J. Nepal Chem. Soc., Vol. 38, 2018

Corrosion Inhibition of Mild Steel in Acidic Medium using High Altitude Plant Extract

Roshan Lama[1], Anju Kumari Das[1], Brahamdeo Yadav[4], Yogesh Chaudhary[1], Prakash Chandra Lama[2], Suman Lal Shrestha[3*], Dipak K Gupta[2], Nabin Karki[1] and Amar P Yadav[1]

[1]Central Department of Chemistry, Tribhuvan University, Kirtipur, Nepal
[2]Department of chemistry, Tri-Chandra Multiple Campus, Kathmandu, Nepal
[3]Department of chemistr, Patan Multiple Campus, Tribhuvan University Lalitpur, Nepal
[4]Depart of Chemistry, RR Multiple Campus, Tribhuvan University, Janakpur, Nepal
Email: sumsrt2015@gmail.com

Abstract

Corrosion inhibition of methanol extract of Artemisia vulgaris on the corrosion of mild steel in 1M H_2SO_4 has been investigated using weight loss measurements. The inhibition efficiency increases with increase in concentration and decreases with increase in temperature beyond 308 K. Adsorption of extract on metal follows Langmuir adsorption isotherm. The activation and free energies for the inhibition reactions support the mechanism of physical adsorption. Values of enthalpy and entropy supports that the process is endothermic and spontaneous. Surface and protective film analysis have been carried out by energy dispersive x-ray (EDX) and scanning electron microscopy (SEM).

Keywords: *Artemisia, inhibitor, mild steel , thermodynamic*

Introduction

Mild steel has wide spread application in a broad field of industry and machinery due to its availability and low cost. Acid solutions are extensively used in the processes such as acid pickling, cleaning of boilers, descaling and drilling operations in oil and gas industries. Base metal applied in these processes undergoes undesirable dissolution. In order to reduce metal dissolution, various means like surface modification, alloy formation are adopted[1]. However, more accepted practice for the reduction of corrosion is the use of inhibitors which when added in small amount retards rate of corrosion significantly and prevents from economic loss due to metallic corrosion[2]. A substance to be used as corrosion inhibitor must fulfil some requirements. An inorganic compounds must be able oxidize the metal, forming a passive layer on its surface. Organic molecules should have feature like a large structure, double bonds, an active centre or groups which gives them to be adsorbed on metal surface by displacing water molecules and cover a large area of a metal surface with a compact barrier film[3]. In chemisorption, electron transfer from inhibitor to metal to form coordinate covalent bond is facilitated by the presence of lone pairs or π electrons in inhibitor molecules[4].

Many organic and synthetic chemical containing oxygen, sulphur, nitrogen are studied as corrosion inhibitor and found effective as well. Unfortunately, most of them are hazardous to human and

---

[*] *Corresponding author*

environment during their synthesis or application. This motivates investigations to develop non toxic, biodegradable, environmentally acceptable, renewable and cheap inhibitor as the demand of recent awareness of green chemistry. These requirements may be achieved in the inhibitor prepared from different parts of plant extracts. Phytochemicals present in plant extracts have similar molecular and electronic structures to the conventional organic inhibitor molecules. Many investigations reveals that plant extracts can be used as effective green inhibitor such as henna[5], coconut coir[6], olive[7], Cassia auriculata[8], Aloes[9], *Hunteria umbellata*[10], *Progostemon benghalesis*[11] etc. Plant extracts shows inhibitions efficiency due to presence in their composition of complex organic species such as alkaloids, flavoniods, polyphenol, tannins, nitrogen bases, carbohydrates, protein as well as hydrolysis products.

Like in chemical reactions, rate of corrosion increases with increase in temperature. Acid pickling is done usually at elevated temperature up to 60 °C in HCl and up to 90°C in H_2SO_4 [12]. Some conclusion regarding mechanism or inhibiting action can be drawn from the temperature dependence of the inhibitor efficiency and the comparison of the obtained thermodynamic data of the corrosion process in both presence and absence of inhibitor. So, the effect of temperature on a corrosion process has practical and theoretical importance.

Experimental Methods

Preparation of specimens

A flat sheet of mild steel available from mild steel supplier of Kathmandu valley was cut into coupons of diameter 4 cm×4 cm×0.15cm. The coupons were polished with silicon carbide paper of different grades, starting with coarse one (100 grade) and proceeding in steps to finest (1500 grade). Dimension of each coupons were measured with digital vernier calliper, ultrasonicated in ethanol, dried and stored in moisture free desiccators.

Preparation of methanol extract

Aerial parts of *Artemisia vulgaris* were collected from Gundu, Bhaktapur, shade dried and powdered. 200 g of powder was extracted with methanol for 72 hrs followed by filtration to obtain extract as filtrate. Process was repeated until colourless extract was obtained. The extract was initially concentrated using rotary evaporator then dried on water bath to obtain solid residue.

Preparation of solution

1 M H_2SO_4 was prepared by diluting 55.6 mL concentrated H_2SO_4 in 1 litre volumetric flask up to the mark with distilled water. 1 g extract was dissolved in 1000 mL 1 M H_2SO_4 at 318 K temperature. Undissolved extract was removed by filtration. Filtrate was taken as 1000 ppm stock solution of acid in presence of inhibitor. Stock solution was diluted with calculated volume of 1M H_2SO_4 to prepare solution of different concentration of 800, 600, 400 and 200 ppm.

Weight loss measurements

The different parameters used for the study by weight loss measurements were effect of time, concentration of inhibitor solution and temperature. Polished coupons were removed from desiccators and weights were taken in an electronic balance. Weighed coupons were immersed in 100 mL acid (1 M H_2SO_4) without and with 1000 ppm concentration of the inhibitor in different beakers for various time intervals (3, 6, 9, 12 and 24 hours) at same temperature 298 K to study the effect of time in inhibition efficiency. To study effect of concentration, weighed coupons were immersed in 100 mL acid (1 M H_2SO_4) without and with different concentrations of inhibitor (1000, 800, 600, 400, 200 ppm) in different beakers for 6 hours at same temperature 298 K. Similarly, effect of temperature was studied by immersing polished coupons in 100 mL acid (1 M H_2SO_4) without and with 1000 ppm concentration of the inhibitor in different beakers for 6 hours at various temperatures (298K, 308K, 318K, 328K, 338K). Temperature in experiments was adjusted by using clifton water bath model no. NE2-4D. After the elapsed time, coupons were taken out, washed thoroughly with distilled water, rinsed with acetone, dried, stored in desiccators and reweighed. All experiments were in triplicates and illustrated data are mean values of obtained results.

The corrosion rate (CR), surface coverage (θ) and inhibition efficiency (IE%) were calculated using following equations :

$$\mathrm{CR} = \frac{87.6\mathrm{W}}{\mathrm{AtD}} \qquad \begin{pmatrix} Where\ W = Weight\ loss\ in\ solution\ (mg) \\ A = Surface\ area\ of\ coupon\ immersed \\ t = Time\ of\ immersion\ (h) \\ D = Density\ of\ mild\ steel\ (g/ml) \end{pmatrix}$$

$$\theta = \frac{W_1 - W_2}{W_1}$$

$$\mathrm{IE\%} = \left(\frac{W_1 - W_2}{W_1}\right) \times 100 \qquad \begin{pmatrix} Where\ W_1\ and\ W_2\ are\ the\ weight\ loss\ in\ absence \\ and\ presence\ of\ inhibitor\ respective\,ly \end{pmatrix}$$

Surface analysis

Three polished coupons were immersed in acid solution without and with inhibitor of 400 and 1000 ppm concentrations for 24 hours. Then coupons were washed, dried and stored in desiccators.

SEM analysis

Surface analysis of mild steel coupons were performed using scanning electron microscope at 500x magnification at three different locations to ensure reproducibility. It was performed by using Bio-Logic M470 Ac-SECM scanning electron microscope.

Energy dispersive x-ray (EDX) analysis

Energy dispersive x-ray (EDX) analysis was carried out with Bio-Logic M470 Ac-SECM scanning electron microscope in conjugation with an energy dispersive spectrometer employing beam of accelerating voltage 15 KV to examine surface film formed on the metal specimen.

Results and Discussion

Effect of immersion time

Corrosion rate and inhibition efficiency by methanol extract of *Artemisia vulgaris* in various time are calculated from weight loss data is shown in table 1 and represented in figure 1. Result shows that corrosion rate is inhibited by extract which is due to adsorption of photochemical present in extract. Inhibition efficiency decreases gradually with increase in time of immersion. It is almost same at 3 and 6 hrs. On the basis of table 1, weight loss for 15 g mild steel coupon with 30 cm^2 surface area is calculated when coupon was immersed in acid with and without inhibitor and plot of weight loss of coupon in different time is shown in figure 2. This data clearly shows that loss of metal by using inhibitor is decreased. This data reveals that adsorbed compounds starts desorption from metal surface after certain time and more metal surface is exposed to acidic media.

Table 1 : Corrosion rate of mild steel and inhibition efficiency of *Artemisia vulgaris* for mild steel corrosion at various time

Time (hours)	Corrosion Rate (mg/cm^2h)		Inhibition Efficiency (%)
	For Acid without inhibitor	For acid with inhibitor	
3	55.47	17.66	68.16
6	59.50	19.15	67.81
9	57.65	22.20	61.50
12	54.04	23.62	56.29
24	50.15	24.37	51.42

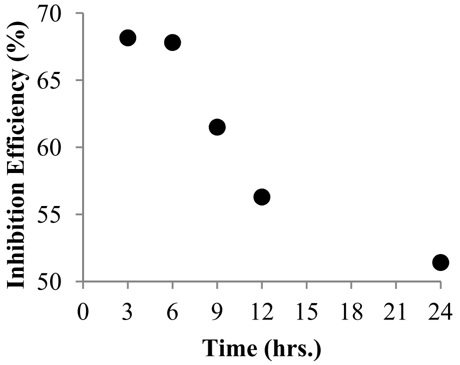


***Figure 1:** Variation of inhibition efficiency with different immersion times of A. vulgaris extract on mild steel surface*

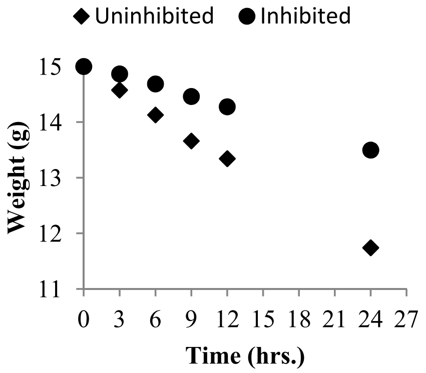


***Figure 2:** Variation in weight of mild steel immersed in acid with and without inhibitor*

Effect of Concentration

Corrosion rate and inhibition efficiency by methanol extract of *Artemisia vulgaris* in various concentration at 298 K for 6 hours are calculated from weight loss data is shown in table 2 and represented in figure 3.

Table 2: Corrosion rate of mild steel and inhibition efficiency of *Artemisia vulgaris* for mild steel corrosion at various concentration

Concentration (ppm)	Corrosion Rate	Inhibition efficiency	Surface Coverage (θ)
Blank (0)	59.50		
200	39.52	33.58	0.336
400	31.30	47.39	0.474
600	26.77	55.00	0.550
800	21.78	63.40	0.634
1000	19.15	67.81	0.678

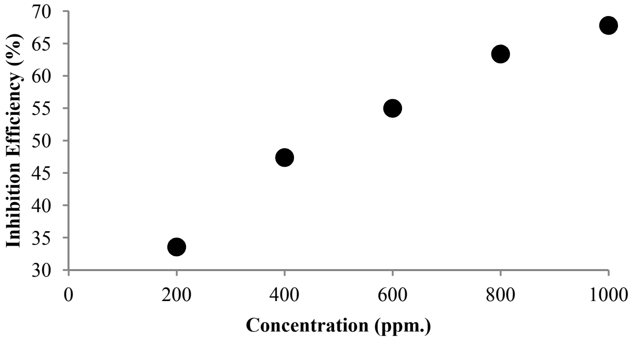


Figure 3: *Variation of inhibition efficiency with different concentration of A. vulgaris extract on mild steel surface*

Results show that inhibition efficiency increases with increase in concentration of inhibition in acid. It is due to the more surface coverage of mild steel with more adsorption of phytochemical compounds on it.

Adsorption isotherm

Adsorption isotherm provides the basic information on the interaction between the inhibitor and mild steel surface since inhibition efficiency is due to adsorption of compounds on metal surface through their polar functions making a barrier for charge and mass transfer between the metal and the environment.

Water molecules are adsorbed on metal surface in aqueous solution. So, the adsorption of inhibitor molecules from aqueous solution is a quasi substitution process[13]. The linear relation between θ value and C_{inh} (concentration of inhibitor) should be known to find the adsorption isotherm. To fit θ Value, attempts were made to various isotherms including Langmuir, Tempkin, Freundlich, El-Awady. Both value of linear correlation coefficient (R^2) and slope is almost equal to 1 in Langmuir adsorption isotherm shown in figure , which indicates that mono-layer of the inhibitor have been adsorbed on metal surface without interaction between the adsorbed molecules .

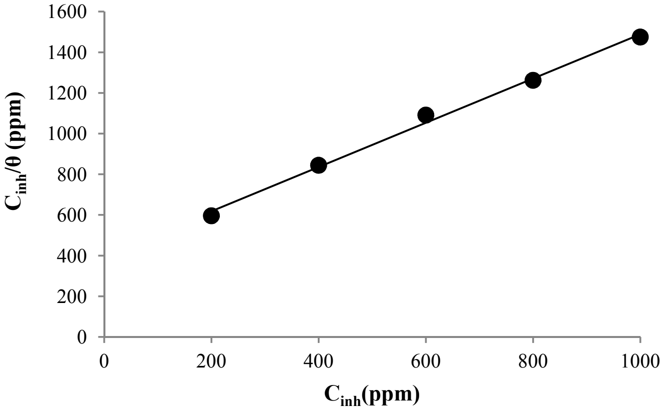


Figure 4: *Langmuir adsorption isotherm plot for mild steel in 1 M H_2SO_4 with different concentration of A. Vulgaris extract.*

According to Langmuir adsorption isotherm equaltion, $\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$, value of adsorption constant K_{ads} is calculated from intercept of straight line. This value can be used in the equation , $\Delta G^o = -RT \ln(55.5K_{ads})$ to calculate the value of free energy of adsorption (ΔG^o), where 55.5 is concentration of water in solution in mol/L and R is universal gas constant (8.314J/mol K). Calculated value of ΔG^o according to relation is -12.22 KJ/mol. which is less than the threshold value -40 KJ/mol required for chemisorption. Value of ΔG^o less than or around -20 KJ/mol means adsorption is physical adsorption. So, adsorption of *Artemisia vulgaris* extract is physical adsorption.

Effect of temperature

Corrosion rate and inhibition efficiency by 1000 ppm methanol extract of *Artemisia vulgaris* in various temperature for 6 hours are calculated from weight loss data is shown in table 3 and represented in figure 5. IE increases with increase in temperature up to 308 K and beyond this IE decreases. Decrease in IE with increase in temperature might be due to desorption or decomposition inhibitor at higher temperature (14). This data also supports the adsorption is physical adsorption.

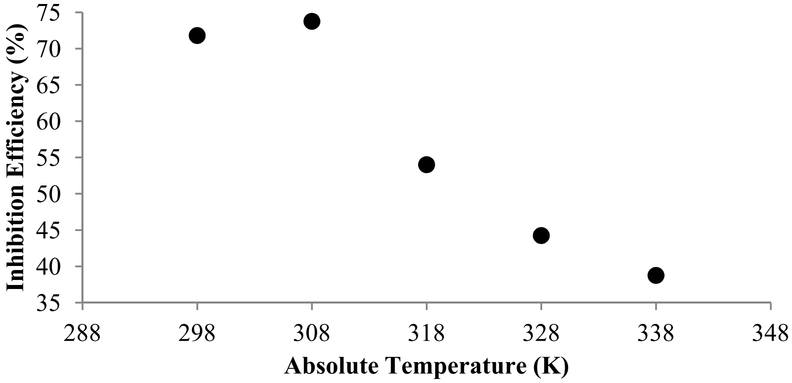


Figure 5: *Variation of inhibition efficiency of A. vulgaris extract on mild steel surface at different temperature.*

Table 3: Corrosion rate of mild steel and inhibition efficiency of *Artemisia vulgaris* for mild steel corrosion at various temperature

Temperatur)	Corrosion Rate (mg/cm^{2}h)		Inhibition Efficiency (%)
	For Acid without inhibitor	For acid with inhibitor	
298	92.40	26.06	71.80
308	136.86	35.91	73.76
318	206.98	95.20	54.00
328	264.48	147.47	44.24
338	332.83	203.85	38.75

Calculation of activation energy and thermodynamic parameters

The activation energy (E_a) can be calculated from Arrhenius plots for corrosion rate at different temperature according to relation : $\log(\text{C.R.}) = \log A - \dfrac{E_a}{2.303\,RT}$

Where, A is the Arrhenius pre-exponential constant, T is absolute temperature.

From the Arrhenius plot shown in figure , Calculated values of E_a for acid without and with inhibitor are 27.09 KJ/mol and 46.38 KJ/mol respectively and value of A for acid without and with inhibitor are 5382697.8 mg/Cm^2 and 3296097122 mg/Cm^2 respectively. Increase in E_a with addition of inhibitor shows the strong adsorption of inhibitor molecules on the metal surface (15). This value is lower than threshold value of 80KJ/mol, required for chemisorption. This indicates that adsorption is physical adsorption.

An alternative form of Arrhenius equation is transition state equation :

$$\log\left(\frac{C.R.}{T}\right)=\left[\log\left(\frac{R}{hN}\right)+\left(\frac{\Delta S^{*}}{2.303R}\right)-\frac{\Delta H^{*}}{2.303\,RT}\right]$$

Where h is plank's constant, 6.6261×10^{-34} Js and N is the Avogadro's number, 6.0225×10^{23} mol^{-1}

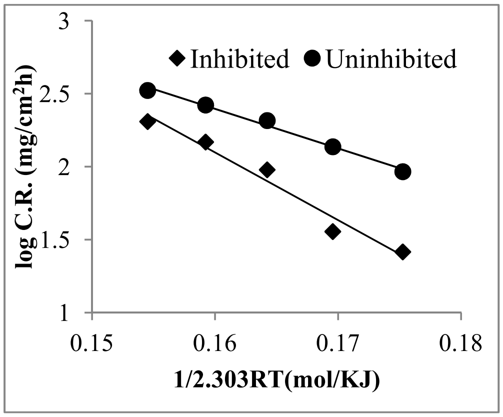


***Figure 6** : Arrhenius plot for mild steel in 1 M H_2SO_4 with and without A. vulgaris extract*

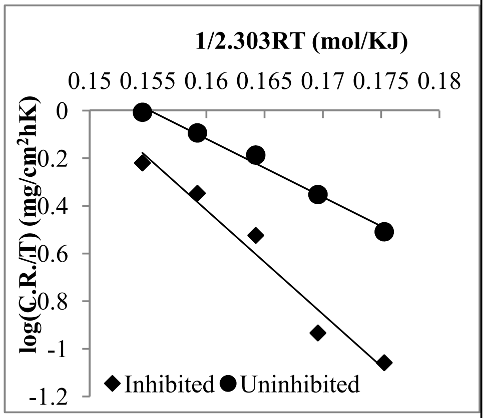


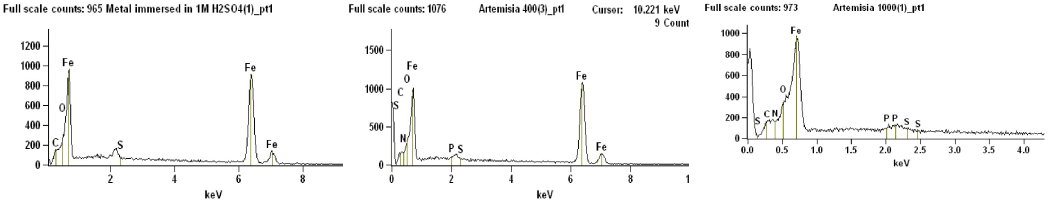
***Figure 7** : Transition state plot for mild steel in 1 M H_2SO_4 with and without A. vulgaris extract*

The slope of straight line obtained by plotting log(C.R./T) vs. 1/2.303T shown in figure is enthalpy of activation (ΔH^{*}) and the entropy of activation (ΔS^{*})can be calculated from its intercept. Calculated values of ΔH^{*} for acid without and with inhibitor are 24.45 KJ/mol and 43.75 KJ/mol respectively. Positive value of ΔH^{*} indicates the endothermic nature of metal dissolution process. Increase in value of ΔH^{*} with addition of inhibitor shows the decrease in corrosion rate is controlled by kinetic parameters of activation. (16). Above calculations show that value of E_a is higher than that of ΔH^{*}, which indicates the involvement of a gaseous reaction, simply the hydrogen evolution reactions, resulting the decrease in the total reaction volume[17]. The corrosion process is unimolecular in the condition, $Ea - \Delta H^{*} = RT$. Here difference in value of $Ea - \Delta H^{*}$ is 2.64 KJ/mol which is nearly equal to RT.

Calculated value of ΔS^{*} for acid without and with inhibitor are –124.91 J/mol K and –71.50 J/mol K respectively. Large and negative values of ΔS^{*} indicates that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that decrease in disordering takes place on going from reactants to the activated complex. In acid, transition state of the rate determining recombination step represents a more orderly arrangement relative to the initial state so a high value for the ΔS^{*} is obtained. In presence of inhibitor, the surface is covered with adsorbed molecules and rate of discharge of hydrogen ions in rate determining step is decreased resulting the system to pass from random arrangement, hence value of ΔS^{*} is increased. The increase in value of ΔS^{*} with addition of inhibitor implies the increase in disorder on going from reactant to activated complex. This behaviour is due to replacement of water molecules during adsorption of extract on metal surface[5].

Surface analysis

Energy dispersive x-ray (EDX) is employed to get the information about the composition of the surface of mild steel sample immersed in acid without and with inhibitor for 24 hours. The results are shown in figure 8. Percentage composition of different elements present in metal surface is listed in table 4. Data shows that there is decrease in iron and increase in N,C and O on surface of mild steel in sample immersed in acid with inhibitor which indicates the formation of protective film due to adsorption of phytochemicals containing N, C and O on surface and inhibit the iron dissolution.

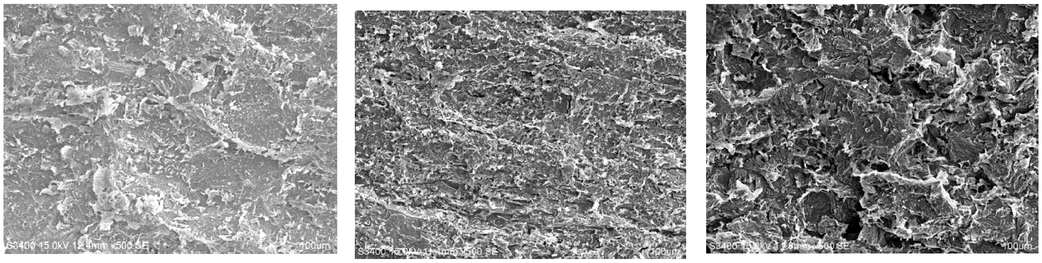


a b c

***Figure 8** : EDX spectra of mild steel coupons after 24 hr. immersion in (a) 1 M H_2SO_4 (b) 400 ppm extract solution in 1 M H_2SO_4 (c) 1000 ppm extract solution in 1 M H_2SO_4*

Table 4 : Percentage of weight of different element on the mild steel surface after immersing in sample in different solution.

Surface dipped in	Iron	Carbon	Nitrogen	Oxygen	Phosphorus
Polished metal sample	100%				
Acid without inhibitor	97.45%	1.72%		0.83%	
Acid with inhibitor of 400 ppm	94.8%	1.78%	1.31%	2.11%	
Acid with inhibitor of 1000 ppm	92.91%	2.27%	1.58%	3.16%	0.07%



a b c

***Figure 9** : SEM micrographs of mild steel coupons after 24 hr. immersion in (a) 1 M H_2SO_4 (b) 400 ppm extract solution in 1 M H_2SO_4 (c) 1000 ppm extract solution in 1 M H_2SO_4*

To study the surface morphology of mild steel, Scanning electron microscope (SEM) images of coupon immersed for 24 hours in acid without and with inhibitor were taken by Bio-Logic M470 Ac-SECM scanning electron microscope. In SEM image of surface of metal sample immersed in acid without inhibitor shown in figure 9, surface was highly porous with deep and large cracks but surface was relatively smooth by the formation of protective film on surface when immersed for same time after addition of inhibitor.

Conclusions

1. Artemisia vulgaris extract acts as a good inhibitor for corrosion of mild steel in 1 M $_2SO_4$ solution.
2. Inhibition efficiency increases with increase in concentration and decreases with increase in temperature beyond 308 K.
3. The adsorption of extract on mild steel follows the Langmuir adsorption isotherm.
4. Values of ΔG^o and Ea indicates the adsorption of molecules on metal surface through physical adsorption.
5. Values of ΔH^* and Ea indicates that the corrosion process is unimolecular and rate is controlled by kinetic parameters of activation.
6. Values of ΔH^*, ΔS^* indicates that adsorption process is spontaneous and endothermic.
7. EDX and SEM confirm the formation of protective film extract on metal surface and inhibit corrosion.

References

1. E.E. Oguzie, Y. Li, F.H. Wang, *Electrochimica Acta*, 2007, **52**, 6988
2. H.A. Sorkhabi, D. Seifzadeh and M.G. Hosseini, *Corros. Sci*., 2008, **50**, 3363
3. S. Muralidharan, K.L.N. Phani, S. Pitchumani, S. Ravichandran, S.V.K. Iyer, *J. Electrochem. Soc*., 1995, **142**, 1478.
4. N. Hackerman, R. M. Hard, *Proc. Int. Congress of Metallic Corrosion*, Butterworth, London, 1962, 166.
5. A. Hamdy, Nour Sh., El-Gendy, *Egyptian Journal of Petrolium* , 2013, **22**, 17.
6. S.A. Umoren, I.B. Obot, A.U. Israel, P.O. Asuquo, M.M. Solomon, U.M. Eduok, A.P. Udoh, *Journal of Industrial and Engineering Chemistry*, 2014, **20**, 3612.
7. A.Y. EL-Etre, *Journal of Colloid and Interface Science*, 2007, **314**, 578.
8. J. Rosaline Vimala, A. Leema Rose, S. Raja, *International Journal of ChemTech Research*, 2011, **3**, 1791.
9. H. Cang, Z. Fei, J. Shao, W. Shi, Q. Xu, *Int. J. Electrochem. Sci*, 2013, **8**, 720.
10. A.S. Fouda, A.S. Abousalem, G.Y. El-Ewady, *Int. J. Ind. Chem*., 2017, **8**, 61.
11. Y. Chaudhary, N. Karki, A.P. Yadav, *J. Nepal Chem. Soc*., 2016, **35**, 139.
12. E.A. Noor, *Int. J. Electrochem. Sci*., 2007, **2**, 996.
13. L.R. Chauhan, G. Gunasekaran, *Corros. Sci.*, 2007, **49**, 1143.
14. F. Bentiss, M. Lebrini, H. Vezin, F. Chai, M. Traisnel, M. Lagrene, *Corr. Sci.*, 2005, **51**, 2165
15. S.K. Shukla, E.E. Ebenso, *Int. J. Electrochem. Sci.*, 2011, **6**, 3277.
16. J.I. Bhat, D.P. Vijaya, V. Alva, Arch. *Appl. Sci. Res.*, 2011, **3**, 343.
17. A.H. Ostovari, S.M. Peikari, S.R. Shadizadeh, S.J. Hashemi, *Corros. Sci.*, 2009, **51**, 1935.