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Anticorrosive efficacy and adsorptive study of guar gum with mild steel in acidic medium

Anjali Peter[1], Sanjay K. Sharma[1*] and Ime Bassey Obot[2]

Abstract

Background: Gums have been found to be good corrosion inhibitors due to their functional group; they form complexes with metal ions and on the metal surfaces. Most gums have -COOH functional groups, which can increase the contribution of electron or charge transfer and hence facilitate inhibition through adsorption.

Methods: The corrosion and inhibition behaviors of mild steel in hydrochloric, sulphuric, and nitric acid in the presence of *Cyamopsis tetragonoloba* (guar gum) have been studied using the weight loss, gas chromatography mass spectrometry (GC-MS), and thermometric techniques.

Results: The temperature studies reflect that the percentage of inhibition efficiency is decreased with increase in temperature and that indicates the mechanism of physical adsorption. The calculated values of activation energy (Ea) also support the physiosorption process. The thermodynamic parameters such as heat of adsorption (Qads) and free energy of adsorption (ΔGads) suggested that the adsorption of inhibitor on the mild steel surface is exothermic and followed by spontaneous process.

Conclusions: The formation of an adsorbed protective film of the inhibitor molecules on the mild steel surface is confirmed by scanning electron micrographs (SEM), which proves that the *guar gum* acts as good inhibitor at 1N acids concentration.

Keywords: *Cyamopsis tetragonoloba* (guar gum), Corrosion, Activation energy (Ea)

Background

Corrosion is as old as the earth itself known to people as rust; corrosion is an undesirable phenomenon which destroys the luster and beauty of the metal and lessens their life. Corrosion is the destruction and deterioration of metals as a result of reaction with environment (Fontana and Greene 1987). It is a major problem that must be confronted for safety, environmental and economic reasons in various chemical, mechanical, metallurgical, biochemical, and medical engineering applications, and more specifically in the design of a much more varied number of mechanical parts which equally vary in size, functionality, and useful lifespan (Desai 2015). One of the most challenging and difficult tasks is to provide the protection of metals from corrosion. Controlling these detritions of metals and alloys is a costly course of action, and industries pay out enormous amounts to manage this crisis. The controlling expense of corrosion in the developed countries such as the USA and European Union is about 3–5% of their gross national product (Bhaskaran et al. 2005).The use of corrosion inhibitors is the most reasonable and realistic way to protect metals from corrosion. Corrosion inhibitors decrease the rate of corrosion when added into the surrounding or solution of metals. They are either synthetic or natural. However, the attractiveness and use of synthetic compounds (Guendouz et al. 2013; Belfilali et al. 2012; Moreira et al. 2014; Ajmal et al. 1994; Lagrenee et al. 2002; El-Maksoud 2004; Elachouri et al. 1996; Kilmartin et al. 2002; Nishimura 1993; Kabanda and Ebenso 2012; Kabanda et al. 2012a; Kabanda et al. 2012b)

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* Correspondence: sk.sharmaa@outlook.com
[1]Green Chemistry & Sustainability Research Group, Department of Chemistry, JECRC University, Jaipur 303905, India
Full list of author information is available at the end of the article

as a corrosion inhibitor is losing ground because of their noxious and hazardous effects on mankind. Therefore, necessities occur to build up a different category of corrosion inhibitors with low poisonous effect, environment friendly and effective efficiency. This new general approach, called green chemistry, was declared which aims for the reduction and replacement of hazardous materials in order to protect the environment and people. Plants have been used by human beings for their basic needs and seem to be a promising source of cheap and harmless corrosion inhibitors. The oldest uses of plants were reported as corrosion inhibitor of *Chelidonium majus* (celandine) and other plants in 1930s (Raja and Sethuraman 2008). After this discovery, natural products drag the attention of scientists around the world for the research on plant extracts for corrosion inhibition. Among others, considered substances are gums, animal proteins, herbs, and even fruit peals (Africa 2008; Al-Otaibi et al. 2014; Oguzie 2006; Abdel-Gaber et al. 2009; Oguzie 2007; Kliškić et al. 2000; Benabdellah et al. 2006; Abiola et al. 2007; Raja and Sethuraman 2009; El-Etre et al. 2005). Gums have been found to be good corrosion inhibitors due to their functional group; they form complexes with metal ions and on the metal surfaces. Most gums have -COOH functional groups, which can increase the contribution of electron or charge transfer and hence facilitate inhibition through adsorption. Literature on the use of gums as corrosion inhibitors is very little (Eddy et al. 2013; Abdallah 2004; Umoren et al. 2008; Ameh et al. 2012). Guar gum drags special attention because of its safe use and high molecular size. The gas chromatography mass spectroscopy (GCMS) spectra of the gum show the presence of heteroatoms. Gum metal complexes occupy a large surface area, thereby blanketing the surface and shielding the metal from corrosive agents present in the solution. The presence of arbinogalactan, sucrose, oligosaccharides, polysaccharides, and glucoprotein confirms the presence of compounds containing oxygen and nitrogen atoms there, which are the active centers of adsorption (Gardner and Eikerts 1983; Bumgartner et al. 1983; Shah and Walters 1984; Peter et al. 2015).

Even though lots of plants have been reported as anticorrosive agents, still a huge kingdom of plants have not yet been appropriately considered for their anticorrosive activity. As a result, huge possibilities exist to find out green corrosion inhibitors. In persistence of our program for the corrosion inhibitor with high value and efficiency, the present paper explore the use of guar gum as effective corrosion inhibitor for mild steel corrosion in 1N HCl, H_2SO_4, and HNO_3 solutions using weight loss method. The effect at 304 and 313 K temperature on corrosion and corrosion rate process are briefly discussed with adsorption isotherm and temperature measurements.

Methods

Materials

Chemical composition of the tested materials, namely pure mild steel is as following (wt%): 0.23% C, 1.50% Mn, 0.04% S, 0.04% P, 0.02% Al, 0.40% Si, and bal Fe. The mild steel specimens were prepared by cutting mild steel sheet into rectangular-shaped pieces having dimension 3 cm × 2 cm × 0.2 cm containing a small hole of about 0.10 mm diameter near the upper edge. Specimens were polished to mirror finish by using emery paper, washed by distilled water, degreased with acetone, and put it to become dried in a moisture-free desiccators before their use in corrosion studies (Obot et al. 2010).

Solutions

The solutions of 1N HCl, H_2SO_4, and HNO_3 were prepared by dilution of analytical grade acids with distilled water. Gum of guar was obtained by distillation of the seed extract of guar gum plant. After drying, it is available in a form of a powder. We dissolved it in distilled water for subsequent use. We prepared the different concentrations of inhibitor (250, 500, 750, 100 ppm) solutions of guar gum and left it for 24 h to procure dissolved properly in distilled water.

Quantitative measurements (weight loss method)

Weight loss method is the most acceptable method for inhibition efficiency measurement (Obot et al. 2009). This method is considered as a baseline for the assessment in many corrosion monitoring programs (Obot and Obi-Egbedi 2010). For the experiment, a set of beakers with immersion capacity of 250 ml were filled with 100 ml test solution of acid 1N HCl, H_2SO_4, and HNO_3 concentration. Keeping one beaker aside, different concentrations (250, 500, 750, 100 ppm) of guar gum were added to the others at 304 K temperature with appropriate arrangements. Metal plates of defined dimensions (3 cm × 2 cm × 0.2 cm) were polished, weighed, and placed in each beaker. At 6, 24, 48, and 72 h intervals, the metal plates were taken out from the solution, washed with water, dried, and weighed. To observe the atmospheric corrosion course of action, the test coupons were removed from reactors for the period of the exposures for weighing with above prescribed intervals. In order to get more precise results, experiments were carried out in triplets. By this weight loss method, weight of corroded material is measured by subtraction of the final weight from the initial weight.

When this value is obtained, the inhibition efficiency (IE) can be calculated.

(W is the weight loss with (i) or without (0) influence of the inhibitor)

$$\mathrm{IE\%} = \frac{w_0 - w_i}{w_0} \times 100 \qquad (1)$$

As well as the corrosion rate (CR) in millimeters per year was achieved by dividing the weight loss by the surface area, density, and time in hours.

$$\mathrm{CR} = \frac{\text{weight loss}}{\text{Area} \times \text{Time} \times \text{density}} \times 8.76 \times 10^4 \qquad (2)$$

where weight loss is expressed in grams, area expressed in square centimeter, time in hours, metal density in gram per cubic centimeter, and 8.76×10^4 is a conversion factor (Baboian 1995).

GC-MS study

GC-MS analysis was carried out on a GC clarus 500 Perkin Elmer system comprising an AOC-20i auto sampler and gas chromatograph interfaced to a mass spectrometer (GC-MS) instrument. The chromatogram of compounds which were reported in GCMS of guar gum are the following: sucrose, 9,9-Dimethoxybicyclo[3.3.1]nona-2,4-dione, cetene, d-Gala-l-ido-octonic amide, 8-Pentadecanone, E-14-Hexadecenal, 11,14-Eicosadienoic acid, methyl ester, decanamide, N-(2-hydroxyethyl), hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl, octadecanoic acid, 2-hydroxy-1,3-propanediyl, cyclohexanone, 2-pentyl, 8-methyl-6-nonenamide, Bis(2-(dimethylamino)ethyl) ether, 9,12-Octadecadienoyl chloride, (Z,Z)-, Linalol oxide, trimethylsilyl ether, heptacosane, 1,2-15,16-diepoxyhexadecane, oxalic acid, dodecyl 3,5-difluorophenyl ester, and 12-hydroxy-3-keto-bisnor-4-cholenic acid. Interpretation on mass spectrum GC-MS was conducted using the database of National Institute Standard and Technology (NIST) having more than 62,000 patterns. The spectrum of the unknown component was compared with the spectrum of the known components stored in the NIST library.

Surface analysis

Morphological studies of the mild steel surface were undertaken by SEM examination using Nova NanoSEM 450 BRUKER scanning electron microscope from Malaviya National Institute of Technology, MNIT (Jaipur).

Results and discussion

Gravimetric measurements

All the weight loss data, together with the mass increase and metal slaughter values, are provided to make possible quantitative comparisons of the manipulation of the different environmental factors on the atmospheric corrosion of the mild steel. Mass increase is a suitable path to calculate average corrosion assault if the corrosion product composition is known.

Tables 1 and 2 show the comparative data of average metal loss, corrosion rate, and inhibition efficiency of the corroded samples at different temperature and immersion intervals. Weight loss of mild steel have found to decrease with increase in the concentration of guar gum at 303 and 313 K temperature for HCl and H_2SO_4 medium, but in HNO_3 medium, we have noticed a good inhibition at 250 ppm only that means due to hyper oxidative nature of

Table 1 Corrosion parameters of guar gum at 304 K temperature in different acidic medium with mild steel at different immersion time periods

Medium	Inhibitor conc.	6 h			24 h			48 h			72 h		
		Wt.loss (gm)	CR (mm/yr)	IE%	Wt.loss (gm)	CR (mm/yr)	IE%	Wt.loss (gm)	CR (mm/yr)	IE%	Wt.loss (gm)	CR (mm/yr)	IE%
1N HCl	0	0.145	1.92	–	0.518	6.8867	–	0.957	12.71	–	1.727	22.944	–
	250	0.046	0.606	68.46	0.097	1.2881	81.295	0.145	1.9197	84.896	0.319	4.244	81.503
	500	0.040	0.536	72.07	0.094	1.252	81.819	0.134	1.7745	86.038	0.243	3.226	85.94
	750	0.036	0.484	74.82	0.079	1.0478	84.785	0.123	1.6283	87.189	0.208	2.7634	87.956
	1000	0.041	0.549	71.41	0.073	0.974	85.857	0.104	1.3843	89.108	0.163	2.1652	90.56
1N H_2SO_4	0	0.220	29.17	–	0.808	107.38	–	1.991	264.45	–	2.678	355.72	–
	250	0.048	6.409	78.03	0.165	21.954	79.555	0.509	67.56	74.453	0.945	125.59	64.695
	500	0.045	5.924	79.69	0.141	18.724	82.563	0.458	60.91	76.967	0.854	113.47	68.101
	750	0.033	4.415	84.86	0.120	15.971	85.127	0.372	49.432	81.307	0.670	88.943	74.996
	1000	0.030	4.024	86.21	0.102	13.516	87.41	0.324	42.979	83.747	0.496	65.859	81.485
1N HNO_3	0	0.882	117.1	–	1.537	204.14	–	1.212	160.98	–	1.121	148.86	–
	250	0.305	40.53	65.4	0.405	53.748	73.67	0.720	95.64	40.588	0.729	96.826	34.954
	500	0.333	44.17	62.29	0.59	78.393	61.6	0.875	116.24	27.789	0.905	120.24	19.224
	750	0.399	53.06	54.7	0.771	102.49	49.8	0.929	123.36	23.368	0.918	121.92	18.099
	1000	0.427	56.7	51.6	0.818	108.68	46.76	0.937	124.41	22.714	0.943	125.25	15.858

Table 2 Corrosion parameters of guar gum at 313 K temperature in different acidic medium with mild steel at different immersion time periods

Medium	Inhibitor conc.	6 h			24 h			48 h			72 h		
		Wt.loss (gm)	CR (mm/yr)	IE%	Wt.loss (gm)	CR (mm/yr)	IE%	Wt.loss (gm)	CR (mm/yr)	IE%	Wt.loss (gm)	CR (mm/yr)	IE%
1N HCl	0	0.161	2.134	–	0.536	7.118	–	0.967	12.842	–	1.754	23.304	–
	250	0.052	0.693	67.52	0.103	1.3726	80.717	0.167	2.2245	82.679	0.339	4.5021	80.681
	500	0.047	0.621	70.9	0.101	1.345	81.105	0.140	1.8638	85.487	0.264	3.5061	84.955
	750	0.047	0.619	71	0.089	1.1784	83.445	0.129	1.7133	86.659	0.215	2.853	87.758
	1000	0.045	0.592	72.28	0.083	1.1031	84.502	0.117	1.5541	87.899	0.182	2.4245	89.6
1N H_2SO_4	0	0.243	32.26	–	0.841	111.78	–	2.023	268.75	–	2.724	361.84	–
	250	0.058	7.733	76.03	0.192	25.526	77.163	0.639	84.917	68.403	1.084	144.04	60.193
	500	0.054	7.203	77.67	0.176	23.327	79.131	0.531	70.582	73.737	0.966	128.33	64.534
	750	0.043	5.724	82.25	0.138	18.344	83.589	0.471	62.58	76.715	0.800	106.24	70.638
	1000	0.037	4.906	84.79	0.130	17.282	84.54	0.418	55.567	79.324	0.714	94.8	73.8
1N HNO_3	0	0.882	117.1	–	1.537	204.14	–	1.212	160.98	–	1.121	148.86	–
	250	0.305	40.53	62.73	0.405	53.748	71.63	0.929	123.36	38.454	0.729	96.826	31.651
	500	0.333	44.17	60.74	0.59	78.393	59.82	0.937	124.41	25.902	0.905	120.24	17.326
	750	0.399	53.06	50.9	0.771	102.49	48.526	0.875	116.24	21.663	0.918	121.92	15.733
	1000	0.427	56.7	48.6	0.818	108.68	44.468	0.823	109.33	19.805	0.943	125.25	13.253

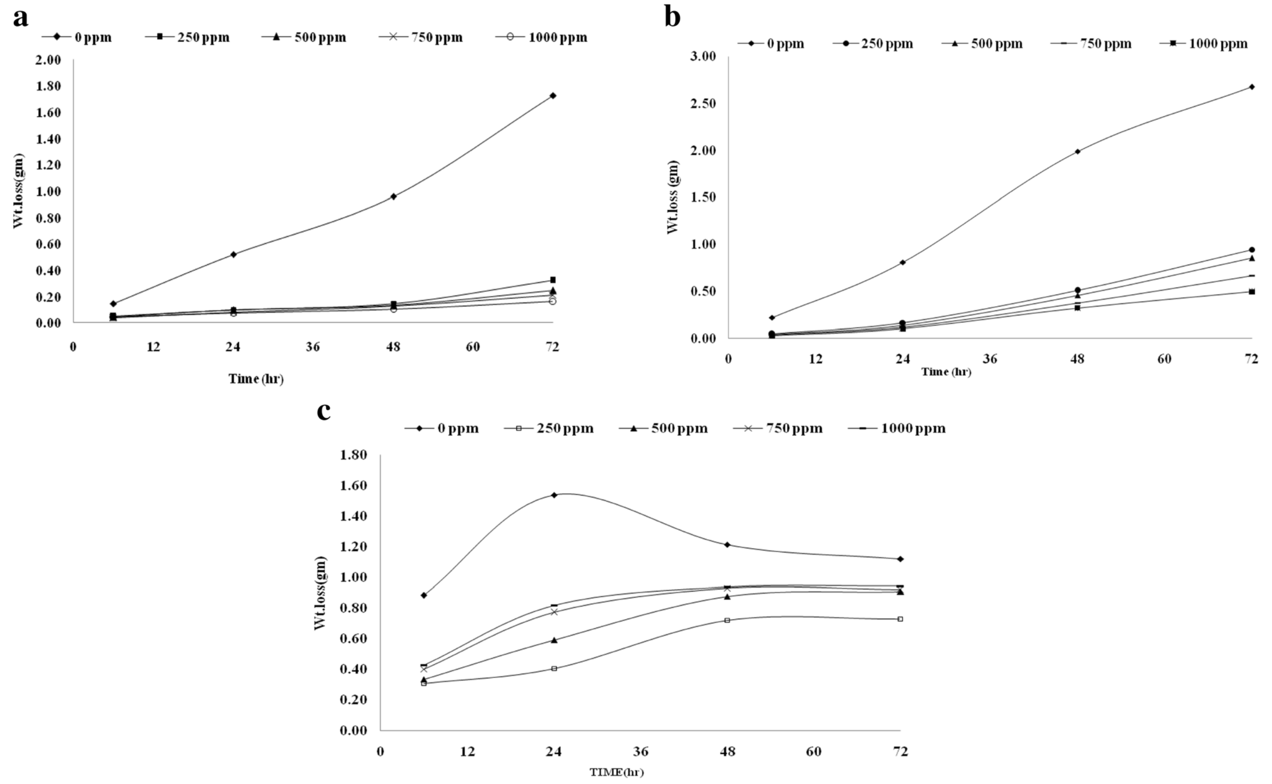

Fig. 1 Weight loss graphs of MS with different concentration of guar gum in **a** 1N HCl, **b** 1N H_2SO_4, and **c** 1N HNO_{30}

HNO_3 acid the inhibition no longer exits. The weight loss of mild steel in the blank solution reported to be higher than comparison with the solutions of HCl, H_2SO_4, and HNO_3 containing a range of concentrations of guar gum. This is a sign that guar gum is an adsorption inhibitor for the corrosion of mild steel in different acids. The assessment between Tables 1 and 2 also discovered that weight loss of mild steel also increase with increasing (313 K) temperature indicating that inhibition efficiency decrease with increase in temperature. Figure 1 comparatively indicates a weight loss of mild steel in [A] 1N HCl, [B] H_2SO_4, and [C] HNO_3 medium with different guar gum concentration at different times. In Fig. 2, the fall in corrosion rate has been observed with the respect of increasing inhibitor concentrations. The result clearly showed that the inhibition mechanism involves blocking of mild steel surface by inhibitor molecules via adsorption. In Fig. 3, exhibits the increase in Inhibition efficiency with increasing concentrations of the inhibitor. The maximum efficiency (90.56%) has been observed at highest inhibitor concentration 1000 ppm at 72 h at temperature 304 K in 1N HCL, 87.4% for 24 h on 1000 ppm in 1N H_2SO_4, and 73.67% for 24 h on 250 ppm in 1N HNO_3 medium. The worth of inhibition falling with high temperature represents physical adsorption mechanism (Eddy et al. 2013). According to finding results, we assume that the adsorption of foremost active elements consist in the inhibitor guard the metal surface at 304 K temperature (Petchiammal et al. 2012). On the other hand, it gets loosen from the metal surface with increase in temperature (313 K).

Kinetic study

A chemical reaction involves breaking of bonds in reacting molecules and formation of new bonds in product molecules. The natures of bonds are different in different substances, and rates of chemical reaction differ a lot from one another. The rate of reaction depends upon structural and energetic factors (Puri et al. 1997).

The kinetics of mild steel corrosion has investigated by drawing the graph between –log (weight loss) and time as given by the following equation (Abdel-Gaber et al. 2006a; Abdel-Gaber et al. 2006b)

$$-log\ (\text{weight loss}) = \frac{\text{k1t}}{2.303} \tag{3}$$

where k1 is the first-order rate constant and t is the time in hours. Figures 4 and 5 show kinetic plots for the

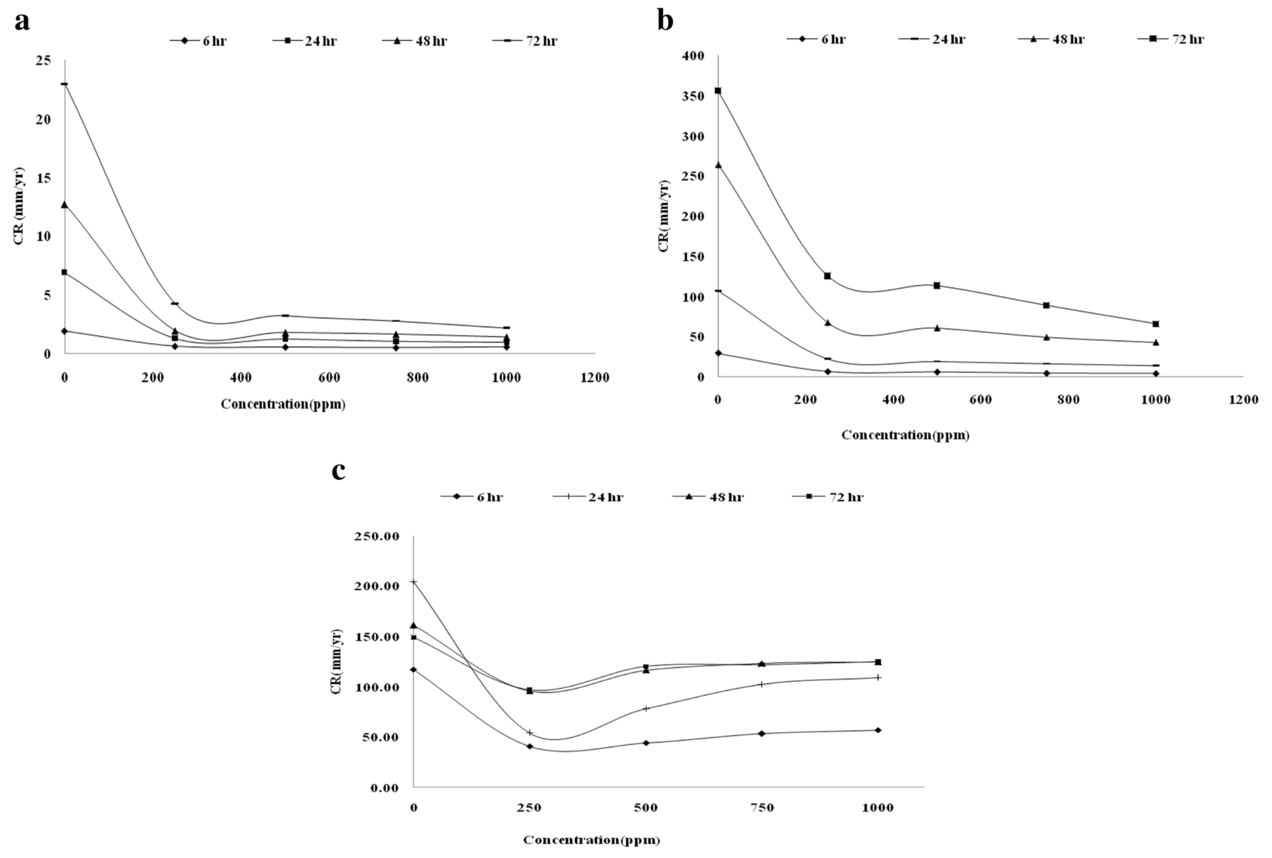

Fig. 2 Corrosion rate graphs of MS with different concentration of guar gum in **a** 1N HCl, **b** 1N H_2SO_4, and **c** 1N HNO_3

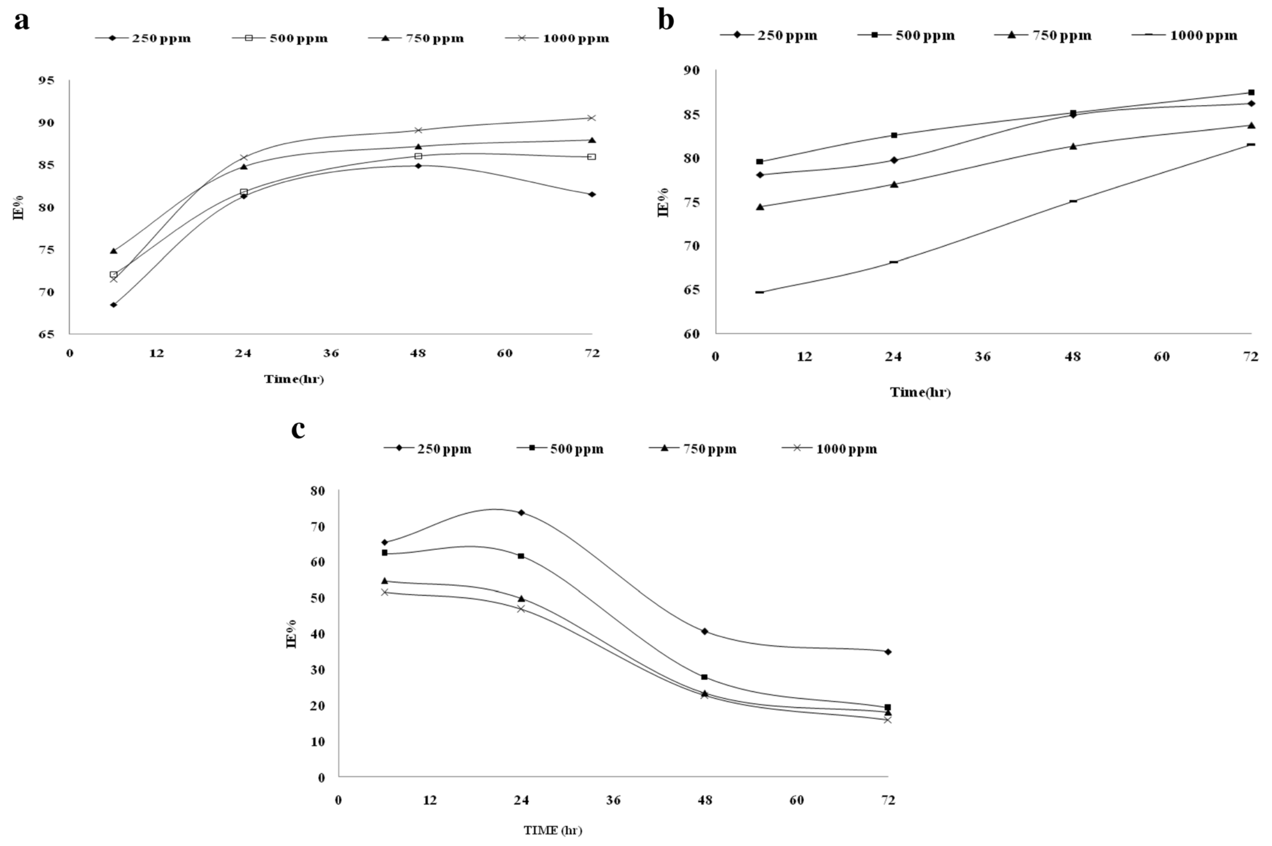

Fig. 3 Inhibition efficiency graphs of MS with different concentration of guar gum in **a** 1N HCl, **b** 1N H_2SO_4, and **c** 1N HNO_3

corrosion of mild steel in solutions of 1N HCl, H_2SO_4, and HNO_3 having different concentrations of guar gum at 304 and 313 K. Obtained straight lines from the plots confirms first order kinetics for the mild steel corrosion inhibition process (Table 3).

Effect of temperature

Values of activation energy for the corrosion reaction of mild steel in the presence and absence of different concentration of guar gum inhibitor have been calculated using Arrhenius equation

$$\mathrm{Ea} = 2.303\mathrm{R} \times \mathit{log}\,(\mathrm{CR1}/\mathrm{CR2})/(\mathrm{T1}-\mathrm{T2}/\mathrm{T1} \times \mathrm{T2}) \quad (4)$$

where Ea is known as activation energy, the reactant molecules having energy less than the threshold energy must acquire the same in order to react to yield a product. CR1 and CR2 are the corrosion rates of mild steel at the temperatures T1 (304 K) and T2 (313 K), respectively. Ea, which ranged from 0.9 to 21.69 kJ mol^{-1} in HCl medium, 1.4 to 32.02 kJ mol^{-1} in H_2SO_4 medium, and 0.79 to 10.12 kJ mol^{-1} in HNO_3 medium with different concentration of inhibitor (Table 4), which are lower than 40.0 kJ mol^{-1} signifying that the inhibitor is physically adsorbed on the metal surface (Ulman 1991). As a result, the adsorption of guar gum on mild steel surface is steady with the mechanism of physical adsorption.

Thermodynamics/adsorption study

Heat of adsorption is essential value of heat which is required for inhibitor to be got adsorb on metal surface. In this work, the heat of adsorption of guar gum has calculated using the following equation:

$$\begin{aligned}\mathrm{Qads} = {} & 2.303R\,[\mathit{log}\,(\theta2/1-\theta2) - \mathit{log}\,(\theta1/1-\theta1)] \\ & \times \mathrm{T1T2}/\mathrm{T2}-\mathrm{T1}\end{aligned} \quad (5)$$

Where θ1 and θ2 are the degrees of surface coverage of the inhibitor at temperatures, T1 (304 K) and T2 (313 K) respectively and *R* is the gas constant. Calculated values of Qads are also recorded in Table 4. These values are negative signifying that the adsorption of guar gum on mild steel surface is exothermic. The adsorption character of guar gum have also investigated by fitting data calculated for the degree of surface coverage of the inhibitor into various adsorption isotherms including Langmuir, Freundlich, and Temkin adsorption isotherms. The adsorption of organic inhibitor molecules from the aqueous solution can be considered as a quasi-

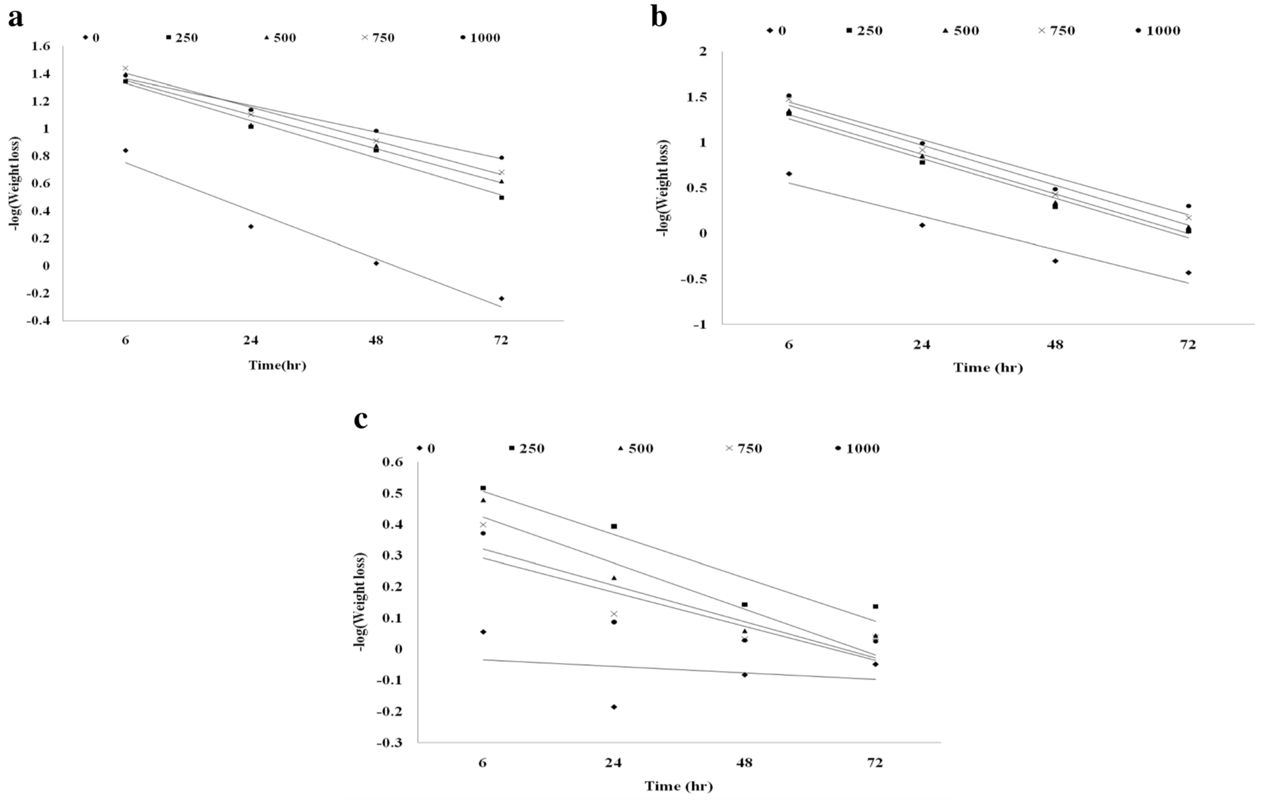

Fig. 4 Variation of –log(weight loss) versus time for the corrosion of mild steel in solutions of **a** 1N HCl, **b** 1N H_2SO_4, and **c** 1N HNO_3 containing various concentrations of guar gum at 304 K temperature

substitution process between the organic compound in the aqueous phase Org(sol) and water molecules associated with the metallic surface H_2O(ads) as represented by the following equilibrium (Eddy and Odoemelam 2008).

$$\mathrm{Org\ (Sol) +\ xH2O\ (ads)} \leftrightarrow \mathrm{Org\ (ads)\ +\ xH2O\ (Sol)}$$

X is the no. of molecules replaced by one organic molecule. In this situation, the adsorption of guar gum was accompanied by desorption of water molecules from the mild steel surface. We calculate the surface coverage (θ) values by using the formula

$$\theta = (\mathrm{w0}–\mathrm{wi})/\mathrm{w0} \tag{6}$$

w0 = weight loss without inhibitor, wi = weight loss without inhibitor

The mechanism of the interaction between inhibitor and the metal surface can be explained using adsorption isotherms. The degree of surface coverage, for the different systems studied, was computed from the weight loss measurements using Eq. (1) and presented in Table 1. The obtained data best fitted into Langmuir isotherm, which may be formulated as

$$(C/\theta)\ =\ C\ +\ 1/\mathrm{Kad} \tag{7}$$

where, *C* is the concentration of the inhibitor (guar gum), θ is the fractional surface coverage, and Kad is the adsorption equilibrium constant. From the intercepts of the straight line Cinh/θ-axis, *K* value was calculated and from graph the value came can be justified by theoretical value. It is based on the assumption that the adsorbed molecule decreases the surface area available for the corrosion reactions to occur. Figures 6 and 7 show the plot of C/θ against *C* for [A] 1N HCl, [B] 1N H_2SO_4, and [C] 1N HNO_3 at 304 and 313 K temperature. Linear plots were obtained indicating that the experimental results fit into Langmuir isotherm. The calculated values of *B* (slope) and *K* (equilibrium constant of adsorption process) obtained from Langmuir are shown in Table 5. ΔGads of the inhibitor on mild steel surface was determined by the following formula:

$$\Delta\mathrm{Gads}\ =\ -\mathrm{RT}\ ln\ (\mathrm{K\ ad} * 55.5) \tag{8}$$

ΔGads = standard free energy of adsorption, Kad = eqillibrium constant of adsorption, and 55.5 = concentration of water in solution (mol l^{-1}). ΔGads values around −20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between charged organic molecules

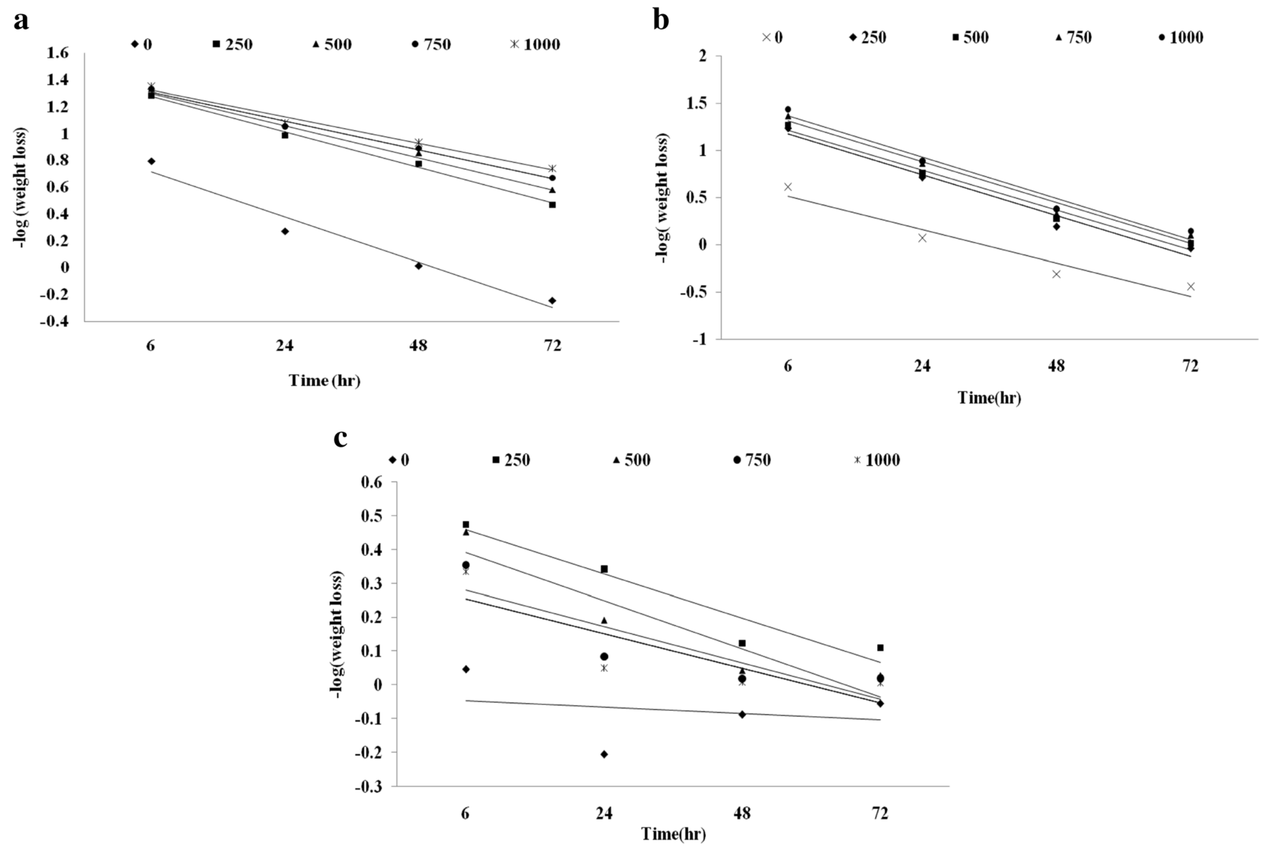

Fig. 5 Variation of –log(weight loss) versus time for the corrosion of mild steel in solutions of **a** 1N HCl, **b** 1N H_2SO_4 and **c** 1N HNO_3 containing various concentrations of guar gum at 313K temperature

and the charged metal surface (physiorption): those around −40 kJ mol^{-1} or higher involve charge sharing or transfer from the organic molecules to the metal surface to form a co-ordinate type of bond (chemisorptions). Our reported values for ΔGads ≤−20 kJ mol^{-1} are less than −20 kJ mol^{-1}, so in our reaction, we reported physiorption. Values of ΔGads and Kad are listed in Table 5.

In case of adsorption by solids from the solutions, mostly the solute is adsorbed on the surface of the solid adsorbent so that the concentration of solute on the

Table 3 Kinetic parameters for the corrosion of mild steel in 1N HCl, H_2SO_4, and HNO_3 medium containing various concentrations of guar gum at 304 K

1N HCl	Cont. (ppm)	B	K	R^2	1N H_2SO_4	B	K	R^2	1N HNO_3	B	K	R^2
	0	−0.35	1.1	0.96		−0.36	0.92	0.93		−0.02	0.01	0.70
	250	−0.27	1.6	0.99		−0.44	1.7	0.98		−0.14	0.64	0.90
	500	−0.25	1.6	0.97		−0.44	1.74	0.98		−0.15	0.57	0.89
	750	−0.25	1.65	0.99		−0.44	1.85	0.98		−0.12	0.44	0.76
	1000	−0.19	1.56	0.99		−0.41	1.86	0.96		−0.11	0.4	0.74
313 K												
1N HCl	0	−0.34	1.05	0.96	1N H_2SO_4	−0.35	0.87	0.94	1N HNO_3	−0.02	0.03	0.93
	250	−0.26	1.54	0.99		−0.43	1.61	0.97		−0.13	0.59	0.92
	500	−0.22	1.52	0.98		−0.42	1.64	0.98		−0.14	0.53	0.87
	750	−0.24	1.54	0.98		−0.43	1.75	0.94		−0.11	0.39	0.74
	1000	−0.2	1.52	0.99		−0.44	1.8	0.97		−0.1	0.36	0.71

Table 4 Calculated values of apparent activation energy (Ea) and Heat of adsorption (Q) of guar gum on mild steel in 1N HCl, H_2SO_4 and HNO_3 medium

Guar gum concentration (ppm)	Medium	Ea (kJ mol^{-1})				Qads (kJ mol^{-1})			
		6 h	24 h	48 h	72 h	6 h	24 h	48 h	72 h
0	1N HCl	9.27250789	2.90507331	0.9139064	1.36911847	–	–	–	–
250		11.848584	5.58216111	12.9549107	5.19003643	−3.75007014	−4.43960607	−5.22802254	−4.21395543
500		12.8788011	6.29318179	4.32023085	7.31956056	−7.53960158	−7.82935384	−9.85802469	−10.7977925
750		21.6914682	10.3215288	4.47333994	2.8048226	−10.0039872	−10.915953	−12.1317652	−14.818384
1000		6.56409778	10.947072	10.1705685	9.94213687	−7.6629907	−10.8511463	−13.051503	−17.5339037
0	1N H_2SO_4	8.8401921	3.52688474	1.41960241	1.50081477	–	–	–	–
250		16.5049372	13.2543419	20.1025875	12.0519032	−6.17484905	−6.84773222	−10.0018618	−11.1406732
500		17.1777765	19.3215751	12.9564535	10.8190683	−6.80674183	−8.4132127	−10.1549509	−12.5647234
750		22.8243155	12.1771338	20.733607	15.6261701	−5.22040277	−5.85683963	−7.75697335	−9.24900021
1000		17.421718	21.6080439	22.5823843	32.02365	−3.34592498	−3.79544558	−5.29988713	−7.99889198
0	1N HNO_3	1.77304033	3.55516654	0.79157225	1.08495861	–	–	–	–
250		8.30698807	10.1277979	3.89375612	5.43939158	−3.36869057	−2.96013092	−2.41242305	−2.20720793
500		5.32116501	7.53342455	3.0589423	3.12703952	−4.84997347	−2.89713752	−2.05965033	−1.9731825
750		8.84421126	5.7499852	2.72675645	3.5886785	−1.79641201	−1.70305171	−1.74738879	−1.82442233
1000		7.05913228	7.25875797	4.03907321	3.7658194	−1.76463022	−1.85561621	−1.92276054	−2.03325308

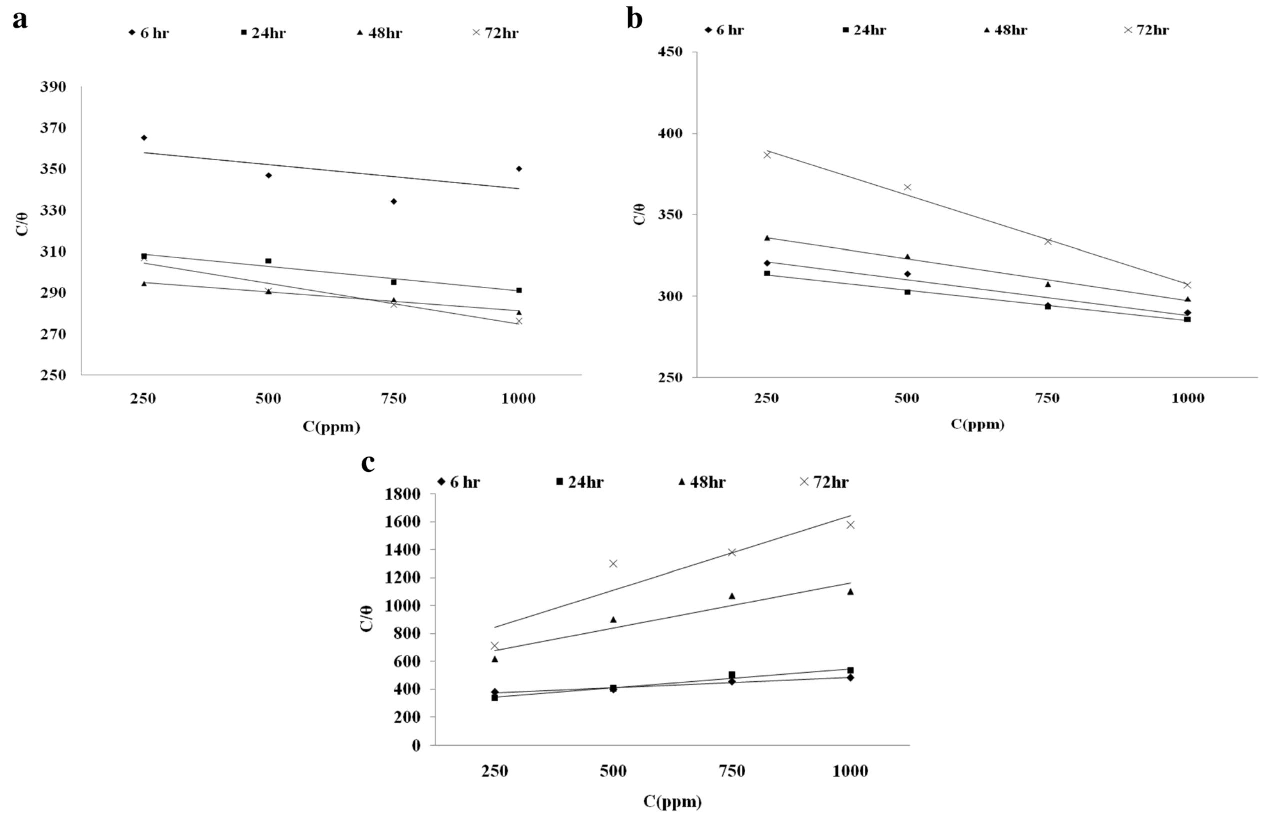

Fig. 6 Adsorption isotherms for the guar gum on mild steel in different acid medium at 304 K temperature. Langmuir isotherm in **a** 1N HCl, **b** 1N H_2SO_4, and **c** 1N HNO_3

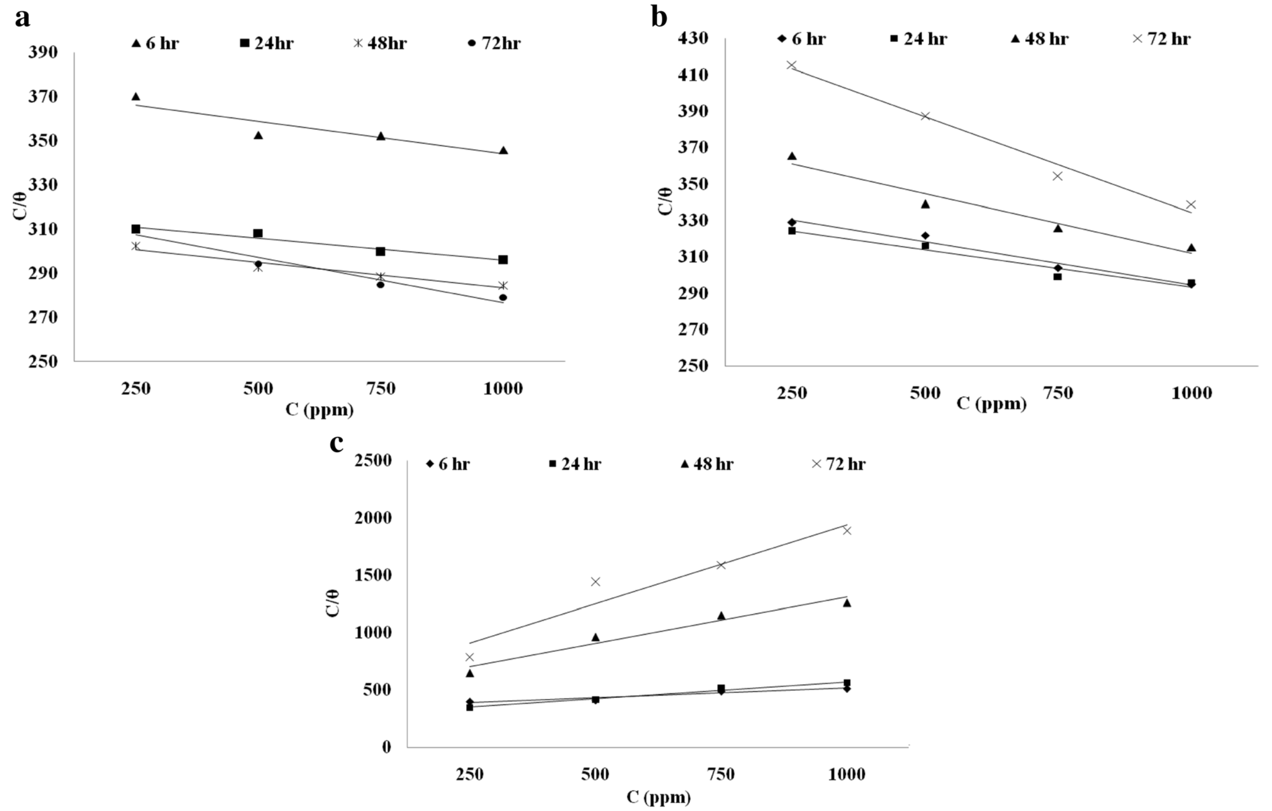

Fig. 7 Adsorption isotherms for the guar gum on mild steel in different acid medium at 313 K temperature. Langmuir isotherm in **a** 1N HCl, **b** 1N H_2SO_4, and **c** 1N HNO_3

surface of the adsorbent is greater than in the bulk. This is known as positive adsorption. In some cases, the solvent from the solution may be absorbed by the adsorbent so that the concentration of the solution increases than the initial concentration. This is called negative adsorption. Hence, if the concentration of the adsorbate is less on the surface of the adsorbent than in the bulk, it is known as negative adsorption.

We observed the low and negative values of ΔG during this study, which show probability of physiosorption. Electrostatic interaction between the charged metal and charged molecules signifies physical adsorption. Applicability of

Table 5 Parameters for the adsorption of guar gum on mild steel surface at 304 and 313 K temperature

		304 K						313 K			
Applied isotherm	Medium	Cont. (ppm)	Time (hours)	B	Kads (ppm^{-1})	R^2	ΔGads ($kJ\ mol^{-1}$)	B	Kads (ppm^{-1})	R^2	ΔGads ($kJ\ mol^{-1}$)
Langmuir adsorption isotherm	1N HCl	250	6	−5.81	363.6	0.95	−25.05	−7.365	373.6	0.82	−25.12
		500	24	−5.97	314.7	0.93	−24.68	−5.026	315.9	0.94	−24.69
		750	48	−4.56	299.48	0.92	−24.56	−5.782	306.3	0.95	−24.61
		1000	72	−9.87	314.16	0.96	−24.68	−10.19	317.4	0.96	−24.70
Langmuir adsorption isotherm	1N H_2SO_4	250	6	−11.03	332.24	0.94	−24.82	−11.98	342.3	0.97	−24.90
		500	24	−9.39	322.65	0.99	−24.75	−26.32	439.6	0.98	−25.53
		750	48	−12.91	348.93	0.99	−24.94	−16.41	377.4	0.96	−25.14
		1000	72	−27.26	416.58	0.99	−25.39	−10.61	334	0.95	−24.83
Langmuir adsorption isotherm	1N HNO_3	250	6	36.25	340.67	0.97	−24.88	42.72	347.1	0.93	−24.93
		500	24	68.21	274.95	0.99	−24.34	73.67	276.8	0.98	−24.36
		750	48	162.4	515.44	0.89	−25.93	202.5	501.5	0.95	−25.86
		1000	72	266.5	577.21	0.86	−26.22	343.5	568.1	0.92	−26.18

Langmuir adsorption isotherm of adsorption of guar gum confirms formation of multi-molecular layer of adsorption where there is no interaction between adsorbate and adsorbent.

Adsorption mechanism

The process of mild steel dissolution in acidic medium i.e., (1N HCl, 1N H_2SO_4, and 1N HNO_3) depends on concentration of anions in the solution as observed

$$\mathrm{Fe} + \mathrm{Cl} \leftrightarrow (\mathrm{FeCl}^-)_{\mathrm{ads}} + e^-$$

$$(\mathrm{FeCl}^-)_{\mathrm{ads}} \leftrightarrow (\mathrm{FeCl})_{\mathrm{ads}} + e^-$$

$$(\mathrm{FeCl})_{\mathrm{ads}} \leftrightarrow \mathrm{FeCl}^+ + e-$$

$$\mathrm{FeCl}^+ \leftrightarrow \mathrm{Fe}^+ + \mathrm{Cl}^-$$

when we add guar gum (GG) as inhibitor to acid solution, different additional steps are involved depending on the nature of the electrolyte in mechanism of anodic dissolution

$$(\mathrm{FeCl}^-)_{\mathrm{ads}} + \mathrm{H}^+\mathrm{GG} \leftrightarrow (\mathrm{FeCl}^- \ \mathrm{H}^+\mathrm{GG})_{\mathrm{ads}}$$

$$(\mathrm{FeCl}^- \ \mathrm{H}^+\mathrm{GG})_{\mathrm{ads}} \leftrightarrow (\mathrm{FeH}^+\mathrm{GG})_{\mathrm{ads}} + \mathrm{Cl}^-$$

In acidic medium reduction, mechanism is not affected by the presence of the inhibitor because hydrogen evolution is activated controlled step. Due to this, there is retardation in the rate of cathodic reaction by the inhibitor and the possible pathways of the cathodic reaction are the following

$$\mathrm{Fe}^+\mathrm{H}^+ + e^- \leftrightarrow (\mathrm{FeH})_{\mathrm{ads}}$$

$$\mathrm{Fe} + (\mathrm{H}^+\mathrm{GG}) + e^- \leftrightarrow (\mathrm{FeH\,GG})_{\mathrm{ads}}$$

$$(\mathrm{FeH})_{\mathrm{ads}} + (\mathrm{FeH\,GG})_{\mathrm{ads}} \leftrightarrow \mathrm{Fe} + \mathrm{H}_2$$

By all this reaction mechanism, we get to know that there is competition between H^+ and H^+GG (protonated inhibitor) for the same active site to get adsorbed on the surface.

Abovementioned mechanism is applicable to HCl, H_2SO_4, and HNO_3. In Fig. 8, we are showcasing comparative inhibition capacity of guar gum inhibitor for mild steel corrosion in all acidic mediums. Where we found that in 1N HCl inhibitor efficacy increases with increasing concentration but in 1N H_2SO_4 and 1N HNO_3, it increases up to maximum limit and after that, it falls. It is noted that, the obtained inhibition results are comparatively better in HCl and H_2SO_4 in comparision of HNO_3.

Guar gum has been found to be a good corrosion inhibitor. The corrosion control potential of this gum can

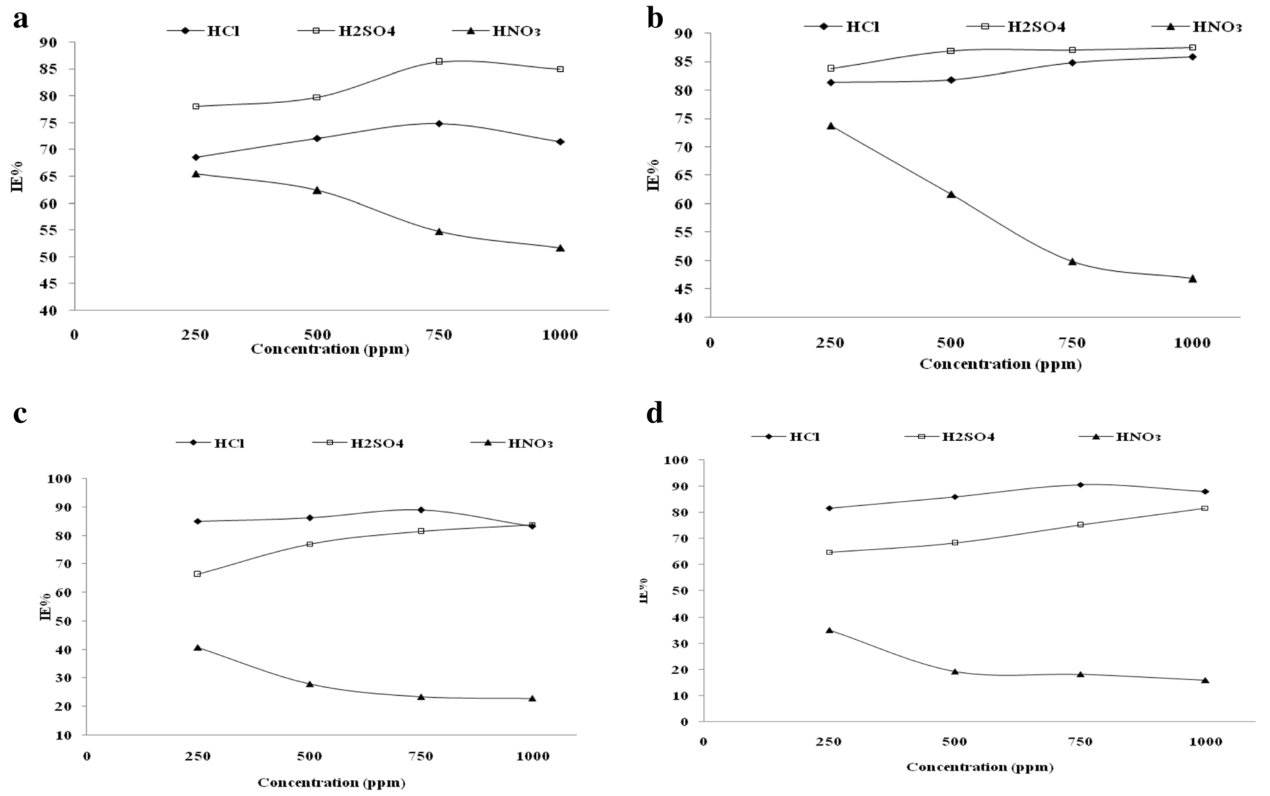

Fig. 8 Comparative analysis graphs of mild steel corrosion 1N HCl, H_2SO_4, and HNO_3 at **a** 6 h. **b** 24 h. **c** 48 h. **d** 72 h

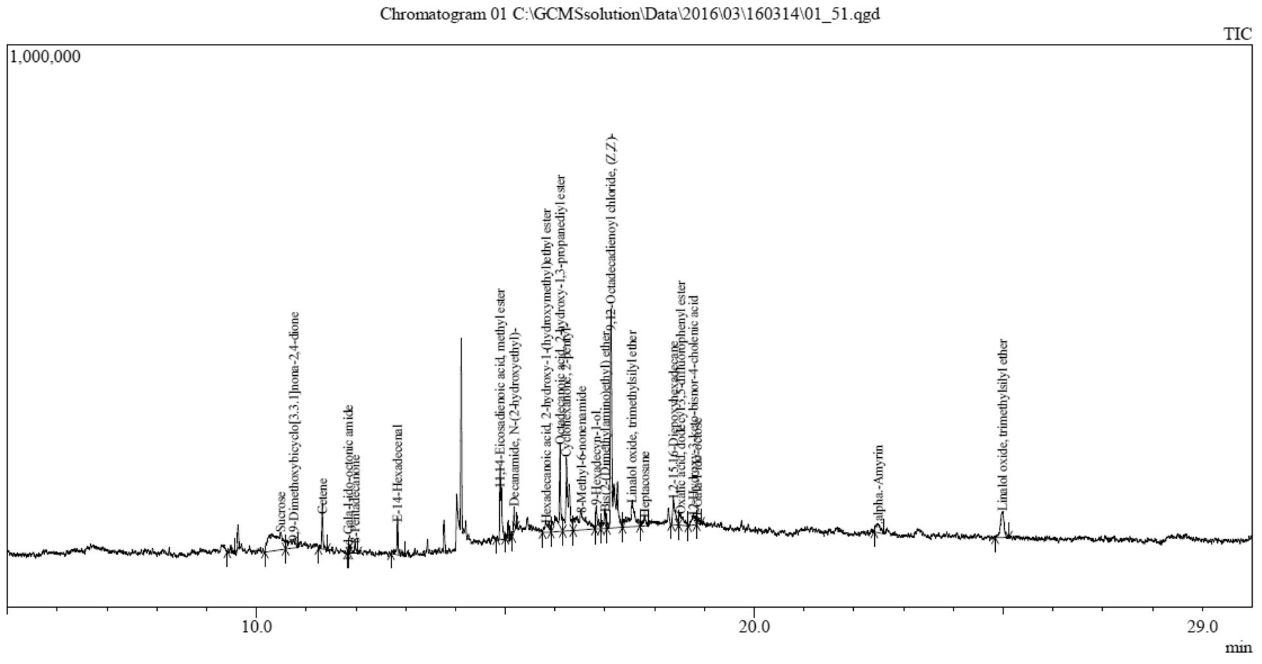

Fig. 9 GCMS spectrum of guar gum (*Cyamopsis tetragonoloba*)

Table 6 GC-MS spectrum details of guar gum

Peak	R. time	F.Time	Area	Area %	A/H	Name
1.	10.492	10.590	555735	9.86	18.66	Sucrose
2.	10.755	10.830	157038	2.79	12.29	9,9-Dimethoxybicyclo[3.3.1]nona-2,4-dione
3.	11.328	11.415	127449	2.26	1.91	Cetene
4.	11.850	11.865	17081	0.30	1.53	d-Gala-l-ido-octonic amide
5.	11.985	12.045	66373	1.18	3.54	8-Pentadecanone
6.	12.840	12.990	144423	2.56	2.42	E-14-Hexadecenal
7.	14.904	15.090	386001	6.85	4.08	11,14-Eicosadienoic acid, methyl ester
8.	15.182	15.210	65176	1.16	1.79	Decanamide, N-(2-hydroxyethyl)-
9.	15.825	15.915	106873	1.90	6.04	Hexadecanoic acid, 2-hydroxy-1-(hydroxymethyl
10.	16.101	16.155	451646	8.01	3.88	Octadecanoic acid, 2-hydroxy-1,3-propanediyl
11.	16.230	16.365	541503	9.61	4.94	Cyclohexanone, 2-pentyl-
12.	16.530	16.800	401248	7.12	12.34	8-Methyl-6-nonenamide
13.	16.830	16.920	122353	2.17	3.10	9-Hexadecyn-1-ol
14.	17.010	17.040	105093	1.86	3.35	Bis(2-(Dimethylamino)ethyl) ether
15.	17.126	17.355	1192462	21.16	3.49	9,12-Octadecadienoyl chloride, (Z,Z)-
16.	17.550	17.700	335697	5.96	7.72	Linalol oxide, trimethylsilyl ether
17.	17.803	17.880	67532	1.20	4.16	Heptacosane
18.	18.379	18.480	179897	3.19	3.74	1,2-15,16-Diepoxyhexadecane
19.	18.525	18.675	112550	2.00	6.01	Oxalic acid, dodecyl 3,5-difluorophenyl ester
20.	18.778	18.840	96726	1.72	6.02	12-Hydroxy-3-keto-bisnor-4-cholenic acid
21.	18.855	18.930	36498	0.65	2.66	-Gala-l-ido-octose
22.	22.493	22.605	101434	1.80	6.76	.alpha.-Amyrin
23.	24.984	25.110	229530	4.07	5.14	Linalol oxide, trimethylsilyl ether

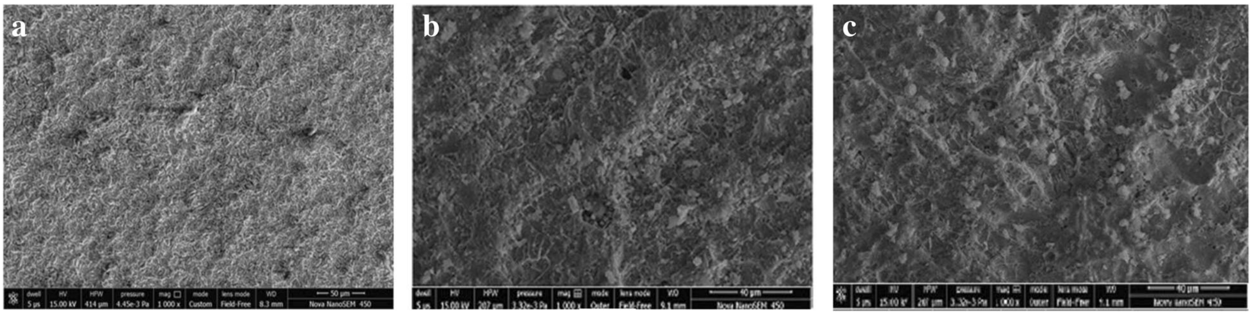

Fig. 10 SEM images of mild steel with HCl on 40-μm **a** Polished MS, **b** MS without inhibitor, and **c** MS with inhibitor (1000 ppm, 72 h)

be defined in expressions of interaction between the metal and the gum. Most efficient corrosion inhibitors are long carbon chain or aromatic compounds that have heteroatoms (N, S, P, and O) in their system. The present of π-electron rich functional groups have also been found to enhance inhibition efficiency of a corrosion inhibitor. Figure 9 and Table 6 show the GCMS chromatograph of guar gum and the corrosion product, respectively.

SEM analysis

The surface morphology of treated mild steel examined by scanning electron microscope is shown in Fig. 10 for samples treated with 1N hydrochloric acid solution, Fig. 11 for samples treated with 1N sulfuric acid solution, and Fig. 12 for sample treated with HNO_3 solution. Each figure shows scanning electron micrographs of the tested surfaces with and without inhibitor. Besides all, three figures show the surface morphology of plain mild steel. Scanning electron micrograph of plain mild steel shows analogous grooves with moderately light areas, which were identified as clean surface. Figure 10 shows the surface morphology of plain mild steel and mild steel exposed to 1N hydrochloric acid without inhibitor or with inhibitor on best potent efficiency (1000 ppm, 72 h), Fig. 11 shows the surface morphology of plain mild steel and mild steel exposed to 1N H2SO4 in the without inhibitor or with inhibitor on best potent efficiency (1000 ppm, 24 h), and in Fig. 12, we obtained the surface morphology of plain mild steel and mild steel exposed to 1N HNO_3 in the without inhibitor or with inhibitor on best potent efficiency (250 ppm, 24 h). Uniform severe corrosion can be observed in the absence of inhibitor for the three acids (Figs. 10, 11, and 12) showing fanatic shapeless corrosion products.

Despite the fact that the obtained SEM results for mild steel in existence of inhibitor suggests that the metal surface is moderately envolved with inhibitor, it is noticeable that the surface is more covered with inhibitor in company of hydrochloric acid (Fig. 10) as compared with the other two acids (Figs. 11 and 12).

Conclusions

- Guar gum inhibitor adsorption follows the Langmuir adsorption isotherm with all three acids at 304 and 313 K temperature.
- In HCl solution, inhibition efficiency gradually increases with increasing concentration of inhibitor up to 1000 ppm at 72 h.
- In H_2SO_4 solution, inhibition efficiency rapidly increases with increasing concentration up to (1000 ppm, 24 h). After that there is fall in inhibition due to limited adsorption site or overlapping of inhibitor molecules. But fall of

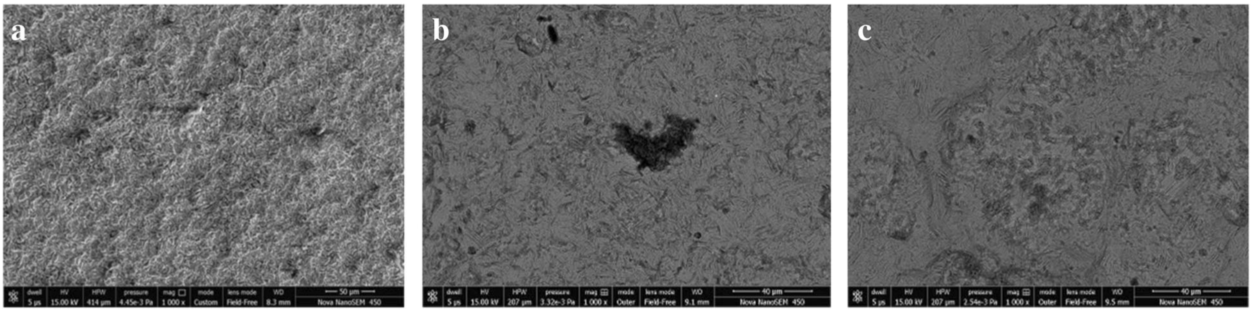

Fig. 11 SEM images of mild steel with H_2SO_4 on 40-μm **a** Polished MS, **b** MS without inhibitor, and **c** MS with inhibitor (1000 ppm, 24 h)

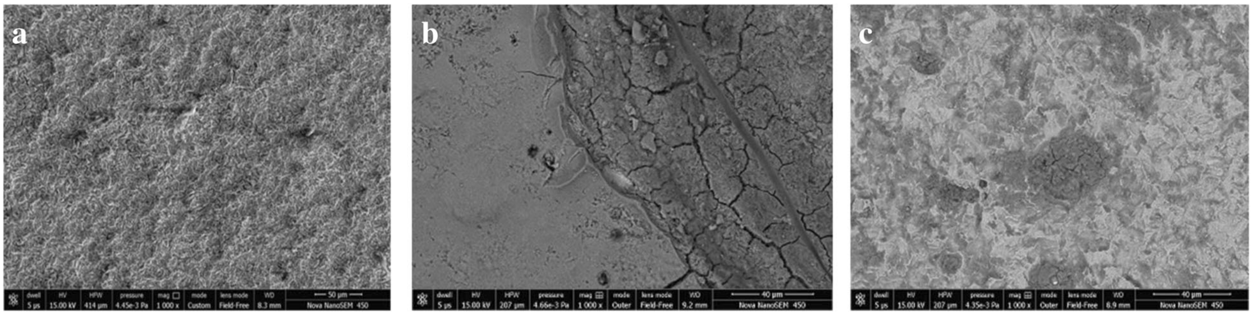

Fig. 12 SEM images of mild steel with HNO_3 on 40-μm **a** Polished MS, **b** MS without inhibitor, and **c** MS with inhibitor (250 ppm, 24 h)

inhibition maintains the increasing mode of inhibition with low inhibition values.

- In HNO_3 solution, inhibition efficiency reported high on initial level (6 h, 500 ppm) after that collapse in inhibition due to hyper oxidizing nature of HNO_3 acid.
- According to obtained result, guar gum adsorption on metal surface was spontaneous, exothermic, and supported the mechanism of physical adsorption.
- Comparatively guar gum work as effective inhibitor in HCl solution as compared to H_2SO_4 and HNO_3.

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Authors' contributions

All experimental works were done by AP. SKS contributed in the results and discussions. IBO contributed in the isothermal studies. All contributing authors have approved the manuscript for submission.

Competing interests

This work is originally done by us and not submitted elsewhere for publication. We also confirm that the authors declare that they have no competing interests.

Author details

[1]Green Chemistry & Sustainability Research Group, Department of Chemistry, JECRC University, Jaipur 303905, India. [2]Centre of Research Excellence in Corrosion, King Fahd University of Petroleum and Minerals, Dhahran 31261, Kingdom of Saudi Arabia.

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