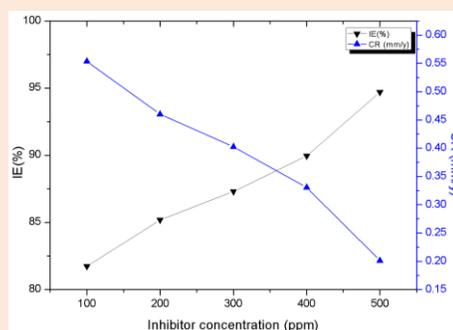


Research Article

Inhibition of Steel Corrosion in Acid Medium by Ethanolic Extract of *Cassia Fistula*Kavitha Rose^{1,2}, Monikandon Sukumaran³, Kesavan Devarayan^{1,4,*}, Kalyanaraman Rajagopal⁵, Sankar Arumugam^{2,*}¹Department of Chemistry, Dhirajlal Gandhi College of Technology, Salem, India²Department of Chemistry, Kandasamy Kandar's College, Salem 638182, India³Department of Basic Engineering, College of Fisheries Engineering, Tamil Nadu Fisheries University, Nagapattinam 611 001, Tamil Nadu, India⁴Department of Basic Sciences, College of Fisheries Engineering, Tamil Nadu Fisheries University, Nagapattinam 611 001, Tamil Nadu, India⁵Department of Biotechnology, Vels University, Chennai 600117, India**Abstract**

For the first time, the homogeneous adsorption of inhibitor molecules of *Cassia Fistula* on steel surface is reported in this study. The ethanolic extract of *Cassia Fistula* is evaluated as potential inhibitor against the corrosion of steel in 1.0 M HCl. The inhibitive nature of the inhibitor is evaluated by means of weight loss measurements and electrochemical studies. A maximum of 94.7% inhibition efficiency was observed for 500 ppm of inhibitor at 289 K. Further scanning electron microscopic images and Langmuir's adsorption isotherm indicated predominant physical adsorption as the mechanism of the corrosion inhibition. In addition, the energy dispersive X-ray spectral elemental mapping revealed homogeneous distribution of the nitrogen, which indicated for the presence of inhibitor molecules on the steel surface.



Keywords: Corrosion, inhibition, *Cassia fistula*, steel, plant extract.

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Introduction

Steel corrosion is one of the widely studied research topic since most of the households and industrial structures are made up using it. Though corrosion is a spontaneous natural process, it can be controlled by using suitable inhibitors. Since the first report on corrosion inhibitors by Speller [1], there have been several researches that suggest for successful application of inhibitors [2]. Initially chromium based inhibitors gained popularity. However, due to its non-eco friendliness and harmful effects on humans, organic inhibitors were on demand [3]. Among organic inhibitors, compounds derived from plant extracts, also known as green inhibitors, attracted more attention due to its eco-friendliness, economy, and inhibition efficiency.

As a part of exploration for efficient inhibitors, the authors evaluated several organic inhibitors [4-14]. *Cassia Fistula* is a common plant available in countries such as India, Sri Lanka, and other South East Asian countries. In view of availability, environmental friendliness, and economy in this study, the ethanolic extract of *Cassia Fistula* (CF) is evaluated for inhibition of steel corrosion in 1.0 M HCl.

Experimental**Preparation of the inhibitor**

The fresh leaves of CF (1 kg) were collected and dried under shadow for 7 days. The dried leaves were crushed into

powder using a mixer grinder. The CF powder was soaked in 95% ethanol for 3 days. Then the extract was filtered through a Whatman20 filter paper and the solvent was evaporated under *vacuo* to yield a green colored oily product (35 g).

Weight loss measurements

The weight loss measurements were performed according to our previous reports [8-10] using the steel specimens with the composition of C, 4.93%; Mn, 1.09%; Si, 1.78%, and the remainder being Fe were used for this study. The inhibition efficiency (*%IE*), corrosion rate (*CR*), and surface coverage (θ) were calculated using the following equations 1-3.

$$IE\% = \frac{(W_o - W)}{(W_o)} \times 100 \quad (1)$$

$$\theta = IE\% / 100 \quad (2)$$

The corrosion rate (*CR*) was calculated according to ASTM standard [15] and it is given by equation 3.

$$CR = \frac{W_o}{AtD} \quad (3)$$

Where, *CR* – corrosion rate (mm/y), *W_o* – weight difference (g) before and after weight loss measurements; *A* – exposed area of the specimen, *t* – immersion time (h), and *D* – density of the specimen (g/cm³). The weight loss measurement values were used to plot adsorption isotherms such as Langmuir adsorption isotherm and to calculate the thermochemical parameters.

Electrochemical Studies

Electrochemical measurements such as potentiodynamic polarization studies and electrochemical impedance spectroscopy were performed according to our previous reports [8-10].

The *IE%* from polarization studies were calculated as given in equation 4.

$$IE\% = \frac{(I'_{corr} - I_{corr})}{(I'_{corr})} \times 100 \quad (4)$$

The electrochemical impedance spectroscopy (EIS) was recorded in the frequency range of 10 mHz to 100 kHz with a potential amplitude of 10 mV. The *IE%* was calculated from the charge transfer resistance (*R_{ct}*) using the equation (5).

$$I.E(\%) = \frac{(R_{ct} - R'_{ct})}{(R_{ct})} \times 100 \quad (5)$$

where *R'_{ct}* and *R_{ct}* are the charge transfer resistance of 1.0 M HCl with and without the inhibitors respectively.

Surface Characterization

The surface morphologies of the steel specimens both in presence and absence of the inhibitor were analyzed using a JSM-5900 scanning electron microscopy (SEM) coupled with an energy dispersive X-ray spectroscopy (EDS) instrument.

Results and Discussion

Weight loss measurements

The inhibitor concentrations were varied from 100 to 500 ppm (**Figure 1** and **Table 1**). The concentration of the inhibitor had linear relationship with the IE%. The CF inhibitor exhibited a maximum of 94.7% inhibition efficiency at 500 ppm of CF inhibitor concentration at 298 K and the corrosion rates were drastically decreased to 13.5 folds. This is attributed to the complete coverage of the steel surface by the CF inhibitor molecules.

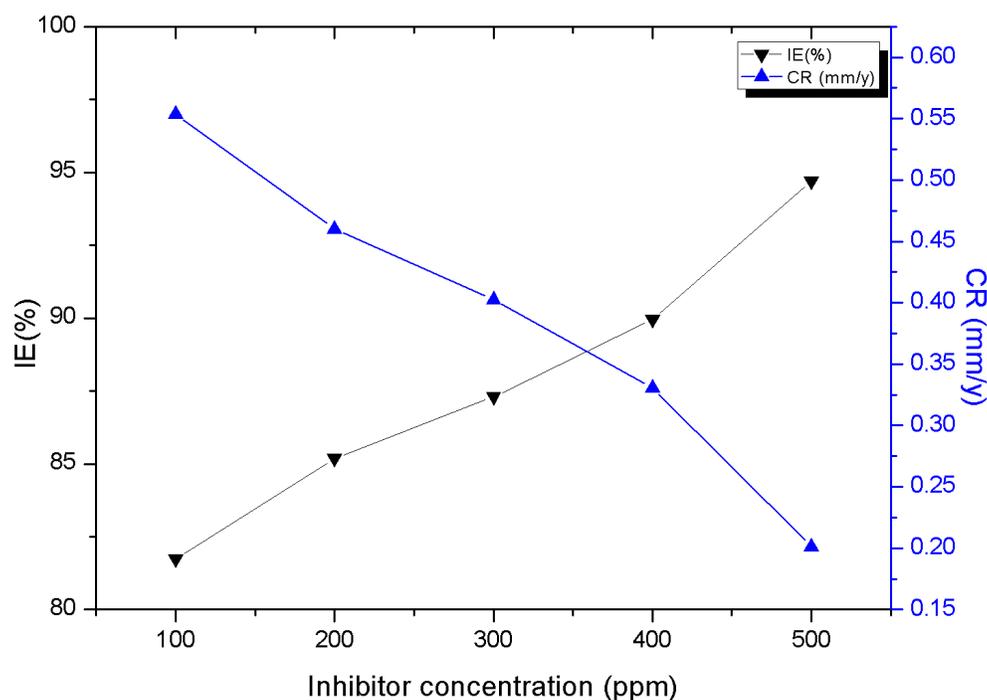


Figure 1 Effect of CF inhibitor concentration on corrosion of steel in 1.0 M HCl at 298 K.

Adsorption isotherms and thermodynamic parameters

The weight loss data were subjected to different adsorption isotherms such as Langmuir, Temkin, Freundlich, Bokrisswinkle, and Frumkin isotherms. However, only Langmuir's adsorption isotherm was found to fit with correlation coefficient more than 0.99 (**Figure 2**). Langmuir adsorption isotherm is explained based on a linear relationship between surface coverage and the inhibitor concentration as shown in equation (6).

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (6)$$

Where, K_{ads} is the equilibrium constant of adsorption process.

Table 1 Corrosion parameters for inhibition of corrosion of steel specimen in 1.0 M HCl by inhibitor at 298 K.

C (ppm)	Surface Coverage (θ)	IE%	CR (mm/y)	K_{ads} (kJ/g)	ΔG_{ads} (kJ/g)
0	0	0	2.718		
100	0.817	81.746	0.554	44.8	-19.5
200	0.852	85.185	0.460	28.7	-18.4
300	0.873	87.302	0.403	22.9	-17.8
400	0.899	89.947	0.331	22.4	-17.8
500	0.947	94.709	0.201	35.8	-18.9

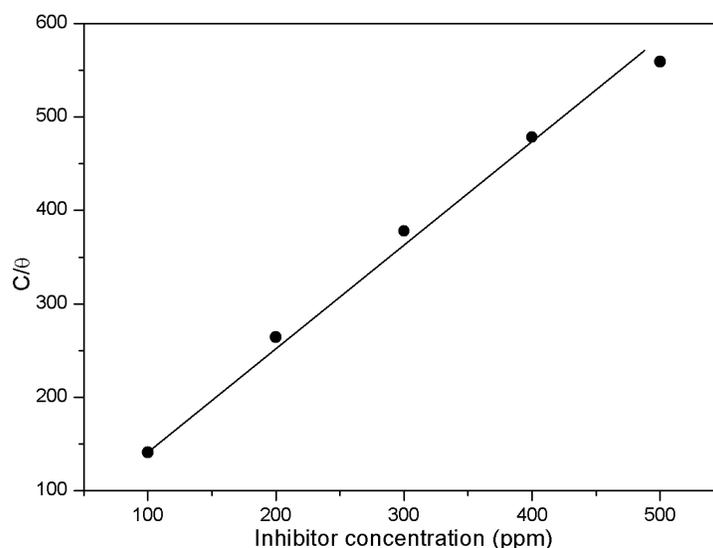


Figure 2 Langmuir adsorption isotherm for adsorption of CF inhibitor molecules on steel surface in 1.0 M

The correlation coefficient was close to 1, which indicated that there was no interaction between the inhibitor molecules adsorbed on the surface of the steel. This was due to the predominant physical adsorption of the inhibitor molecules on the surface of the steel. In generally, plant extracts contain alkaloids and flavonoids [2], which possess aromatic rings, hetero atoms such as O, S, and/or N in the structure.

Further the weight loss data were used to calculate equilibrium constant (K_{ads}) and free energy of adsorption using equations (6) and (7), respectively (Table 1).

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

where R is the gas constant, T is the temperature, and the value of 55.5 is the concentration of water in the inhibitor solution. The determined ΔG_{ads} values were between -17.8 to -19.5 kJ/g, which indicated for predominant electrostatic interaction between the CF inhibitor molecules and the steel surface. The above discussion indicated that the adsorption of the inhibitor molecules proceeds mainly via physical adsorption [16, 17].

Electrochemical studies

The EIS curves for the steel both in presence and absence of the inhibitor was shown in **Figure 3** and data were shown in **Table 2**. Upon introduction of the 500 ppm inhibitor the diameter of the EIS curve has decreased drastically which is attributed to the coverage of the steel surface by the inhibitor molecules which prevented the acid attack and thus decreased the conductivity. Further, the double-layer capacitance (C_{dl}) was also calculated by the following equation (8).

$$C_{dl} = \frac{1}{(2\pi f_{max} R_{ct})} \quad (8)$$

where f_{max} is the frequency at which the imaginary component of the impedance ($-Z''$) is maximal. The effect of 500 ppm of inhibitor decreased the C_{dl} from 267.4 to $20.3 \times 10^{-3} \mu\text{F cm}^{-2}$. This is due to lowering of the dielectric constant of the steel by the introduction of the inhibitor molecules.

The Tafel polarization results for the steel both in presence and absence of the inhibitor was shown in **Figure 4** and **Table 3**. The results indicated that the I_{corr} values observed for the steel specimen in presence of inhibitor was lower than that was observed in the absence of the inhibitor. It was also noted that the difference between the E_{corr} values of the steel in presence an absence were lesser than ± 85 mV which indicated that the inhibitor suppresses both cathodic and anodic reactions and thus the inhibitor was classified as mixed-type inhibitor [18].

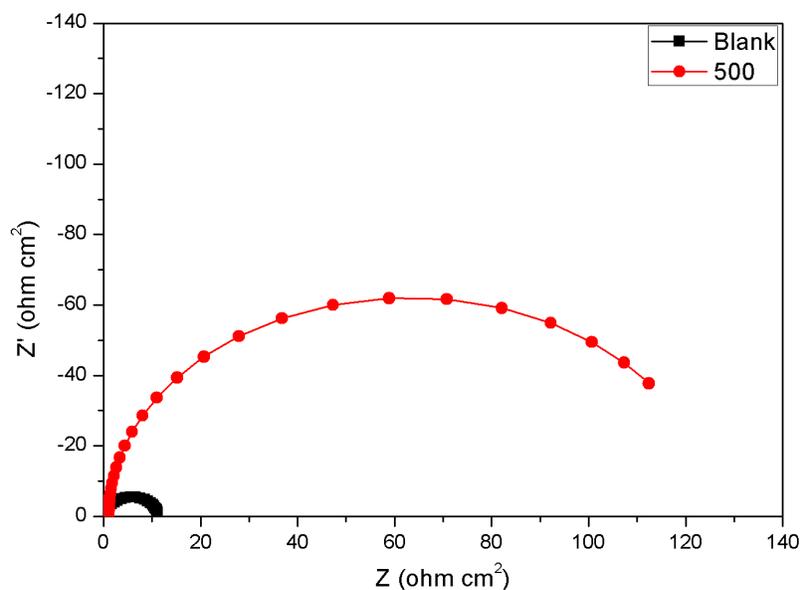


Figure 3 Electrochemical impedance spectra of steel specimen both in presence of 500 ppm of inhibitor and absence of inhibitor

Table 2 EIS parameters of steel specimen in presence of absence of inhibitor in 1.0 M HCl at 298 K

Inhibitor	Concentration (ppm)	R_{ct} (Ω cm 2)	f_{max}	C_{dl} (μ F cm $^{-2}$) 10^{-3}	Θ	IE%
Blank	0	11.1	5.38	267.4	-	-
1.0 M HCl + Inhibitor	500	126.7	61.9	20.3	0.913	91.3

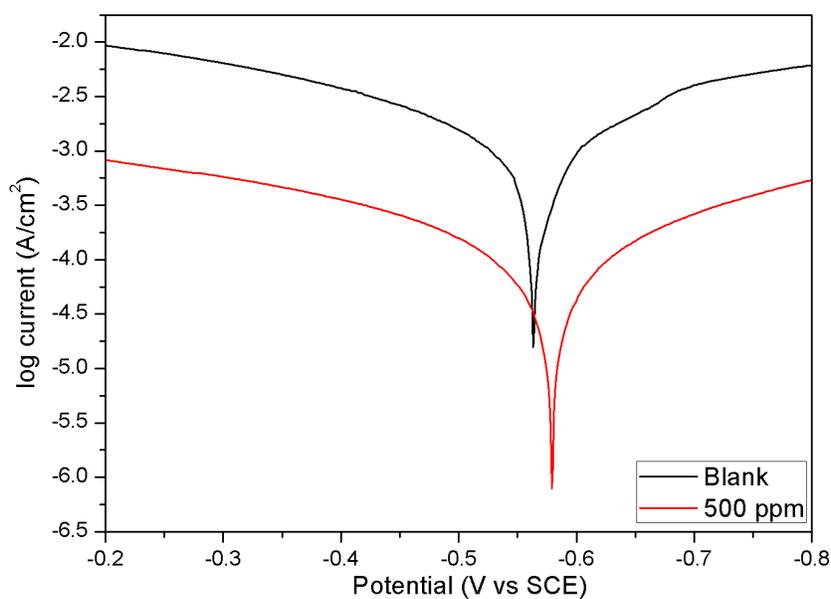


Figure 4 Tafel polarization curves of steel specimen in presence and absence of CF inhibitor in 1.0 M HCl at 298 K

Table 3 Tafel polarization parameters for steel specimen in presence and absence of CF inhibitor in 1.0 M HCl at 298K

Inhibitor	Concentration (ppm)	b_c (mV/decade)	b_a (mV/decade)	$-E_{corr}$ (mV vs SCE)	I_{corr} (μ A/cm 2)	Θ	IE%
Blank	-	5.687	4.292	0.562	673.3	-	-
1.0 M HCl + 2.0 Inhibitor	500	5.291	4.884	0.579	59.2	0.912	91.2

Surface analysis

Figure 5 exhibits the SEM morphologies and EDS results of the fresh steel, acid-treated steel, and inhibitor-treated steel. The elemental composition of the steel specimens was presented in **Table 4**. The fresh steel specimen exhibited a relatively smooth surface, whereas the acid-treated steel exhibited a rough surface due to the acid attack. Further the composition of the acid-treated steel showed higher content of oxygen. The inhibitor-treated steel showed relatively better surface that consisted of 15.52% of nitrogen which was evidence for the presence of the inhibitor molecules on the steel surface.

The EDS mapping shown in **Figure 6**, exhibited highly homogeneous distribution of nitrogen on the steel surface. This result indicated for the homogeneous adsorption of the inhibitor molecules on the surface of the steel specimen which actually inhibited the corrosion.

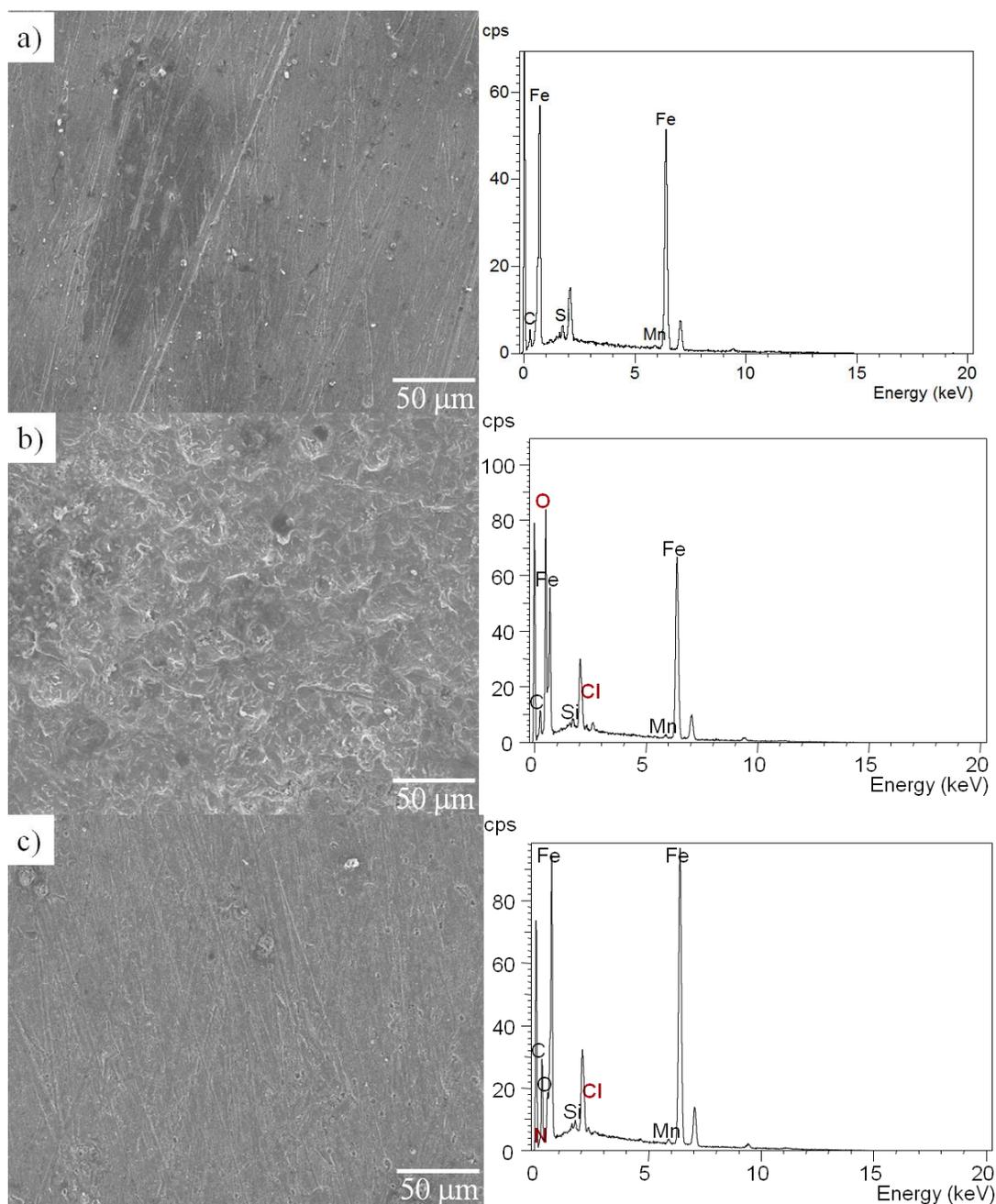
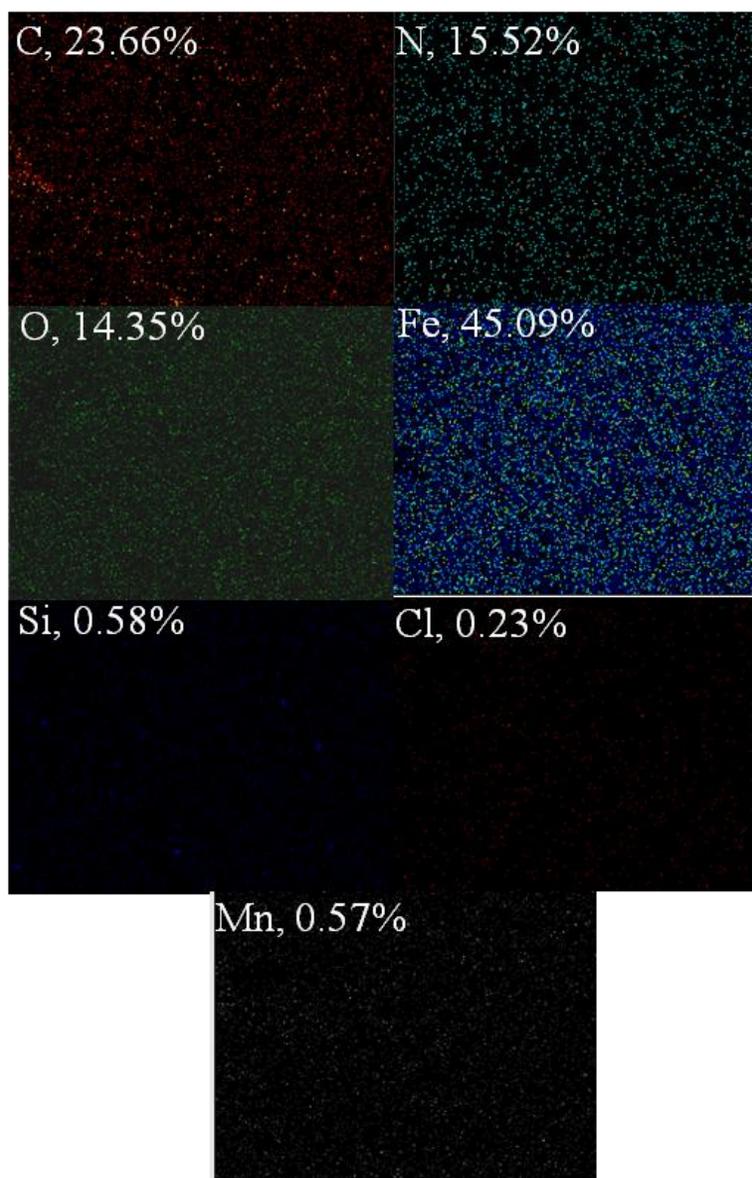


Figure 5 SEM and EDS of abraded steel specimen (a, b), 1.0 M HCl treated-steel specimen (C, d), and 1.0 M HCl + 50 ppm of inhibitor treated-steel specimen (e, f)

Table 4 SEM-EDS composition analyses of abraded steel specimen and steel specimens in presence and absence of inhibitor in 1.0 M HCl

Sample	Composition						
	Fe	O	C	Mn	Si	Cl	N
Fresh steel specimen	92.2	0	4.93	1.08	1.79	0	0
Blank	68.23	23.35	3.37	0.63	0.86	3.56	0
1.0 M HCl + Inhibitor	45.09	14.35	23.66	0.57	0.58	0.23	15.52

**Figure 6** EDS mapping of 1.0 M HCl + 500 ppm of inhibitor treated – steel specimen

Conclusion

In this study, the inhibitive nature of the ethanolic extract of *Cassia Fistula* against corrosion of steel in 1.0 M HCl was evaluated. A maximum of 94.7% inhibition efficiency was observed for the inhibitor against steel corrosion in 1.0 M HCl at 298 K. The electrochemical studies indicated that the inhibitor suppresses both anodic and cathodic reactions. The energy dispersive X-ray spectroscopic analysis revealed the homogeneous distribution of the inhibitor molecules on the surface of the steel which is evident for adsorption mechanism of the inhibitor.

Acknowledgement

Kesavan Devarayan and Monikandon Sukumaran thank College of Fisheries Engineering, Tamil Nadu Fisheries University for their encouragement for research. Kavitha Rose thanks the management of Dhirajlal Gandhi College of Technology for their encouragement for research. Sankar Arumugam and Kavitha Rose as well thank the management of Kandasamy Kandar's College for their support for research.

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Publication History

Received	01 st Sep 2016
Accepted	20 th Sep 2016
Online	30 th Oct 2016