

Corrosion inhibition of steel in sulphuric acid by aqueous extracts of *Rose* and *Rose water*

Aisha M Al-Turkustani

Chemistry Department, Sciences Faculty for Girls, King Abdulaziz University, Jeddah, Saudi Arabia

E-mail: a.m.turkustani@hotmail.com, amalturkestani@kau.edu.sa

Received 24 February 2014; accepted 21 September 2014

The corrosion inhibition of steel in 2 molar sulphuric acid solution by *Rose* extract and/or *Rose water* has been studied at 30°C using chemical (weight loss and hydrogen evolution) and electrochemical (impedance and polarization) measurements. It is found that all methods give consistent results, the inhibition efficiency increases with increasing concentration of the extract, and it shows that *rose* extract is a better corrosion inhibitor for steel than *rose water*. The polarization curves indicate that *rose* extract and *rose water* act as mixed-type inhibitors. The adsorption of inhibitor on the steel surface is found to obey the Langmuir adsorption isotherm model for *rose* extract and Freundlich adsorption isotherm for both *rose* extract and *rose water*. Thermodynamic data for the adsorption process (K_{ads} and G°_{ads}) were calculated and discussed.

Keywords: Corrosion, Inhibition, Steel, Sulphuric acid, *Rose*, *Rose water*, Electrochemical.

Acids are widely used in many industries. Some of the important areas of application are industrial acid cleaning, acid pickling, acid descaling and oil well acidizing¹. One of today's most important considerations in industry is the reduction of overall costs by protection and maintenance of materials used. Because steel is the backbone of industrial constructions, the inhibition of iron corrosion in acidic solutions has been studied in considerable detail².

Corrosion of metals by acids is a major problem that must be confronted for safety, environment, and economic reasons. Among the several methods of corrosion control and prevention, the use of corrosion inhibitors to reduce the rate of dissolution of metals, is very popular. Many investigations were conducted to examine extracts from natural substances to slow or inhibit the corrosion process. The extracts contained mixtures of compounds having oxygen, sulphur and nitrogen elements, which help in the corrosion inhibition process. Natural compounds used as inhibitors to develop new cleaning chemicals for green environments have been selected because they are environmentally friendly, readily available, and renewable sources for a wide range of needed inhibitors³⁻⁹.

Scientific corrosion literature has descriptions and lists of numerous plant products that exhibit inhibitive properties for mild steel in acidic solutions¹⁰⁻²¹.

The present work continues to focus on the application of plant extracts for metallic corrosion control and reports on the inhibiting effects of the *Taif rose* and *rose water* on steel corrosion in acidic solution at 30°C using chemical (HE and ML) and electrochemical (PDP and EIS) techniques.

The city of Taif in the western region of the Kingdom of Saudi Arabia is characterized with its beautiful roses from the species of *Rosa Damascus*. *Taif rose* and *rose water* are very famous and considered the best in the Middle East and the world for their quality (Fig. 1).

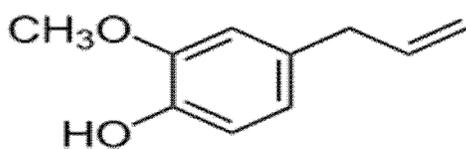
There are three main compounds represented in 61.07% of *Taif rose* oil components, they are, citronellol 31.27%, geraniol 19.52% and nonadecane ($C_{19}H_{40}$) 10.25%. Whereas phenyl ethyl alcohol which has high percentage in the other *rose* oil represents 3.13% about twelve compounds have percentage between 1% and 10%. Others compounds which are about fifty have than 1%²². Table 1 represents the structure of some compounds in *Taif rose*.

Rose has several benefits, tightens skin and purifies the pores face and makes it masks after mixing its water with natural ingredients such as flour, oats, etc., and can also be used in washing the face and eyes²³. *Rose water* is a traditional remedy for the heart and stomach ailments. It is also used for cleaning the skin and face²⁴.

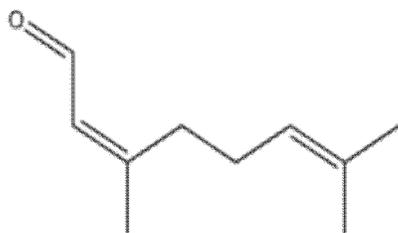


Fig. 1 — The tree of *Taif rose* and *rose water*.

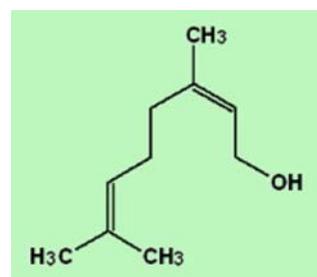
Table 1 — The structure of some compounds in *rose*.



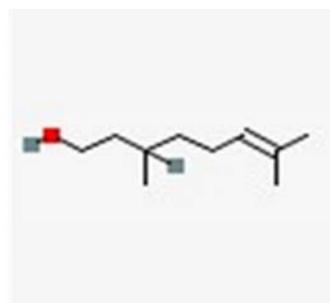
Eugenol



Citral (3,7-dimethylocta-2,6-dienal)



Geraniol



Citronellol (3,7-dimethyloct-6-en-1-ol)

Experimental Section

Preparation of extract

Cut flowers of *roses* were obtained from a commercial grower in Taif, Saudi Arabia. Flowers were dried in an air after the removal of unwanted material (sepals, pollens and anthers) and petals were kept under shade at room temperature for the removal of extra moisture and were then ground well into powder using a manual blender. From this, 10 g of the rose plant was refluxed in 100 mL distilled water for 1 h. The refluxed solution was then filtered carefully, the stock solution was prepared from the collected filtrate and the concentration of the stock solution was expressed in terms of % (v/v). From the stock solution, 5-20% concentrations of the *rose* extract were prepared using 2M sulphuric acid, and 5-40% concentrations of the *rose water* were prepared.

Similar kind of preparation has been reported in studies using aqueous plant extracts in the recent years²⁵⁻³⁴.

Material and methods

Steel specimen having a composition of 0.10 wt % C, 0.34 wt % Mn, 0.08 wt % P, and the remaining Fe with the dimensions 5 cm × 1 cm was used for chemical methods, hydrogen evolution and mass loss. The specimen was polished with different emery papers, cleaned with acetone and doubly distilled water and finally dried. The electrochemical experiments were performed in three electrode cell assembly with steel as the working electrode, platinum as the counter electrode and saturated calomel electrode (SCE) as the reference electrode³⁵.

Analar grade sulphuric acid (Merck) and doubly distilled water were used to prepare 2 M acid solution for all experiments. Weight loss (WL) and hydrogen evolution (HE) experiments were done with different inhibitor concentration range 5, 7, 10, 15, 20 and 40%v/v at 30°C, Tafel polarization potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from -800 mV to -200 mV relative to open circuit potential with a scan rate of 20 mV/min. The corresponding corrosion current I_{corr} , were recorded. Tafel plots were constructed by plotting E versus log I; corrosion potential E_{corr} , corrosion current density I_{corr} , cathodic and anodic slopes (β_c and β_a) were calculated according to known procedures. Electrochemical impedance measurements were carried out in a frequency range from 10 to 10000 Hz using an

amplitude of 10 mV peak to peak using an AC signal at the open circuit potential. The impedance diagrams were plotted in the Nyquist representation. Charge transfer resistance (R_{ct}) values were given by subtracting the high frequency impedance from the low frequency.

Results and Discussions

Chemical methods (weight loss and hydrogen evolution)

Weight loss and hydrogen evolved are obtained from the chemical measurements of the steel specimen before and after the immersion in the acid solution with and without the plant extracts. Different concentrations of *rose* extract and *rose water* (5-40%v/v) are added to the H_2SO_4 and the specimen is immersed in the solution for 1 h at 30°C. The results are summarized in Figs. 2 and 3 and Tables 2 and 3 for *rose* extract and *rose water*, respectively.

Inhibition efficiency obtained from HE & ML increases with increasing concentration of the extract (*rose* extract and/ or *rose water*). Maximum inhibition efficiencies from HE and ML 75.78, 71.01% and 56.07, 63.11% for *rose* extract and *rose water* were achieved at 20%v/v and 40%v/v, respectively. A further increase in concentration did not cause any appreciable change in the performance of the inhibition efficiency. This may be due to the reason that the total surface coverage is accomplished by the acid concentration and beyond that any further addition will not yield any increase in the inhibition efficiency. At constant temperature the inhibition

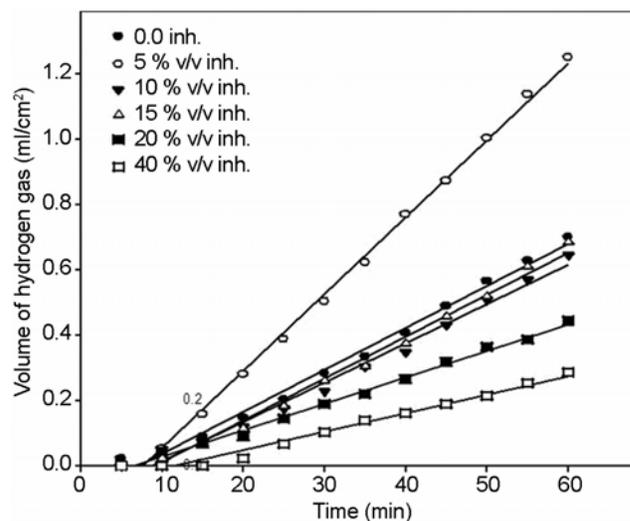


Fig. 2 — Hydrogen gas/time curves for steel corrosion in 2 M H_2SO_4 in the absence and presence of different concentrations of aqueous extract of *rose* at 30°C.

efficiency increases as the concentration of the studied extract increases, explained on the basis of increased adsorption of the compound on the metal surface are shown in Figs. 4 and 5.

Adsorption Isotherm

Basic information on the interaction between the inhibitor (*rose* extract and/or *rose* water) and steel

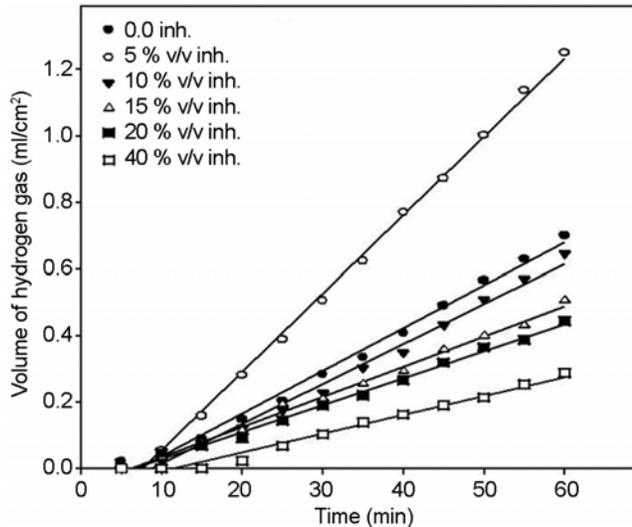
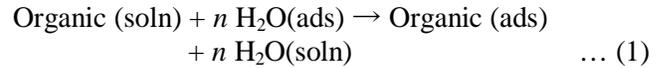


Fig. 3 — Hydrogen gas/time curves for steel corrosion in 2 M H_2SO_4 in the absence and presence of different concentrations of *rose* water at 30°C.

surface can be proved by the adsorption isotherm and in general, inhibitors can function either by physical (electrostatic) adsorption or chemisorptions with the metal.

The adsorption of organic substance in the inhibitor at the metal/solution interface may be written according to the following displacement reaction



where n is the number of water molecules removed from the metal surface for each molecule of inhibitor adsorbed. Clearly, the value of n depends on how the molecule arrange on the surface due to the surface roughness, and the interaction among the molecules. A correlation between surface coverage (θ) defined and the concentration of inhibitor ($C_{inh.}$) in electrolyte can be represented by the Langmuir adsorption isotherm,

$$C_{inh.} / \theta = 1 / K + C_{inh.} \quad \dots (2)$$

where, K is the adsorption constant. Surface coverage values (θ) for the inhibitor were obtained from HE and ML measurements for various concentrations of *rose* extract and *rose* water at 30°C as shown in Tables 2 and 3. The best fitted straight line is obtained for the plot of $C_{inh.} / \theta$ versus $C_{inh.}$ with slopes around

Table 2 — Corrosion rate and Inhibition efficiency for steel corrosion on 2.0 M H_2SO_4 in the presence of different concentrations of *rose* extract at 30°C.

Inhibitor concentration (% v/v)	Corrosion rate		Inhibition efficiency			
	RML $\times 10^5$ (g. cm. / min.)	RHE $\times 10^2$ (ml. cm. / min.)	Inh. _{ML} %	θ_{ML}	Inh. _{HE} %	θ_{HE}
0.0	2.9559	1.2835	--	--	--	--
5	2.8884	1.1621	2.284	0.0228	9.375	0.0938
7	2.2446	0.8639	24.02	0.2402	32.81	0.3281
10	1.6757	0.5683	43.31	0.4331	46.09	0.4609
15	1.2913	0.5023	56.35	0.5635	60.94	0.6094
20	0.8568	0.3147	71.01	0.7101	75.78	0.7578

Table 3 — Corrosion rate and Inhibition efficiency for steel corrosion on 2.0 M H_2SO_4 in the presence of different concentrations of *rose* water at 30°C.

Inhibitor concentration (% v/v)	Corrosion rate		Inhibition efficiency			
	RML $\times 10^5$ (g. cm / min.)	RHE $\times 10^2$ (mL. cm / min.)	Inh. _{ML} %	θ_{ML}	Inh. _{HE} %	θ_{HE}
0.0	2.9559	1.2835	--	--	--	--
5	5.3135	2.3516	-79.76	-0.7976	-83.22	-0.8322
10	2.6879	1.2028	9.067	0.0907	6.288	0.0629
15	2.1312	0.9568	27.90	0.2790	25.45	0.2545
20	1.6535	0.8081	44.06	0.4406	37.04	0.3704
40	1.0903	0.5644	63.11	0.6311	56.07	0.5607

unity for rose extract and the plot of $\log C$ versus $\log \Theta$ for *rose* extract and *rose water*. This suggests that the adsorption of the studied inhibitors on metal surface follows the Langmuir adsorption isotherm for *rose* extract (Fig. 6) and Freundlich adsorption isotherm for both *rose* extract and *rose water* (Figs. 7 and 8), respectively. From the intercept of the straight lines C_{inh}/Θ -axis for *rose* extract, K values were calculated and are equal to $0.0553 \text{ L mol}^{-1}$ and $0.0570 \text{ L mol}^{-1}$ from HE and ML, respectively. The most important thermodynamic adsorption parameters are the free energy of adsorption (G_{ads}^0).

The adsorption constant, K, is related to the standard free energy of adsorption, G_{ads}^0 with the following equation:

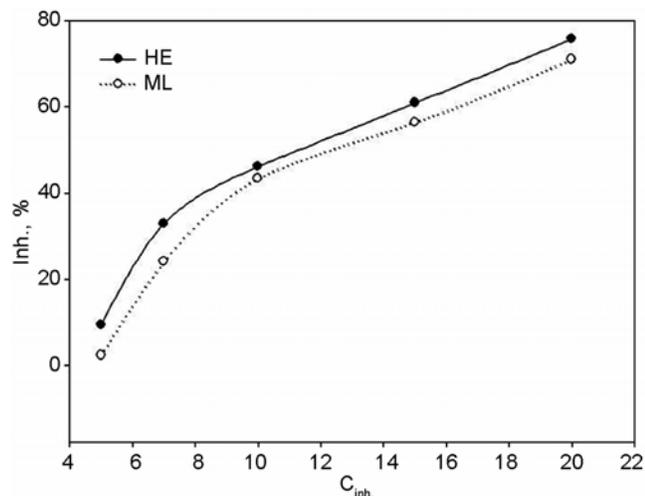


Fig. 4 — Variation in Inhibition efficiency with different inhibitor concentrations of *rose* extract for steel in $2 \text{ M H}_2\text{SO}_4$ at 30°C .

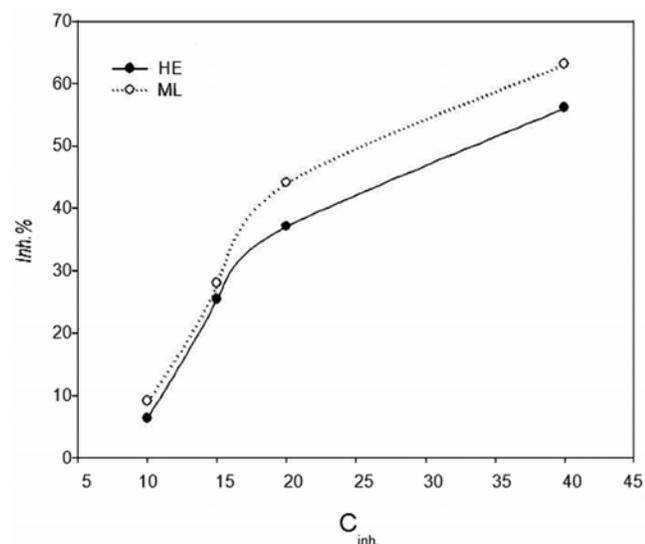


Fig. 5 — Variation in Inhibition efficiency with different inhibitor concentrations of *rose water* for steel in $2 \text{ M H}_2\text{SO}_4$ at 30°C .

$$G_{ads}^0 = -RT \ln (55.5 K_{ads}) \quad \dots (3)$$

where 55.5 is the water concentration of solution in mol/L.

Generally, the magnitude of ΔG_{ads}^0 around -20 kJ/mol or less negative is assumed for electrostatic interactions exist between inhibitor and the charged metal surface (i.e., Physisorption). Those around -40 kJ/mol or more negative are indicating of charge sharing or transferring to the metal surface to form a coordinate type of metal bond (i.e., chemisorptions).

The values for G_{ads}^0 are equal $-28.27 \text{ kJ mol}^{-1}$ and $-29.01 \text{ kJ mol}^{-1}$ for *rose* extract from both HE and ML, respectively. The negative values of G_{ads}^0 indicate the

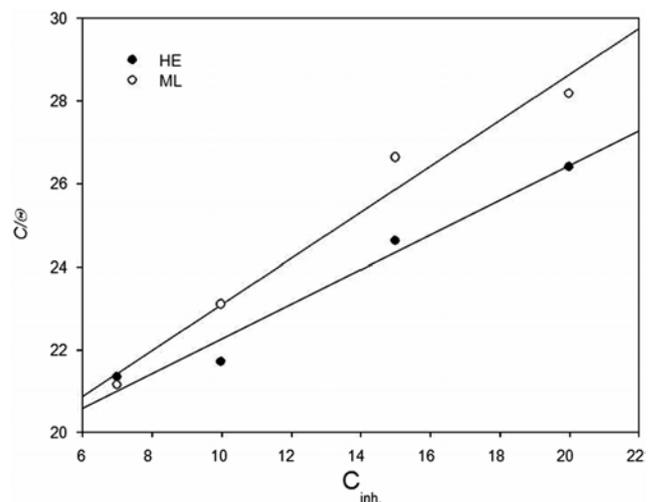


Fig. 6 — Langmuir adsorption isotherm for *rose* extract on steel in $2 \text{ M H}_2\text{SO}_4$ from HE and ML at 30°C .

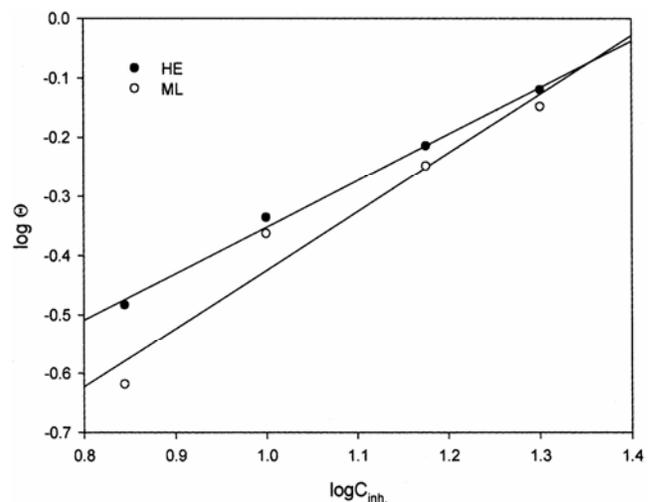


Fig. 7 — Freundlich adsorption isotherm for *rose* extract on steel in $2 \text{ M H}_2\text{SO}_4$ from HE and ML at 30°C .

stability of the adsorbed layer on the steel surface and spontaneity of the adsorption process³⁶.

Regarding the present work, the calculation G_{ads}^0 values for rose extract show that an electrostatic interaction between the inhibitor and charged metal surface (physical adsorption).

Tafel polarization

The potentiodynamic polarization curves of steel in 2 M H₂SO₄ solution in the presence and absence of different inhibitor concentrations are shown in Fig. 9. As can be inferred from the figure that after addition of inhibitor there is a decrease in both cathodic and

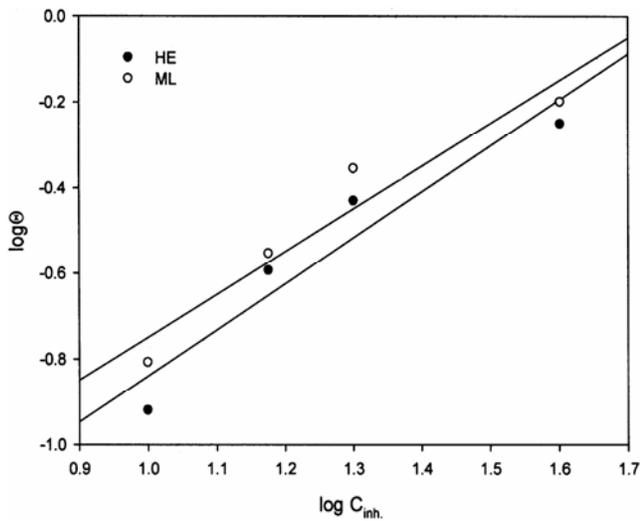


Fig. 8 — Freundlich adsorption isotherm for *rose water* on steel in 2 M H₂SO₄ from HE and ML at 30°C.

anodic current. The electrochemical corrosion kinetic parameters, corrosion potential E_{corr} , cathodic and anodic Tafel slopes (β_c and β_a) and corrosion current density I_{corr} obtained from the Tafel polarization curves are listed in Table 4. Corrosion current rate decreases with increasing concentration of inhibitor for both *rose extract* and *rose water*. Maximum inhibition efficiency 56.54% for *rose extract* at 20% v/v and 51.41% for *rose water* at 40% v/v, respectively were achieved. It can be clearly seen that the inhibition efficiency increases with increasing concentration. The fact that the polarization curves show no change in corrosion potential with increasing concentration of inhibitors indicated that inhibitors (*rose and rose water*) act as mixed type inhibitors.

Electrochemical impedance spectroscopy (EIS)

The effect of inhibitor concentration on the impedance behavior of steel in 2 M H₂SO₄ solution at 30°C is presented in Fig. 10. The curves show a similar type of Nyquist plot in the presence of various concentrations of inhibitors (*rose extract* and *rose water*). The Nyquist plots contain a depressed semi-circle, which size is increased by increasing the inhibitor concentration. Electrochemical corrosion kinetic parameters, charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) calculated from Nyquist plots are listed in Table 5. Maximum Inhibition efficiency (IE %) for the *rose extract* (56.42%) and *rose water* (54.77 %) was achieved at 20% v/v and 40% v/v, respectively. The corrosion is mainly a charge transfer resistance (R_{ct}) process

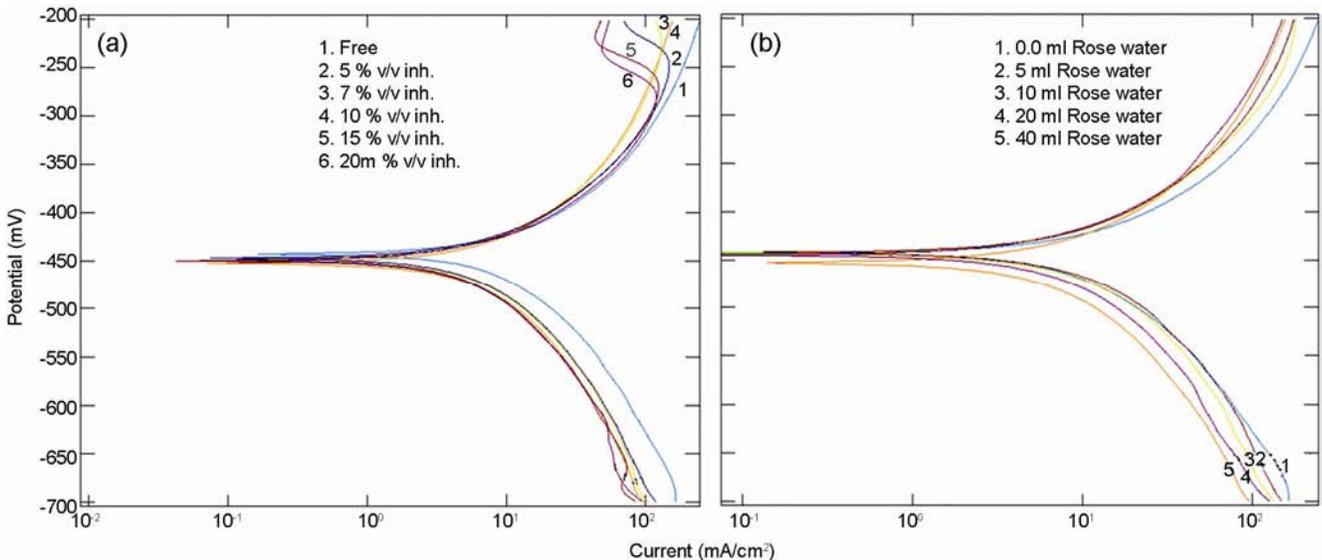


Fig. 9 — Tafel polarization curves of steel 2 M H₂SO₄ at 30°C in presence of different concentration of (a) *rose extract* (b) *rose water*.

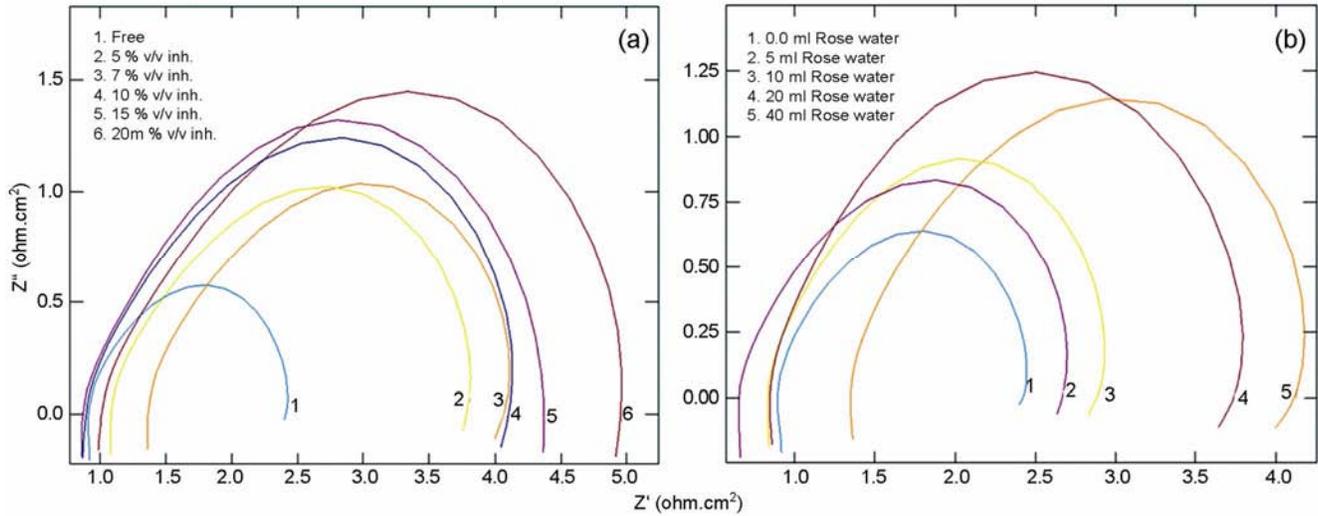


Fig. 10 — Nyquist plots of EIS measurements of steel in 2 M H₂SO₄ at 30°C in the presence of different concentration of (a) *rose extract* and (b) *rose water*.

Table 4 — Inhibition efficiency obtained by Tafel polarisation of steel in 2 M H₂SO₄ containing various concentrations of *rose extract* and/or *rose water* at 30°C.

Inhibitor concentration (% v/v)	$I_{corr.}$ (mA cm ⁻²)	$-E_{corr.}$ (mV vs SCE)	β_c (mV/dec1)	β_a (mV/dec1)	IE (%)	Θ
<i>Rose extract</i>						
Blank	21.319	450.29	127.32	162.73	--	--
5	11.397	446.54	77.052	124.52	46.54	0.4654
7	9.9146	449.03	82.776	123.50	53.49	0.5349
10	9.6326	450.05	84.601	125.91	54.82	0.5482
15	9.4022	450.09	78.565	132.67	55.90	0.5590
20	9.2643	449.70	67.537	120.66	56.54	0.5654
<i>Rose water</i>						
5	18.566	450.13	121.26	148.08	12.91	0.1291
10	15.270	450.02	120.46	132.33	28.37	0.2837
20	14.318	449.95	124.66	112.65	32.84	0.3284
40	10.358	449.72	106.23	143.46	51.41	0.5141

Table 5 — Inhibition efficiency obtained by EIS measurements of mild steel in 2 M H₂SO₄ containing various concentrations of *rose extract* and/or *rose water* at 30°C.

Inhibitor concentration (% v/v)	R_{ct} (Ω cm ²)	$C_{dl} \times 10^3$ (F)	IE (%)	Θ
<i>Rose extract</i>				
Blank	1.615	8.681	--	--
5	3.000	7.194	46.17	0.4617
7	3.042	5.782	46.91	0.4691
10	3.584	5.617	54.94	0.5494
15	3.706	5.493	56.42	0.5642
20	4.311	5.215		
<i>Rose water</i>				
5	2.254	5.907	28.35	0.2835
10	2.555	4.442	36.79	0.3679
20	3.102	3.266	47.94	0.4794
40	3.571	2.357	54.77	0.5477

which increased with increasing inhibitor concentration (*rose extract* and/or *rose water*). On the other hand, the values of C_{dl} are decreased with increase in inhibitor concentration which is most probably due to the decrease in local dielectric constant and/or increase in thickness of the electrical double layer, suggests that the inhibitor acts via adsorption at the metal/solution interface^{37, 38}. It could be assumed that the decrease of C_{dl} values is caused by the gradual replacement of water molecules by adsorption of organic molecules on the electrode surface, which decreases the extent of the metal dissolution.

Conclusion

Rose extract and *rose water* can acts as an effective corrosion inhibitors for steel in 2 M sulphuric acid.

The inhibition efficiency measured through hydrogen evolution, weight loss method, potentiodynamic and EIS reached *rose* extract concentration at 20% v/v and *rose* water concentration at 40% v/v. The potentiodynamic measurement results indicate both anodic and cathodic processes are suppressed. The inhibition is due to the adsorption of the inhibitor molecules on steel surface and blocking is active sites. Beside protective effect by means of adsorbing on metal surface according to the Langmuir isotherm mode, the result demonstrated that the inhibitor under investigation acts as physisorption. The calculation G_{ads}^0 values for *rose* extract show that an electrostatic interaction between the inhibitor and charged metal surface.

References

- Schmitt G, *Brit Corr J*, 19 (1984) 165.
- Makdour L H, Hassanein A M, Ghoneim M M & Eid S A, *Monat- shefte fu" r Chemie*, 132 (2001) 245.
- Raja P B & Sethuraman M G, *Mat Lett*, 62 (2008) 113.
- Benkaddour M M, Hammouti B, Bendahhou M & Aouniti A, *Appl Surf Sci*, 25 (2006) 6212.
- Amin M A, Abd El-Rehim S S, El-Sherbini E E & Bayoumi R S, *Electrochem Acta*, 52 (2007) 3588.
- Jai J W S & Wan A, *International Conference on Environmental Research and Technology*, 1 (2008) 865.
- Okafor P C, Ikpi M E, Uwah I E, Ebenso E E, Ekpe U J & Umoren S A, *Corros Sci*, 50 (2008) 2310
- Abdel-Gaber A M, Abd-El-Nabey B A, Sidahmed I M, El-Zayady A M & Saadawy M, *Corros Sci*, 48 (2006) 2765.
- El-Naggar M M, *Corros Sci*, 49 (2007) 2226.
- Li X, Deng S & Fu H, *J Appl Electrochem*, 40 (2010) 1641.
- Patela N, Rawat A, Jauhari S & Mehta G, *Eur J Chem*, 1 (2010) 129.
- da Rocha J C, Gomes J A P & D'Elia E, *Corros Sci*, 52 (2010) 2341.
- Kalaiselvi P, Chellammal S, Palanichamy S & Subramanian G, *Mater Chem Phys*, 120 (2010) 643.
- Quraishi M A, Singh A, Singh V K, Yadav D K & Singh A K, *Mater Chem Phys*, 122 (2010) 114.
- Okafor P C, Ebenso E E, Ekpe U J, *Int J Electrochem Sci*, 5 (2010) 973.
- Ekanem U F, Umoren S A, Udousoro & Udoh A P, *J Mater Sci*, 45 (2010) 5558.
- Eddy N O, Odiongenyi A O, *Pigm Resin Technol*, 39 (2010) 288.
- Shyamala M & Kasthuri P K, *Int J Corrosion*, 2011 (2011) 11.
- Loto C A, Loto R T & Popoola A P I, *Int J Phys Sci*, 6 (15) (2011) 3689.
- Shyamala M & Kasthuri P K, *Int J Corrosion*, 2012 (2012) 13 pages
- Ashok Kumar S L, Iniyavan P, Saravana Kumar M, Sreekanth A, *J Mater Environ Sci*, 3 (3) (2012) 461.
- Sqil Z M, Master Thesis, 2004.
- www. Html. 115- Taif-Rose/frangrantica.com/notes
- www. Htmi.roses/saudicaves.com/saudi
- Quraishi M A & Yadav D K "Corrosion and its control" by some green inhibitors," in *Proceedings of the 14th National Congress on Corrosion Control*, 2008.
- El-Etre A Y, *J Colloid Interf Sci*, 314 (2) (2007) 578.
- Abdel-Gaber A M, Abd-El-Nabey B A, Sidahmed I M, El-Zayady A M & Saadawy M, *Corros Sci*, 48 (9) (2006) 2765.
- Abdel-Gaber A M, Abd-El-Nabey B A & Saadawy M, *Corros Sci*, 51 (5) (2009) 1038.
- Anand B & Balasubramanian V, *E-Journal of Chemistry*, 8 (1) (2011) 226.
- Hussin M H & Kassim M J, *J Phys Sci*, 21 (2010) 1.
- Al-Turkustani A M, *Mod Appl Sci*, 4 (2010) 105.
- Rajendran S, Agasta M, Devi R B, Devi B S, Rajam K & Jeyasundari J, *Za`stita Materijala*, 50 (2009) 77.
- Selvi J A, Rajendran S, Sri V G, Amalraj A J & Narayanasamy B, *Portugaliae Electrochim Acta*, 27 (2009) 1.
- Ilayaraja G, Sasieekhumar A R & Dhanakodi P, *E-J Chem*, 8 (2) (2011) 685.
- Kumar S L A, Gopiraman M, Kumar M S, Sreekanth A, *Ind Eng Chem Res*, 50 (2011) 7824.
- Dahmani M, Touhami A, Al-Deyab S S, Hammouti B, Bouyanzer A, *Int J Electrochem Sci*, 5 (2010) 1060.
- Mernari B, Elattari H, Traisnel M, Bentiss F, *Corros Sci*, 40 (1998) 391.
- Ramesh S V & Adhikari A V, *Mater Chem Phys*, 115 (2009) 618.