an emerging area of research. In this work, alkaloids were successfully extracted from the stems of *Crotalaria spectabilis* by a solvent extraction method. Qualitative characterization of extracted alkaloids was performed using chemical test methods and the Fourier Transformed Infrared Spectroscopy (FTIR) technique. The alkaloids extracted were tested as corrosion inhibitors on mild steel (MS) exposed to 1.0 M H<sub>2</sub>SO<sub>4</sub>, and their effectiveness was evaluated using gravimetric and electrochemical techniques. The study used the weight loss method to examine how inhibitor concentration, immersion time, and working temperature affect corrosion inhibition efficiency. The results showed a maximum inhibition efficiency of 90.38% for mild steel immersed in a 1000 ppm alkaloid solution for 6 hours at 25 °C. Similarly, polarization measurements indicated a maximum inhibition efficiency of 92.86%. The alkaloids demonstrated effective inhibition efficiency at temperatures up to 45 °C. The studies on adsorption isotherm, activation energy, and free energy of adsorption suggested that the alkaloids follow the Langmuir adsorption isotherm through physisorption. Overall, the findings indicate that the extracted alkaloids have the potential to serve as environmentally friendly inhibitors for mild steel corrosion.

**Keywords:** *Crotalaria spectabilis*, Green inhibitor, Mild steel, Sulphuric acid, Thermodynamics, Weight-loss.

## Introduction

Mild steel (MS) is popular due to its appealing properties and cost but low corrosion resistance in acidic environments. The MS is used in petrochemical and chemical plants where acidified solutions are used, and one of the most challenging tasks for industries is to protect mild steel from corrosion [1-4]. The most recent practice is using inhibitors to protect mild steel used in petrochemical and chemical plants [5, 6]. Synthetic or natural chemicals can be used as corrosion inhibitors, effectively

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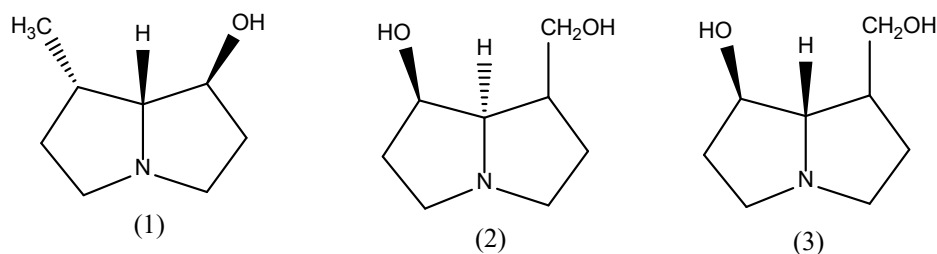
decreasing the corrosion rate when added to an aggressive environment [7]. Large numbers of synthetic inhibitors are enlisted in corrosion literature, but interest in synthetic compounds diminishes due to the strict environmental regulations and toxic effects on living beings [2, 8]. Natural products such as corrosion inhibitors attract more attention in research works because they are environmentally friendly, easily available, and good efficiency [9, 10]. Natural product extracts contain biodegradable phytochemicals, and their inhibition performance is linked to phytoconstituents like tannins, flavonoids, alkaloids, etc. [11, 12]. These metabolites contain polar functional groups with nitrogen, sulfur, or oxygen atoms, along with conjugated double or triple bonds that act as absorption centers [13, 14]. The effectiveness of green inhibitors in reducing corrosion is influenced by several factors, including their chemical structure, the presence of functional groups, the electron density at the donating atom, and the characteristics of their orbitals. The trend for inhibition performance based on the donating atom is as follows:  $O < N < S < P$  [14, 15].

The extract of different plants exhibits inhibitive properties for mild steel in acidic solutions. The methanol extracts of plants such as *Lantana camara* [4], *Artemisia vulgaris* [2], *Euphorbia royleana* [14], *Bamboo* [16], *Ficus hispida* [17], *Ginkgo* [18], *Shorea robusta* [19], *Murraya koenigii* [20] are reported with promising inhibition efficiency. Similarly, alkaloid extract from *Aniba rosaeodora* [21], *Annona squamosa* [22], *Solanum tuberosum* & *Artemisia vulgaris* [23], *Rhynchosyilis retusa* [24], *Acacia catechu* [25], *Coriaria nepalensis* [26], *Solanum xanthocarpum* [15], *Alnus nepalensis* [27], *Ageratina adenophora* [28] are also reported to have good inhibition efficiency.



Fig 1. Flowering twig of *Crotalaria spectabilis*

The *Crotalaria spectabilis* is an erect, branched annual to perennial legume plant as shown in Figure 1, also known as rattle pods in English [29]. The stem and leaf of *Crotalaria spectabilis* contain pyrrolizidine alkaloids, flavonols, tannins, unsaturated sterols, and organic acids in methanolic, ethanolic, chloroform, and hexane extract [30-32]. The presence of pyrrolizidine alkaloids like Retronecanol, Platynecine, Retronecine (Scheme 1), etc. in the leaf, stem, and seed extract of *Crotalaria spectabilis* species have been reported [33, 34]. The retronecanol is the major pyrrolizidine alkaloid found in this species [33].



Scheme 1: Pyrrolizidine alkaloids of *Crotalaria spectabilis* stem, leaf, and seed extract (1) Retronecanol, (2) Platynecine, and (3) Retronecine [33].

Alkaloids are aromatic organic compounds with nitrogen as a heteroatom in the ring [35]. It contains at least nitrogen as a heteroatom on its aromatic ring structure (Scheme 1) as well as oxygen as the functional group. Such atoms are assumed to get adsorbed either by a physical or chemical bond with the MS surface and hence protect the MS surface from an aggressive environment [36-38]. This work explores the effectiveness of the alkaloid extract of *Crotalaria spectabilis* stem as a green

corrosion inhibitor in an acid-cleaning solution. Gravimetric and electrochemical methods have been used to monitor the efficacy of the alkaloids in terms of inhibitors. The nature of adsorption and energy of adsorption has been studied in terms of adsorption isotherms and thermodynamics of corrosion.

## Experimental methods

### Preparation of Mild steel (MS) surface

MS sheets were collected and cut into coupons of dimension  $4 \times 4 \times 0.5 \text{ cm}^3$ . Before each experiment, MS coupons were polished with emery papers (100-2000 grits), washed with distilled water followed by hexane, sonicated in ethanol for 10 minutes, dried in the air, and stored in moisture-free desiccators. The dimensions of each coupon were measured before each experiment using a vernier caliper.

### Extraction and Characterization of Alkaloids

*Crotalaria spectabilis* stems were collected from Kirtipur, (Latitude: 27.65, Longitude: 85.25) Kathmandu, Nepal. The collected stems were washed with distilled water, shade-dried, and ground into a fine powder. A total of 100 g of the dried powder was soaked in 500 mL of hexane for 24 hours to remove unsaturated organic compounds, after which the mixture was filtered. The filtrate was discarded, and the remaining residue was then macerated in 800 mL of methanol. This mixture was allowed to stand for 7 days at room temperature. The mixture was then filtered, and the pH of the filtrate was made acidic by adding tartaric acid solution ( $\text{pH} < 3$ ) where almost all alkaloids form water-soluble salt. It was filtered and made alkaline ( $\text{pH} > 10$ ) adding an ammonia solution. The alkaline solution was treated with  $\text{CHCl}_3$  solution, and the organic layer was separated. The organic layer contains an alkaloid fraction. The alkaloid fraction was collected in a beaker, dried in a water bath at  $40^\circ \text{C}$  up to dryness, and stored in a moisture-free desiccator before use. Extracted alkaloids were characterized using FTIR, Mayer's, and Dragendorff's tests.

### Inhibitor Medium Preparation

A stock solution of inhibitor was prepared by dissolving 1.0 g of alkaloid in 1.0 M  $\text{H}_2\text{SO}_4$  in a 1000 mL volumetric flask. The solution was filtered to remove any undissolved impurities, resulting in a stock solution with a concentration of 1000 ppm. Inhibitor solutions of 200, 400, 600, and 800 ppm were prepared by serial diluting the stock solution.

### Weight Loss Measurement Method

Mild steel coupons were weighed before and after the immersion in acid and inhibitor solution using a four-digit weighing machine (Ohaus Corporation USA, Model: E1RR80). The inhibitor concentration effect was studied by weight loss measurement in inhibitor solutions of 200 ppm, 400 ppm, 600 ppm, 800 ppm, and 1000 ppm. The immersion time effect was studied in 0.5, 3, 6, 9, and 24 h. Similarly, the effect of temperature in corrosion inhibition was recorded at 25, 35, 45, 55, and  $65^\circ \text{C}$  after 6 h of immersion time. The inhibition efficiency (IE%) and corrosion rate (C.R.) of the extracted alkaloids were calculated using the following formula [20, 39]:

$$\text{Corrosion rate (C.R.)} = \frac{K \times W}{A \times T \times D} \quad \dots (1)$$

$$\text{Inhibition efficiency (IE\%)} = \frac{w_b - w_p}{w_b} \times 100 \quad \dots (2)$$

$$\text{Surface Coverage } (\theta) = \frac{w_b - w_p}{w_b} \quad \dots (3)$$

Where,  $K = 87600$ ,  $W$  = weight loss of MS coupon (g),

$A$  = total exposed surface area of MS ( $\text{cm}^2$ )

$T$  = Time of immersion (h),  $D$  = density of mild steel ( $\text{g}/\text{cm}^3$ )

$w_b$  = weight loss in the absence of inhibitors

$w_p$  = weight loss in the presence of inhibitors

## Potentiodynamic Polarization

Potentiodynamic polarization measurements were conducted using a three-electrode cell system with a Hokuto Denko Potentiostat (HA-151, Japan) [24, 28, 39]. During measurement, MS was used as a working electrode, a graphite rod as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. The open circuit potential (OCP) was observed for 30 min for each MS sample before polarization measurements. The polarization measurements were performed at a scan rate of 1 mV/s from the cathodic to the anodic range ( $\pm 0.3$  V Vs OCP). Corrosion current density of each measurement was obtained by extrapolating Tafel curves. Inhibition efficacy and fraction of surface covered ( $\theta$ ) by inhibitor molecules were calculated by using the formula [28, 40],

$$\text{Corrosion inhibition efficiency} = \frac{I_{corr} - I_{corr}^*}{I_{corr}} \times 100 \quad \dots (4)$$

$$\text{Fraction of surface coverage } (\theta) = \frac{I_{corr} - I_{corr}^*}{I_{corr}} \quad \dots (5)$$

Where,  $I_{corr}$  and  $I_{corr}^*$  are corrosion currents in the absence and presence of inhibitors, respectively.

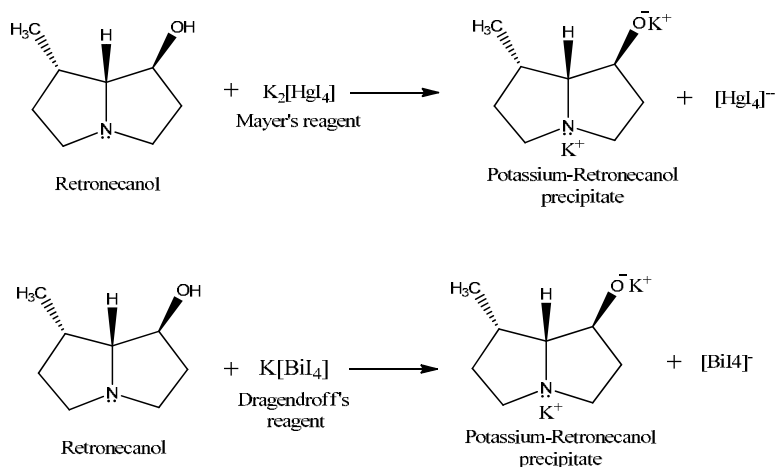
## Results and Discussion

### Characterization of Alkaloids

General chemical and FTIR spectroscopic tests were applied to characterize the extracted alkaloids. Mayer's and Dragendroff's test methods were performed for the chemical test which forms precipitation due to the possible chemical reactions given in Table 1 and Scheme 2 [26, 28, 41]. The color appearance of the precipitate results from charge transfer or electron transfer reactions within the salt [28, 42, 43]. Extracted alkaloids contain a mixture of compounds, however, to demonstrate the chemical reactions involved in chemical tests, a retronecanol molecule of this alkaloid mixture has been used.

**Table 1.** Chemical test of alkaloids

S.N.	Experiment	Observation	Inference
1.	Mayer's Test	Orange color precipitation	Presence
2.	Dragendroff's Test	Orange-red color precipitation	Presence



**Scheme 2:** Possible chemical reactions involved in chemical test of alkaloids, taking Retronecanol as a model alkaloid [24, 41].

FTIR spectroscopic analysis was performed to identify the types of bonding,  $\pi$ -bond conjugate systems, functional groups, and the presence of aromatic and aliphatic structures in alkaloids. The strong peak observed at  $3400-3200$   $cm^{-1}$  (Figure 2) is attributed to the N-H stretching vibrations of primary and secondary ammonium ions, as well as the stretching vibrations of the O-H functional group, which involves intermolecular hydrogen bonding. A peak at  $2328$   $cm^{-1}$  indicates the presence of secondary amine multiple bonds, while the peak at  $1624$   $cm^{-1}$  is associated with the N-H bending vibrations of the amide group. Additionally, multiple peaks in the range of  $1250-1020$   $cm^{-1}$  are due to the C-N stretching of primary, secondary, and tertiary amines [44].

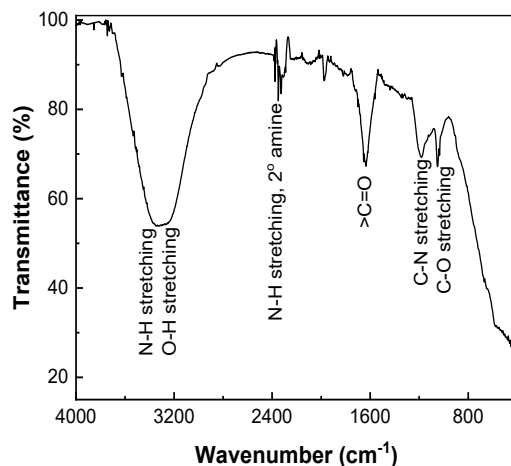


Fig 2. FTIR spectra of alkaloids

### Weight loss measurements

The weight loss measurement of MS coupon was studied in terms of immersion time effect, concentration effect, and temperature effect.

#### Effect of Immersion Time

The weight loss method was employed to study the effect of immersion time on the corrosion rate and inhibition performance of alkaloids. The inhibition efficiency of alkaloids extracted from *C. spectabilis* was examined and calculated at various time intervals, as illustrated in Figures 3a and 3b, respectively. The weight loss of mild steel when treated with inhibitors showed a significant decrease. However, extended exposure of the metal to the acidic medium may lead to desorption, resulting in slight weight loss even in the presence of an inhibitor [24, 40].

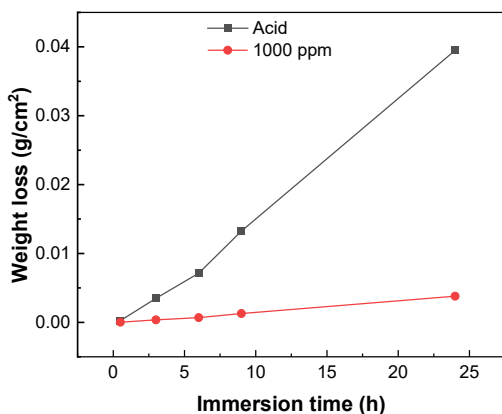


Fig 3. a) Weight loss of mild steel samples immersed in acid and inhibitor solution with respect to time.

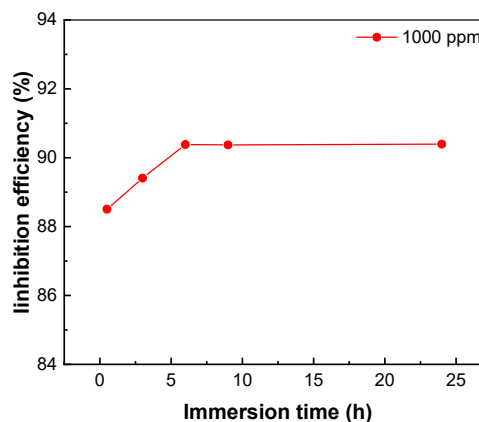


Fig 3. b) Inhibition efficiency of alkaloid solution at different intervals of time

The inhibition efficiency of alkaloids gradually increases from an initial 88.57% to 90.38% after 6 hours of immersion, and then the efficiency remains nearly constant, as shown in Figure 3b. The increase in IE reflects the dissolution of air-formed oxide and an increase in surface roughness followed by enhanced adsorption of the alkaloids on the MS surface. These adsorbed alkaloids protect MS from corrosion. Nearly constant inhibition efficiency after 6 h of immersion indicated that the system got dynamic adsorption-desorption equilibrium as well as the formation of the chelate complex by alkaloids with the dissolved  $\text{Fe}^{3+}$  or  $\text{Fe}^{2+}$  species [45-47].

### Effect of Concentration

The effect of inhibitor concentration has been studied by immersing MS samples in alkaloid solutions of different concentrations for 6 h. The observation showed that at low inhibitor concentrations, weight loss is high, indicating a high corrosion rate. On increasing inhibitor concentration, weight loss gradually decreases and remains almost constant as shown in Figure 4a.

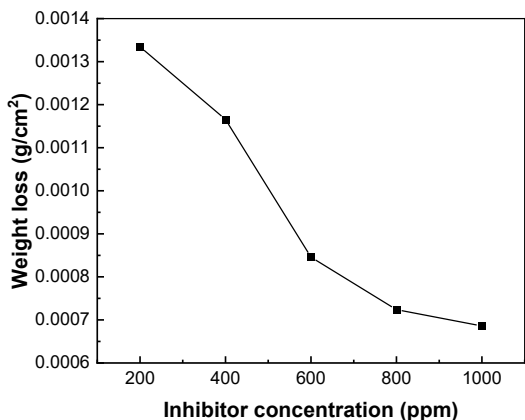


Fig 4 a) Variation of weight loss in the mild steel samples in different concentrations of inhibitor.

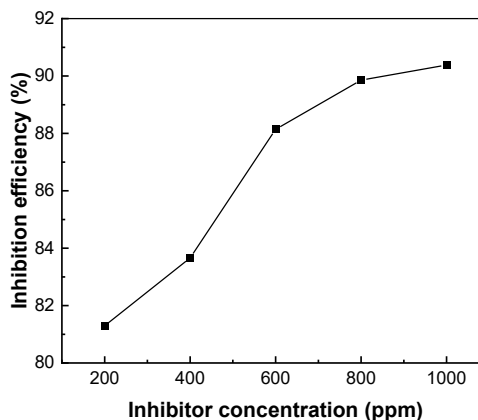


Fig 4 b) Variation of inhibition efficiency in the mild steel samples in different concentrations of inhibitor.

The effect of inhibitor concentration is studied for 200 to 1000 ppm inhibitor concentration for 6 h immersion time. The inhibition efficiency (*IE*) is high as the concentration is increased, and the maximum efficiency observed is 90.38% in 1000 ppm solution as shown in Figure 4b. This change could be due to the availability of a large number of alkaloids in a highly concentrated solution which adsorbed on the surface of MS and enhanced the corrosion inhibition.

### Effect of Temperature

To study the effect of working temperature on the corrosion inhibition of alkaloids, a weight loss method was employed in which metal samples were immersed in acid only and in acid containing a 1000 ppm inhibitor solution separately. Alkaloids reflected good inhibition performance up to 45 °C then decreased as shown in Figure 5a. The inhibition efficiency remained nearly constant at about 90% from 25 °C to 45 °C, but it began to decrease afterward, as shown in Figure 5b. At higher temperatures, the alkaloid present in the solution may lose its adsorptive properties or form a chelate complex with ferrous/ferric ions resulting in a decrease in inhibition efficiency [24, 40, 48].

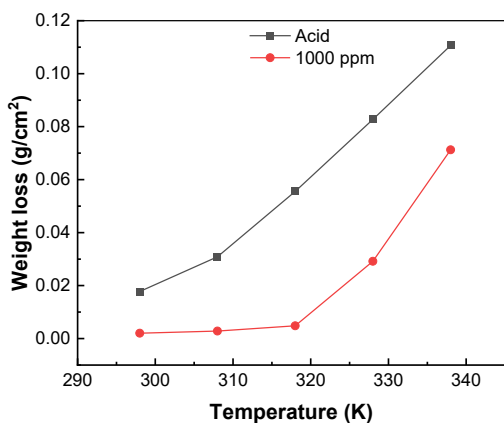


Fig 5 a) Variation of weight loss in mild steel sample at different temperatures

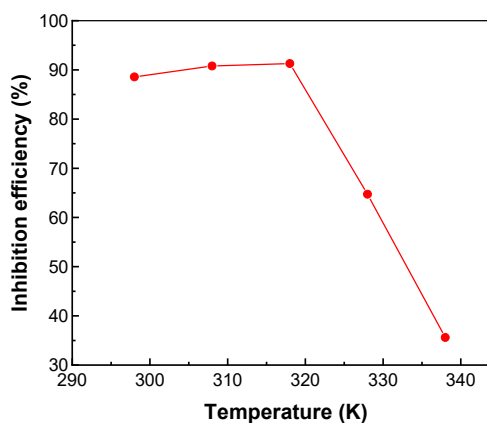


Fig 5 b) Variation of inhibition efficiency of inhibitor in mild steel sample with temperature

### Adsorption Isotherm and Free energy of adsorption

To understand the fundamentals of the adsorptive properties of inhibitor molecules on the mild steel surface, adsorption isotherm models are examined [28, 38]. Fraction of surface covered ( $\theta$ ) by inhibitors obtained from the gravimetric method and inhibitor concentration ( $C_{inh}$ ) in the reference of Retronecacol molecule were used to evaluate the adsorption isotherms. Figure 6(a) represents the plot  $C_{inh}/\theta$  versus  $C_{inh}$  (mol/L) from equation (6) was used to evaluate Langmuir adsorption isotherm. A straight line with a regression coefficient ( $R^2$ ) value of unity was obtained. This suggests that complete monolayers of alkaloids formed on the steel surface before the formation of multilayers on the equivalent adsorption sites [25, 28].

$$\frac{C_{inh}}{\theta} = \frac{1}{k_{ads}} + C_{inh} \quad \dots (6)$$

Where  $C_{inh}$  is the alkaloid concentration expressed in mol L<sup>-1</sup> and  $\theta$  denotes the surface of MS covered by alkaloid molecules. The  $k_{ads}$  signifies the equilibrium constant for the Langmuir isotherm. Gibbs free energy ( $\Delta G_{ads}$ ) of adsorption was determined using equation (7), where  $K_{ads}$  was obtained from the intercept of Langmuir adsorption isotherm.

$$\Delta G_{ads} = -RT \ln(55.5 \times k_{ads}) \quad \dots (7)$$

The free energy of adsorption obtained using ideal gas constant value ( $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and adsorption equilibrium constant ( $k_{ads} = 3484.3 \text{ L mol}^{-1}$ ) is  $-30.13 \text{ kJ mol}^{-1}$  at 298 K. The obtained value of  $\Delta G_{ads}$  is intermediate between physisorption and chemisorption. This suggests that there is a weak electrostatic interaction between the alkaloid molecules and the steel surface. A chemical interaction occurs as the lone pair of electrons from the electronegative sites of the alkaloid molecules interacts with the steel, forming a thin protective layer on the surface of the mild steel [19, 28].

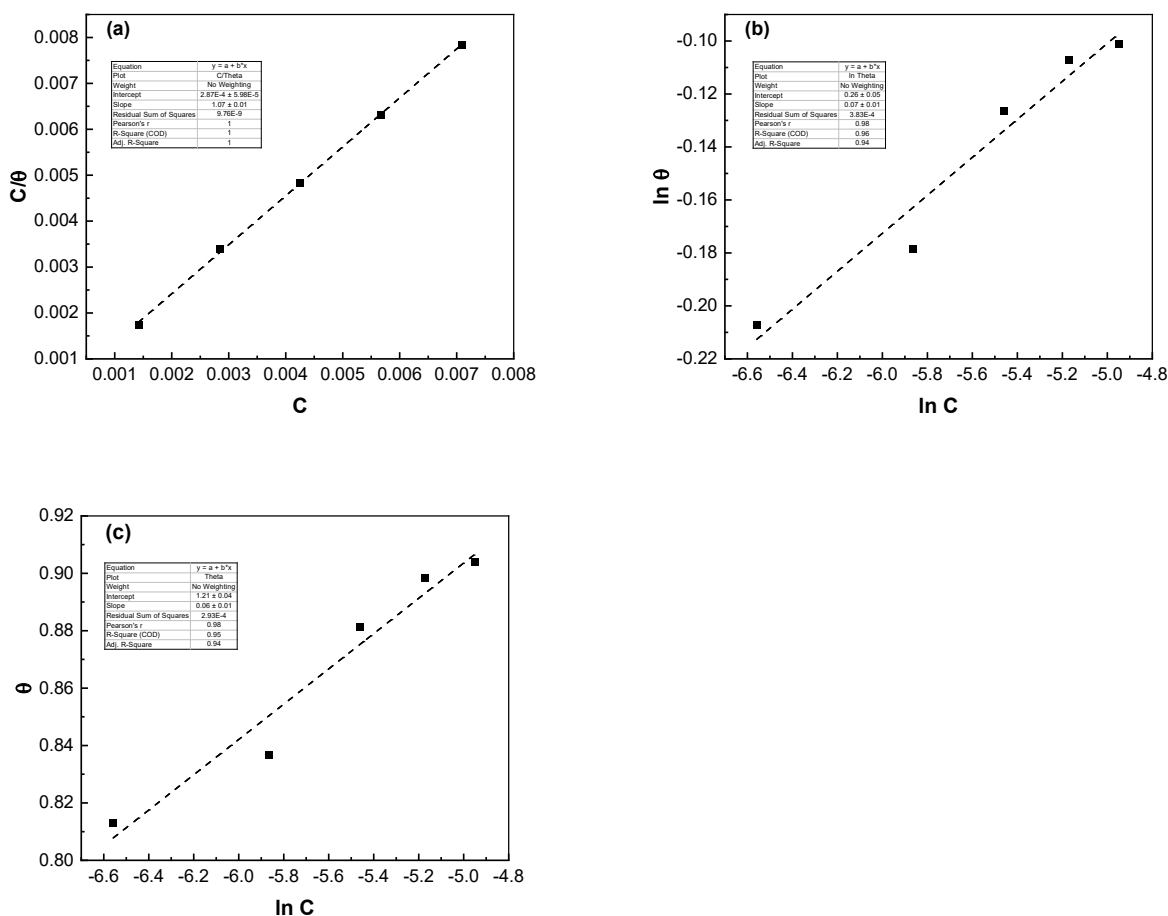


Fig 6. Adsorption isotherm plots of a) Langmuir, b) Freundlich, and c) Temkin

The interacting nature of alkaloid molecules with surface and among themselves, and the spontaneity of adsorption were studied by Freundlich and Temkin isotherms. The plot of  $\ln \theta$  versus  $\ln C$  obtained from Freundlich equation (8) gave a straight line with slope ( $1/n = 0.07$ ) and  $R^2$  coefficient 0.96 as shown in Figure 6(b). This suggests that the adsorption process is spontaneous as the value of  $1/n$  lies between 0 and 1 [25, 28].

$$\ln \theta = \ln k + \frac{1}{n} \ln C_{inh} \quad \dots (8)$$

$$\theta = -\frac{1}{2a} \ln k - \frac{1}{2a} \ln C_{inh} \quad \dots (9)$$

Where  $a$  is an interaction parameter. The interacting parameters  $a$  and  $k$  from the intercept and slope of Temkin plot ( $\theta$  versus  $\ln C$ , Equation 9) as in Figure 6(c) were found to be  $-8.33$  and  $5.73 \times 10^8$  indicating the strong interaction of the alkaloid molecules with the steel surface[28, 49].

### Corrosion Inhibition Kinetics

The corrosion inhibition kinetics and thermodynamics were determined by the weight loss measurement method. The activation energy ( $E_a$ ) of alkaloid adsorption was calculated using the linear Arrhenius equation (10),

$$\text{CR} = \log A - \frac{E_a}{2.303RT} \quad \dots (10)$$

Where, pre-exponential factor  $A$  is constant but absolute working temperatures ( $T$ ) may vary based on the experimental setup. Plotting  $\log \text{CR}$  against  $1/2.303RT$ , activation energies were calculated from the slope of straight lines. The activation energy of the acid-steel reaction was  $39.05 \text{ kJ mol}^{-1}$ , but when an inhibitor was present, it was  $78.42 \text{ kJ mol}^{-1}$ . This increase in activation energy implies a decrease in the dissolution of steel in acid. These calculated values lie very close to physisorption indicating that the adsorption of alkaloids on the steel surface is physisorption-dominant [2, 25, 40].

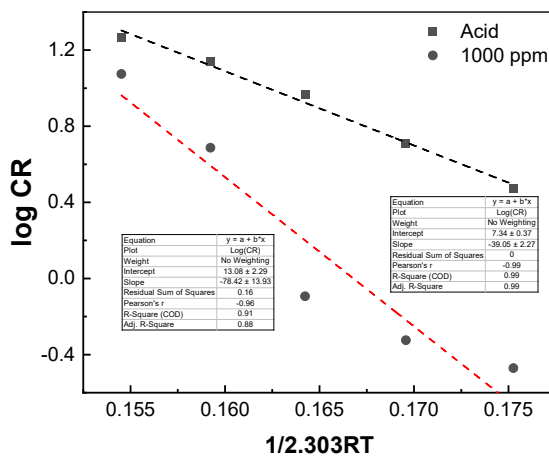


Fig 7. Arrhenius plot for the steel sample immersed in acid and inhibitor solution

### Thermodynamics of Corrosion

Enthalpy and entropy of adsorption at the transition state were determined using the transition state equation (11),

$$\log \left( \frac{\text{CR}}{T} \right) = \log \left( \frac{R}{hN} \right) + \left( \frac{\Delta S^\circ}{2.303R} \right) - \left( \frac{\Delta H^\circ}{2.303RT} \right) \quad \dots (11)$$

Where  $h$  is plank constant ( $6.62 \times 10^{-34} \text{ Js}$ ),  $N$  is Avogadro's number ( $6.022 \times 10^{23}$ ). Enthalpy of adsorption ( $\Delta H^\circ$ ) was determined from the slope of the straight line while the entropy of adsorption ( $\Delta S^\circ$ ) was determined from the intercept of the line in graph ( $\log \text{CR}/T$  versus  $1/2.303RT$ ) as shown in Figure 8.



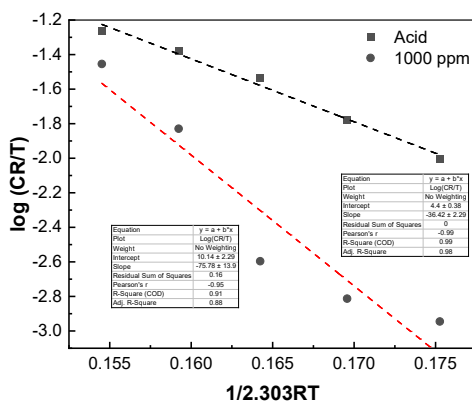


Fig 8. Transition state plot for the MS sample in acid and inhibitor solution

The enthalpy of the reaction in an acid solution is 36.42 kJ mol<sup>-1</sup> and in the presence of an inhibitor is 75.78 kJ mol<sup>-1</sup>. The positive enthalpy values for both reactions indicate that adsorption occurs through an endothermic process, which minimizes the corresponding corrosion rate [47]. Likewise, entropies calculated from intercepts are found to be -113.33 J mol<sup>-1</sup> K<sup>-1</sup> in acid and -3.34 J mol<sup>-1</sup> K<sup>-1</sup> in the presence of inhibitor solution. The presence of inhibitor molecules increases entropy due to greater randomness in the transition state, resulting from the formation of an activated complex and the movement of free protons in the solution [28]. This occurs because alkaloid molecules replace water molecules on the steel surface during adsorption [26, 28]. The calculated values of E<sub>a</sub>, ΔH°, and ΔS° are presented in Table 2 which suggests that the adsorption of alkaloids on steel surfaces is physisorption-dominant [26, 28, 40].

Table 2. Activation parameters of steel dissolution in acid and inhibitor solutions

Medium	E <sub>a</sub> (kJ mol <sup>-1</sup> )	ΔH° (kJ mol <sup>-1</sup> )	E <sub>a</sub> - ΔH°	ΔS° (J mol <sup>-1</sup> K <sup>-1</sup> )
Acid	39.05	36.42	2.63	-113.33
Inhibitor	78.42	75.78	2.64	-3.34

### Electrochemical Behavior

Before potentiodynamic polarization measurement, the OCP of each cell system was recorded. Generally, all the systems attained an equilibrium state after 5 minutes but OCP was recorded for 30 minutes. From Figures 9a and 9b, it can be shown that the OCP for the mild steel coupons in the presence of *Crotalaria* extract is slightly shifted to positive as compared to 1 M H<sub>2</sub>SO<sub>4</sub> solution, however, shifting is lower than 85 mV showing the mixed corrosion behavior of inhibitor [40, 48].

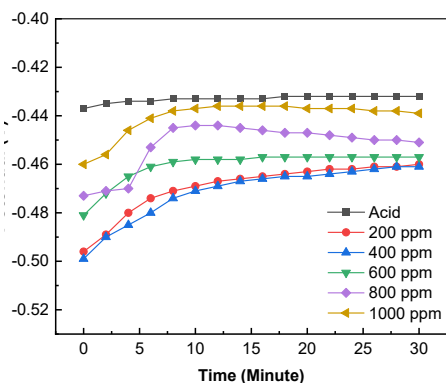


Fig 9 a): OCP variation of mild steel sample recorded before polarization measurement (as immersed).

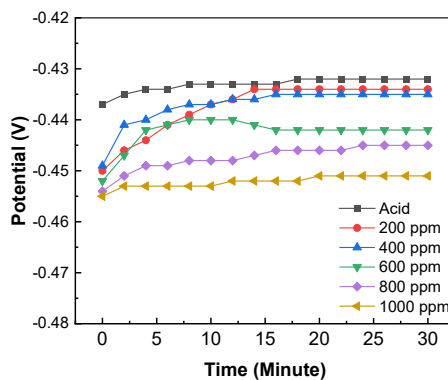
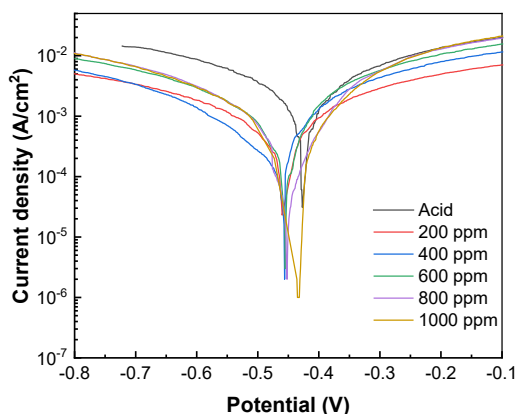
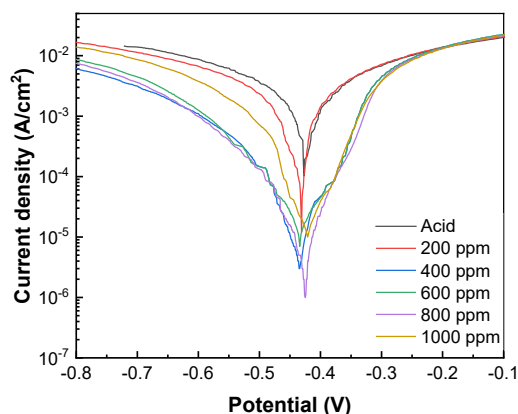


Fig 9 b): OCP variation of mild steel sample recorded before polarization measurement (after 3 h of immersion).



**Fig 10 a:** Potentiodynamic polarization curves for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> having different concentrations of inhibitor, when polarization was done in an immersed condition



**Fig 10 b:** Potentiodynamic polarization curves for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> having different concentrations of inhibitor, when polarization was done after 3 hours of immersion

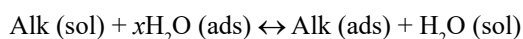
The potentiodynamic polarization of the MS sample was performed with different concentrations of alkaloids and without alkaloids in 1M H<sub>2</sub>SO<sub>4</sub> solution as shown in Figure 10a. Figure 10b shows the polarization curve of 3 h of immersed mild steel samples with and without alkaloids in 1M H<sub>2</sub>SO<sub>4</sub> solution. The corrosion potential was shifted in both directions indicating a mixed type of inhibition [24, 40, 47, 48]. It was seen that the shift in potential was more enunciated when the polarization of MS was done for 3 h immersed samples. There is a lowering current density upon the alkaloid addition, which reflects the inhibition behavior of the inhibitor. The current density decreased with the increment of inhibitor concentration however the effective decrease in current density was found in 3 h immersed samples. Thus, it can be said that the inhibitor acts more effectively after 3 h immersion. The detailed inhibition efficiency of as immersed and 3 h immersed samples for different inhibitor concentrations are tabulated in Table 3.

**Table 3:** Inhibition efficiency of *Crotalaria spectabilis* Alkaloid (CSA) for as immersed and immersed condition

Conditions	Inhibition efficiency of (200-1000) ppm alkaloids in 1M H <sub>2</sub> SO <sub>4</sub> solution				
	200	400	600	800	1000
As immersed	53.17	61.73	69.82	76.53	82.82
3 h Immersed	81.60	87.68	89.58	91.38	92.86

## Corrosion Inhibition Mechanism

Corrosion inhibition by inhibitor molecules generally occurs through an adsorption process. However, this process is not straightforward. Inhibitor molecules adhere to the surface of mild steel, forming a protective layer. This layer reduces the corrosion rate by increasing the activation energy of both the anodic and cathodic reactions. The adsorption of alkaloid molecules occurs by displacing water molecules in what is known as a quasi-substitution process.



Where, Alk (sol) and Alk (ads) represent the solvated and adsorbed alkaloid molecules, respectively. And,  $x$  stoichiometric coefficient of H<sub>2</sub>O (ads) denotes the size ratio, i.e. how many water molecules are replaced by one alkaloid molecule [24, 26, 47].

The metal surface becomes positively charged in the presence of an inhibitor. The positively charged surface interacts with sulfate ions (SO<sub>4</sub><sup>2-</sup>), resulting in a negative charge on the surface. Then the positively charged protonated alkaloids attract sulfate ions through electrostatic forces. After releasing hydrogen molecules (H<sub>2</sub>), the protonated alkaloids revert to their neutral form [27, 40, 47]. In alkaloids, the highest occupied molecular orbital (HOMO) group specifically the lone pair of electrons on the nitrogen interacts with the vacant d-orbital of iron to form a coordinate covalent bond. This interaction leads to the gathering of an extra negative charge on the metal surface. To neutralize this charge, electrons are transferred back to the lowest unoccupied molecular orbital (LUMO), particularly to the antibonding orbital of nitrogen in the alkaloid molecule, creating a process known

as back-bonding. This retro-donation not only strengthens the bond but also facilitates the chemical adsorption of inhibitors [24, 26, 27, 47].

## Conclusions

The extraction of alkaloids from the *Crotalaria spectabilis* stem was successfully and efficiently carried out and characterized by qualitative chemical method and FTIR spectroscopic technique. The maximum inhibition efficiencies of the extracted alkaloids are 90.38 % and 92.86 % obtained via weight loss method and polarization method, respectively. As an inhibitor, extracted alkaloids are effective up to 45 °C and for up to 6 hours of immersion. The data are best fitted for Langmuir adsorption isotherm. The free energy of adsorption, along with the entropy and enthalpy values determined from weight loss measurements, indicates that alkaloids are adsorbed on the steel surface through physisorption. Due to the effective performance demonstrated by the extracted alkaloids, they can serve as effective inhibitors to prevent corrosion in industrial cleaning processes.

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