Research Article

Effect of Green Inhibitors on Acid Corrosion of AISI 1022 Steel

Vivekananthan Shanmuga Sundaram,[1] Sakunthala Pitchai,[2] Kesavan Devarayan,[1] Gopiraman Mayakrishnan,[1] Alexramani Vincent,[2] and Sulochana Nagarajan[1]

[1]Department of Chemistry, National Institute of Technology, Tiruchirappalli 620 015, Tamil Nadu, India.

[2]Department of Chemistry, St. Joseph's college, Tiruchirappalli, Tamil Nadu 620 015, India.

Abstract

The methanolic extract of the flowers from *Millingtonia hortensis* and *Cleome chelidonii* were studied against the corrosion of mild carbon steel in 1 M HCl by different techniques. Weight loss and electrochemical studies showed that these eco-friendly inhibitors efficiently diminish the corrosion rate of the steel specimen in 1 M HCl. The extract from *Cleome chelidonii* exhibited a maximum inhibition efficiency of 91.5% for 400 ppm concentration at 300 K, whilst the extract from *Millingtonia hortensis* showed 83.4% inhibition efficiency for 1000 ppm. Langmuir adsorption isotherm suggested for physisorption mechanism, whereas the ΔG_{ads} indicated that the inhibition process proceeds *via* both physisorption and chemisorption mechanism.

Keywords: Corrosion, Inhibition, Green Inhibitors, Millingtonia hotensis, Cleome chelidonii, Steel

Introduction

Mild or low-carbon steels are the most frequently used alloys due to the high ductility, which allows it for easier machining and welding [1]. Corrosion of metals/alloys is a natural phenomenon that can be controlled upon introducing small quantities of suitable inhibitors into the corrosion system. Different types of inhibitors were studied including heavy metals and plant extracts. Due to the toxic nature of the metal inhibitors, eco-friendly inhibitors are prefered and studied more in recent years [2]. There were several succeeding reports on non-toxic, eco-friendly/green inhibitors [3–14].

Plants are economical and ubiquitous biomaterials, which can be used for the purpose of corrosion inhibition. Different parts of the plants contain different organic compounds. Moreover, extraction of natural products from plants is rather easier than any complex synthetic procedure. Thus plant extracts merits for investigation as potential eco-friendly/green inhibitors. Earlier, our research group reported *Clematis gouriana* [7], *Brugmansia suaveolens*, *Cassia roxburghii* [8], *Polycarpaea corymbosa* [12], and *Desmodium triflorum* [12] as potential corrosion inhibitors for corrosion of mild steel in HCl. 3-hydroxyflavone [5] and 2,3-dihydroxyflavanone [10] were also studied as the simple, representative models for plant extracts to understand the mechanism of inhibition.

In view of inhibition of potential, cost-effectiveness, and eco-friendliness of plant extracts, in the present study, the methanolic extracts of flowers from *Millingtonia hortensis* and *Cleome chelidonii* were investigated against the corrosion of mild steel in 1 M HCl. The inhibition potentials were evaluated by weight loss method and electrochemical impedance spectroscopic techniques. The inhibition mechanism was studied by fitting the experimental data to different adsorption isotherms and the results are presented in the following sections.

Experimental

Materials

Inhibitor Preparation [7, 8, 12]

(1) *Millingtonia hortensis* (MH)

The flowers of *Millingtonia hortensis* (250 g) was dried under shadow, crushed and then stored in powder form. The flower-powders were extracted with methanol (3 x 200 mL) by means of cold percolation method. The solvent was completely removed under vacuo to yield crude, oily substance (2 g). The crude product (hetherto inhibitor) was dissolved in appropriate volume of double distilled water to prepare 10% stock solution of the inhibitor. Different concentrations of the plant extract were prepared from the stock solution by appropriate dilution using double distlled water.

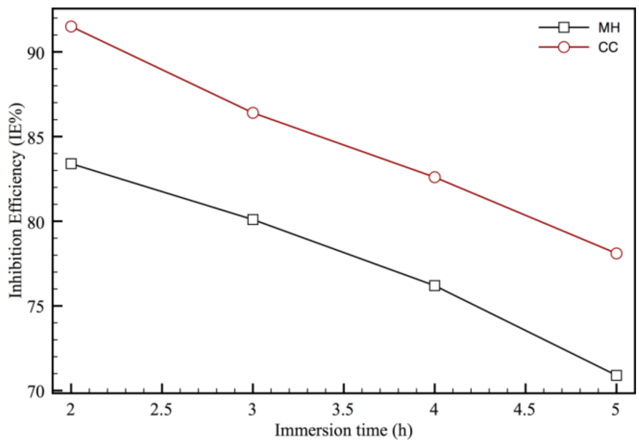
(2) *Cleome chelidonii* (CC)

Fresh flowers (1 kg) of *Cleome chelidonii* were extracted with methanol (5 x 500 mL) by means of cold percolation method. The methanol extract was concentrated in vacuo and left on an ice chest for few days. The crude, oily product (5.4 g) was dissolved in appropriate volume of double distilled water to prepare 10% stock solution of the inhibitor. Similar to MH-extract, different concentrations of CC-extracts were prepared.

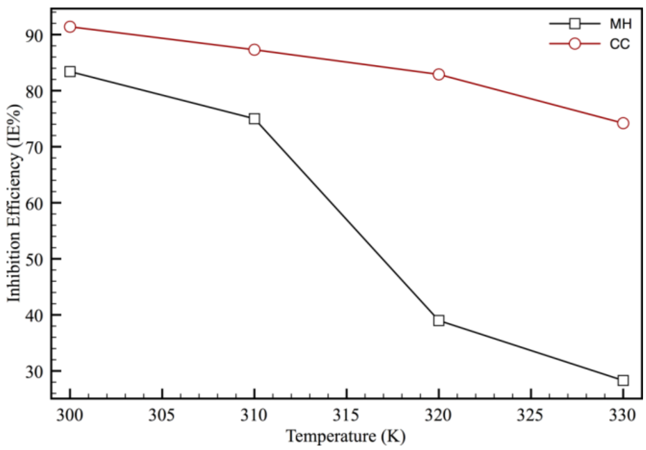
Table 1 Effect of inhibitor concentration on inhibition efficiency at 300 K

Inhibitor	Conc. (ppm)	IE%	θ	$\sigma_{IE\%}$
MH	250	72.0	0.720	0.04
	500	75.8	0.758	0.03
	750	78.7	0.787	0.07
	1000	83.4	0.834	0.01
CC	100	83.0	0.830	0.08
	200	86.2	0.862	0.05
	300	89.4	0.894	0.06
	400	91.5	0.915	0.04

* $\sigma_{IE\%}$ – standard deviation for IE%



(a)

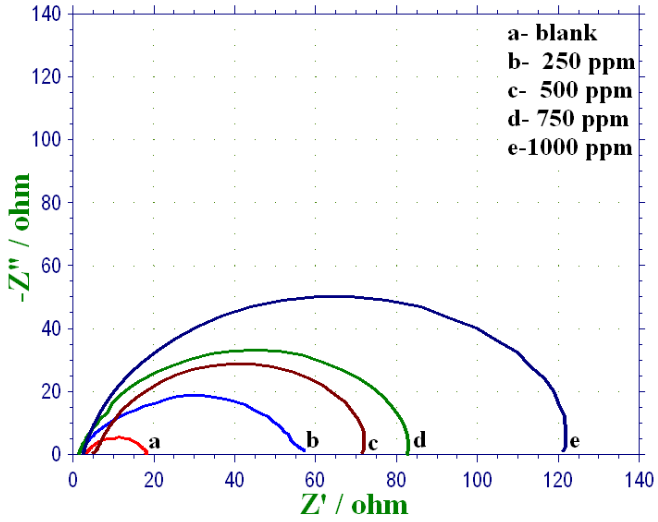


(b)

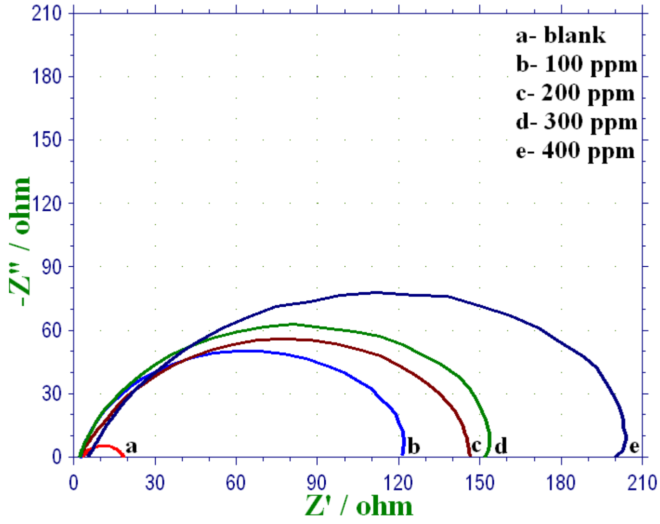
Figure 1 Effect of immersion time (a) and temperature (b) on inhibition efficiency. An optimum concentration of **MH** (1000 ppm) and **CC** (400 ppm) were used to determine the effect of prolonged immersion time and elevated temperature

Mild Steel Specimen Preparation

The mild steel having compositions of C = 0.22%, Mn =0.22%, Cr = 0.22% and Fe = 99.34% has been purchased and classified as 1022 steel according to AISI standards [1]. The mild steel specimens having dimensions 1.0 cm x 1.0 cm x 0.06 cm were used for weight loss study. The specimens with an exposed area of 1 cm^2 were used for electrochemical studies. The coupons are abraded with a series of emery papers from 400 to 1200 grade and washed thoroughly with double distilled water, degreased with acetone and then air dried. The solutions are prepared by dilution of analytical grade 37% HCl with double distilled water in the absence and presence of inhibitors.



(a)



(b)

Figure 2 Electrochemical behaviour (Nyquist plots) for mild steel specimens in 1 M HCl in presence and absence of inhibitors MH (a) and CC (b) at 300 K

Table 2 Impedance parameters for the corrosion of mild steel in 1 M hydrochloric acid in presence and absence of inhibitor

Inhibitor	Conc. (ppm)	R_{ct} (Ω cm^2)	IE%	θ	$σ_{IE\%}$
MH	250	56.3	73.3	0.733	0.02
	500	67.3	77.7	0.777	0.01
	750	81.6	81.6	0.816	0.08
	1000	120.5	87.5	0.875	0.05
CC	100	119.4	87.4	0.874	0.03
	200	144.7	89.6	0.896	0.02
	300	152.3	90.1	0.901	0.03
	400	199.2	92.5	0.925	0.02
Blank	-	15.0	-	-	-

Weight Loss Measurements

The weight loss experiments were performed similar to our previous reports [7, 8, 12]. The polished mild steel specimens were immersed into 100 mL of 1 M HCl for 2 h at 300 K to determine the weight loss values of blank run. The results of weight loss measurements are the mean of three such runs that are performed separately. The experiments were performed both in the presence and absence of inhibitors at temperatures ranging from 300–330 ± 1 K. The immersion time also varied (2–5 h) to understand the inhibitive action of the inhibitors as well as the machanism of inhibition. The inhibition efficiency (IE %) and surface coverage (Θ) from weight loss measurements were calculated using the following equations

$$\theta = \frac{(W_0 - W)}{(W_0)} \quad (1)$$

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

where W_0 and W are the mass loss of the mild steel in the absence and presence of inhibitors, respectively.

Electrochemical Impedance Spectroscopy

AC electrochemical impedance spectrocopic measurements (EIS) were carried out at the range from 100 kHz to 10 mHz at an amplitude of 10 mV. The impedance diagrams were given as Nyquist representation. The electrical equivalent circuit for the system is shown in Figure 1. The IE% was calculated from the charge transfer resistance (R_{ct}) (Equation 3).

$$IE(\%) = \frac{(R_{ct} - R'_{ct})}{(R_{ct})} \times 100 \quad (3)$$

where R_{ct} and R'_{ct} are charge transfer resistances in the absence and presence of inhibitor.
In the given electrical equivalent circuit, R_s is the solution resistance, R_{ct} is the charge transfer resistance, and C_{dl} is the double layer capacitance.

Fourier Transform – Infrared Spectroscopy

The mild steel specimens were immersed in solutions containing 1 M HCl and optimised amount of inhibitor (i.e. 2000 ppm of **MH** or 400 ppm of **CC**) for 2 h at 300 K. The specimens were washed with distilled water and acetone, and then dried in vacuo for 24 h at 40 °C. On one hand, the inhibitors (**MH**, **CC**) adsorbed on the surface of the mild steel specimens were scrapped with the help of a knife. The scrapped samples were named as **Fe-MH** and **Fe-CC**. Then the inhibitors and the scrapped samples were subjected to FT-IR (Perkin Elmer) spectroscopies.

Results and Discussion

Effect of Inhibitor Concentration

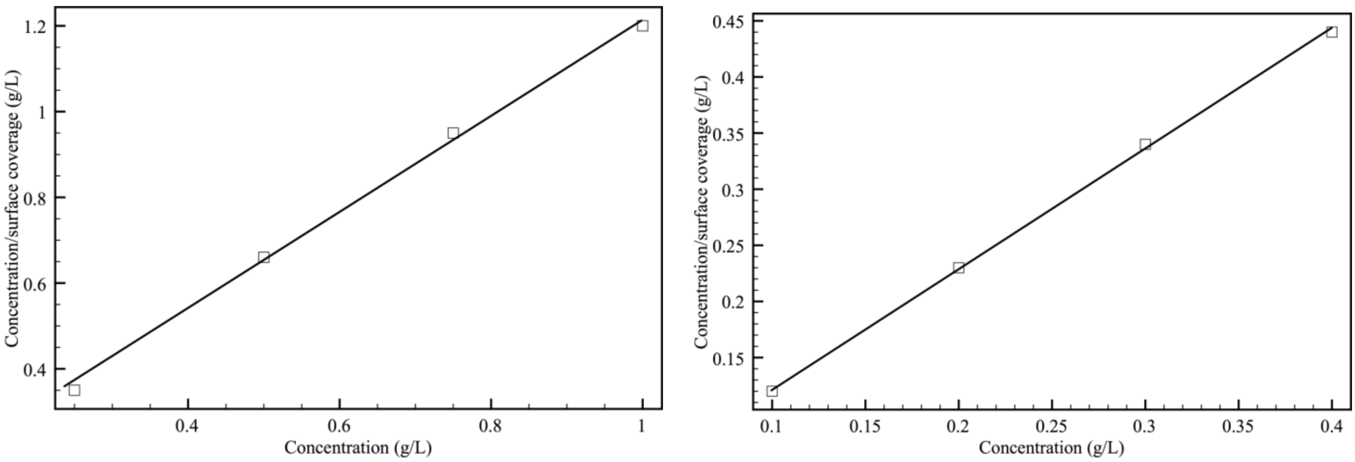
The weight loss measurements were performed for mild steel in 1 M HCl at different conditions by varying concentrations of inhibitors (**MH**, **CC**), immersion time, and temperature. The results of weight loss experiments conducted at 300 K are presented in **Table 1** and **Figure 1**. 2 h of immersion time was required for both the inhibitors to reach their maximum efficacy. Inhibitor **MH** showed 83.4% of IE at 1000 ppm, where as **CC** exhibited 91.5% of IE at 400 ppm. Further increase of the inhibitor concentrations (>1000 ppm for **MH**, >400 ppm for **CC**) did not yield any significant increase in the IE%. Therefore, the concentrations of 1000 ppm for **MH** and 400 ppm for **CC** were considered as optimum concentrations for further studies. As a general nature for any inhibitors, for **CC** and **MH** also upon increasing the inhibitor concentrations IE% increases.

Effect of Immersion Time

The immersion time for weight loss measurements were varied from 2–5 h. **CC** showed rather higher efficiency than **MH** as shown in Table 1. At all the immersion times, **CC** exhibited more than 78% of IE, where as more than 71% of IE was observed for **MH**. Apparently, IE% of both inhibitors decreases significantly upon increasing the immersion time. A likely explanation is that the **MH** and **CC** inhibit the corrosion rate by physisorption phenomenon. There may be a partial desorption of the inhibitor molecules from the mild steel surface due to the prolonged immersion time, which is attributed to the weak van der Waals forces and/or electrostatic interactions.

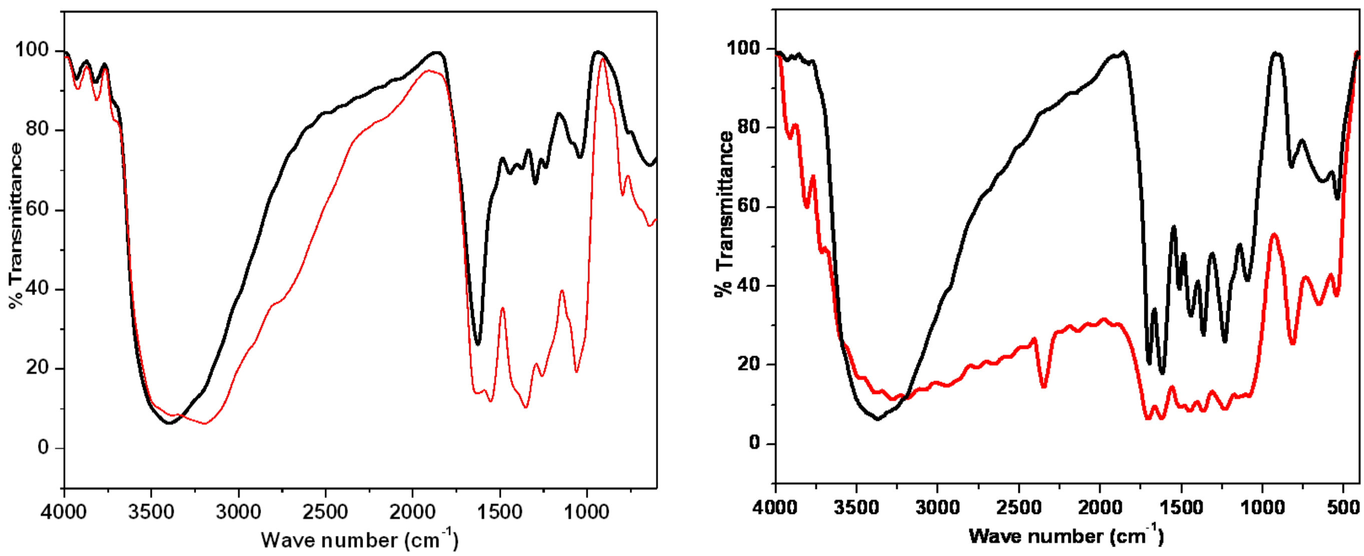
Effect of Temperature

In order to understand the mode of interaction of the inhibitor molecules with the mild steel surface, the temperature of the corrosion system was varied. In the case of **MH** the inhibition efficiencies has decreased drastically with increasing temperatures. At 330 K, inhibitor **MH** showed IE of 28.3% only, where as **CC**



(a) (b)

Figure 3 Langmuir isotherm for adsorption behaviour of **MH** (a) and **CC** (b) on mild steel surface at 300 K



(a) (b)

Figure 4 FT-IR spectrum of MH (top spectrum) & MH-adsorbed on mild steel (Fe-MH) (bottom spectrum) (a) and CC (top) & CC-adsorbed on mild steel (Fe-CC) (bottom)

Table 3 Thermochemical parameters for mild steel in 1 M hydrochloric acid in the absence and presence of the inhibitors

Inhibitor	Methods	Temperature (K)	R^2	Slope	ΔH_{ads} (kJ mol^{-1})	ΔS_{ads} (JK^{-1} mol^{-1})	ΔG_{ads} (kJ mol^{-1})
MH	Weight loss	300	0.995	1.140	102.1	91.4	-27.2
	EIS	300	0.998	1.072	-	-	-
CC	Weight loss	300	0.996	1.054	43.45	46.48	-31.4
	EIS	300	0.999	1.064	-	-	-

exhibited 74.2% of IE. A plausible explanation for the different behaviors of inhibitors is that the **MH** inhibitor molecules inhibit predominantly via physisorption, where as, a comparatively stronger interaction is suggested between the molecules of **CC** and mild steel surface. Chemisorption phenomenon is dominant at higher temperatures where as both chemisorption and physisorption exists at lower temperatures.

EIS Studies

The electrochemical impedance spectroscopic results are presented in the form of Nyquist plots as shown in **Figure 2**. The impedance parameters like R_{ct} and C_{dl} are given in **Table 2**. For both the inhibitors the trend of increasing IE% was observed with increasing inhibitor concentrations. The Nyquist plots shown in figure 2 contain depressed semi-circle with the center under the real axis, whose size increases with the inhibitor indicating a charge transfer process mainly controlling the corrosion of mild carbon steel.

Such a behavior, characteristic for solid electrodes and often referred to as frequency dispersion that has been attributed to roughness and other in homogeneities of the solid surface [15]. The impedance response of mild steel in uninhibited acid solution has significantly changed after the addition of the plant **S**extract in the corrosion solutions, which indicated that the impedance of the inhibited substrate has increased with increasing concentration of inhibitor. This situation was the result of increase in the surface coverage by the plant extract, which lead to an increase in the inhibition efficiency. Similar to the weight loss data, the EIS results of **CC** exhibited maximum IE% more than 92% at 400 ppm, where as **MH** showed over 87% of IE.

Mechanism of Inhibition

Generally, inhibitors act via adsorption to retard the corrosion rate. By fitting the weight loss data to different isotherms such as Langmuir, Temkin, or Frumkin, mode of interaction between the inhibitor molecules and the steel surface can be revealed. The plots obey Langmuir adsorption isotherm (**Figure 3**) with correlation values, **MH** = 0.995 and **CC** = 0.996, indicating that there were smaller degree of interaction between the inhibitor molecules, which is originally prohibitted by Langmuir isotherm.

The thermochemical parameters such as ΔH_{ads}, ΔS_{ads}, and ΔG_{ads} were calculated similar to our previous reports [7, 8, 12] (**Table 3**). The negative sign of ΔG_{ads} indicates the sponteinity of the adsorption process besides the stability of the adsorbed layer on the steel surface at room temperature. The magnitude of ΔG_{ads} values for **MH** and **CC** were -27.2 kJ/mol and -31.4 kJ/mol, suggesting that the inhibition occurs via both chemisorption and physisorption mechanisms. The exothermic nature of the inhibition process was indicated by the negative values of ΔH_{ads}. The negative values for the ΔS_{ads} are suggesting for associatively activated inhibition process.

The FT-IR spectra were taken for both inhibitors **MH** and **CC** and the inhibitors' adsorbed on the steel surface (**Figure 4**). Adsorption bands for C=O (~1650 cm^{-1}), N-H (~3200 cm^{-1}), O-H (~3400 cm^{-1}) groups were mainly observed for the inhibitors, since these plant extracts were known to contain several natural products that have different functional groups. The inhibitor molecules-adsorbed on the steel surface showed shifts in the C=O, N-H, and O-H stretching bands, indicating that the inhibitors were adsorbed on the mild steel either via chemisorption, physisorption or both mechanisms.

Conclusion

Two plant extracts (**MH** and **CC**) were evaluated against the corrosion of mild steel in hydrochloric acid medium, and found to be effective inhibitors at given circumstances. The adsorption of inhibitors was both via chemisorption and physisorption. At all the tested conditions, **CC** was better inhibitor than **MH** both in terms of inhibition efficiency and inhibitor concentration. The major reason for the better inhibitive properties of CC may be attributed to the different chemical constituents of the extracts, which may be revealed by phytochemical analysis of the two plant extracts. Finally, both the plant extracts are efficient, economical, eco-friendly inhibitors for corrosion inhibition of mild steel.

References

[1] Galvery WL, Marlow, FM (2001) Welding essentials: Questions and Answers, Industrial Press Inc., New York, Extended 1st edition, 2001

[2] Kesavan D, Gopiraman M, Sulochana N (2012) Green inhibitors for corrosion of metals: A review. *Che Sci Rev Lett* 1:1–9

[3] Raja PB, Sethuraman MG (2008) Natural products as corrosion inhibitor for metals in corrosive media-A review. *Mater Lett* 62:113–116

[4] Negm NA, Zaki MF (2009) Synthesis and evaluation of 4-diethylamino benzaldehyde Schiff base cationic amphiphiles as corrosion inhibitors for carbon steel in different acidic media. *J Surf Deterg* 12:321–329

[5] Lavanya M, Kesavan D, Prabhavathi N, Sulochana N (2009) Studies on inhibitive effect of 3-hydroxyflavone on the acid corrosion of mild steel. *Surf Rev Letts* 16:845–853

[6] Bothi Raja P, Sethuraman MG (2009) Strychnosnux-vomica an eco-friendly corrosion inhibitor for mild steel in 1 M sulfuric acid medium. *Mater Corros* 60:22-28

[7] Gopiraman M, Sakunthala P, Kanmani R, Alex Ramani V, Sulochana N (2011) Inhibitive action of Clematis gouriana extract on the corrosion of mild steel in acidic medium. *Ionics* DOI:10.1007/ s11581-011-5480584-9

[8] Gopiraman M, Sakunthala P, Kesavan D, Alexramani V, Kim IS, Sulochana N (2011) An investigation of mild carbon steel corrosion

inhibition in hydrochloric acid medium by environment friendly green inhibitors. *J Coat Technol Res* DOI 10.1007/s11998-011-9374-6
[9] Negm NA, Kandile NG, Mohamad MA (2011) Synthesis, characterization and surface activity of new eco-friendly Schiff bases vanillin derived cationic surfactants. *J Surf Deterg* 14:325–331
[10] Gopiraman M, Sathya C, Vivekananthan S, Kesavan D, Sulochana N (2011) Influence of 2,3-dihydroxyflavanone on corrosion inhibition of mild steel in acidic medium. *J Mater Eng Perform* doi:10.1007/s11665-011-9925-0
[11] Kesavan D, Muthu Tamizh M, Gopiraman M, Sulochana N, Karvembu R (2012) Physicochemical studies of 4-substituted *N*-(2-mercaptophenyl)-salicylideneimines: Corrosion inhibition of mild steel in an acid medium. *J Surfact Deterg* doi:10.1007/s11743-012-1338-z
[12] Sakunthala P, Vivekananthan S, Gopiraman M, Sulochana N, Alex Ramani V (2012) Spectroscopic investigations of physicochemical interactions on mild steel in an acidic medium by environmentally friendly green inhibitors. *J Surf Deterg* doi: 10.1007/s11743-012-1405-5
[13] Negm NA, El Garargy AFM, Mohammed DE, Mohamad HN (2012) Environmentally friendly nonionic surfactants derived from tannic acid: Synthesis, characterization and surface activity. *J Surf Deterg* 15:433–443
[14] Negm NA, Kandile NG, Badr EA, Mohammed MA (2012) Gravimetric and electrochemical evaluation of environmentally friendly nonionic corrosion inhibitors for carbon steel in 1 M HCl. *Corr Sci* 65:94–103
[15] Goncalves RS, Azambuja DS, Serpa Lucho AM (2002) Electrochemical studies of propargyl alcohol as corrosion inhibitor for nickel, copper, and copper/nickel (55/45) alloy. *Corros Sci* 44:467–479

Received	:	11th February 2013
Revised	:	25th February 2013
Accepted	:	03rd March 2013
Online	:	16th May 2013