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Differences in the corrosion inhibition of water extracts of *Cassia fistula* L. pods and *o*-phenanthroline on steel in acidic solutions in the presence and absence of chloride ions

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ABSTRACT

The corrosion inhibition of water extract of *Cassia fistula* L. pods and *o*-phenanthroline on mild steel in acid solution in the absence and presence of 0.1 M NaCl have been investigated using weight loss measurements in addition to the potentiodynamic polarization technique. FTIR and GC-mass were used to identify the chemical composition of *C. fistula* L. pods. The inhibition efficiencies of *C. fistula* L. pods were 95.19% in 2 M H_2SO_4 and 86.13% in 0.5 M nitric acid solutions in the presence of chloride ions, while *o*-phenanthroline recorded 86.09 and 72.76% for the above acid solutions, respectively. All the ΔG_{ads} were negative which indicates spontaneous adsorption on the steel surface. Consequently the relationship between log (c/ϑ) and log c indicates that the adsorption of inhibitor onto steel surface follows the Langmuir adsorption isotherm.

Keywords: Steel; Weight loss; Polarization; Acid corrosion; *C. fistula*; *o*-phenanthroline

1. Introduction

Steel is the most important engineering and construction material in the world. It is widely used in many applications, which have resulted in the research of its corrosion resistance in various aggressive environments. Corrosion inhibition is receiving more research attention nowadays in order to find solutions for metal corrosion and to avoid the attack of all kinds of corrosive media. Using inhibitors has been considered an effective method to control the corrosion of metals by numerous scientists. Inorganic substances such as phosphates, chromates, dichromates, nitrites, nitrates, and sulfides of alkali metals as well as the salts of arsenic and cadmium have been found as the effective inhibitors of metal corrosion; however, a major disadvantage is their toxicity and as such, their use has been a sufficient subject to severe criticism [1,2]. Organic compounds containing polar groups with nitrogen, oxygen, or sulfur atoms in a conjugated system have been reported as effective inhibitors to the corrosion of mild steel in acidic media [3–6]. Their inhibitive action is connected to several factors including the structure and charge distribution of the molecule [7–11], the number and types of adsorption sites, and the

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nature of interaction between the molecule and the metal surface [5].

Most of the materials used as corrosion inhibitors are of chemical origin [12–15] and only a few are of natural resource including: plant extracts, animal proteins, and coal tar [16]. *Opuntia* extract, *Aleoeru* leaves, orange, and mango peels gave adequate protection to steel in 5 and 10% HCl at 25 and 40˚C, respectively. Tobacco, black pepper, caster oil seeds, acacia gum, and lignin were good inhibitors for steel in an acidic medium. Flour, yeast, and some byproducts of food industries were used for restraining iron corrosion in acid media. Molasses treated in alkali solution inhibited the corrosion of steel in HCl. Caffeine and nicotine was used in the inhibition of steel corrosion in neutral media. Herbs (such as coriander, hibiscus, anise, black cumin, and garden cress) were provided as a new type of green inhibitors for acidic corrosion of steel. On the other hand, most corrosion inhibitors have side effects on living organisms and poison the environment and therefore, pose an increasing concern regarding their toxic effects [12–15]. Furthermore, the uses of naturally occurring compounds are of interest because of their cost effectiveness, abundant availability, and their environmental acceptability [17]. Due to these advantages, extracts of some common plants and plant products have been tried as corrosion inhibitors for metals and alloys under different environments. Accordingly, plants become an important source of a wide range of ecofriendly (green) corrosion inhibitors. This endless increasing search for environmentally friendly corrosion inhibitors such as some natural products obtained from plant extracts is investigated by many authors [18–29]. In many studies, the use of water extract of pods of *C. fistula* L. for the inhibition of the corrosion of mild steel in H_2SO_4 and HNO_3 solutions is not cited. *C. fistula* L. tree is found in many countries. It is cultivated as an ornamental flowering tree and is sometimes planted for its medicinal properties [30]. In full bloom, *C. fistula* L. is laden with an 8–18 inch hanging racemes of pure yellow. The ensuing pods are one inch thick, and can reach lengths of 24 inches. They are persistent and will turn from green to black and remain on the tree until the next season. *C. fistula* L. is semi-deciduous after flowering, but most trees regain all their leaves by late July. It is an upright, rather narrow tree with an open top, and slightly drooping branches. It is planted in full sun and in a place where it will be noticed. Some communities have planted this tree on their streets. *C. fistula* L. begins flowering about three years after germination. This plant is mostly found in the gardens of Egypt.

The aim of this study is to investigate the inhibitive properties of water extract of *C. fistula* L. pods on the corrosion of mild steel in 2 M H_2SO_4 and 0.5 M HNO_3 solutions and then compare the results obtained with those of *o*-phenanthroline (**1**) under identical conditions. *o*-phenanthroline (**1**) is widely used to chelate metallic ions in aqueous solutions, and hence as corrosion inhibitors for metals [31–36].

2. Experimental

2.1. Materials and instruments

Steel specimens with the following composition: $C \leqslant 0.15\%$, $S \leqslant 0.07\%$, $P \leqslant 0.38\%$, $Mn \leqslant 0.58\%$, and Fe 98.82% (wt.%) were tested and emery paper of different grit size was used for the cleaning of steel specimens. All reagents used for this study were analytically graded and distilled water was used for their preparation. Gas chromatography-Mass Spectroscopy (GC-mass) (Trace DSQ II Ms. with capillary column: Thermo TR-35 MS (30, 0.25 mm, 0.25 μm, 35% phenylpolysilphenylene-siloxane). Fourier transforms infra-red (FTIR) (Perkin–Elmer FTIR spectrum). Four digital analytical balance of precision ±0.1 mg was used for the weight loss measurements. Gill AC instrument (ACM instrument) was used for the electrochemical polarization measurements.

2.2. Methods

2.2.1. Preparation of metal

The experiments were performed with cold rolled steel specimens. The steel sheet was mechanically press-cut to form different coupons, each of dimensions $4.0 \times 2.0 \times 0.2$ cm. These coupons were abraded with emery paper of different grad size, degreased with ethanol, dipped in acetone, removed and washed thoroughly with laboratory distilled water, and allowed to dry in vacuum before use. Prior to each experiment, the specimens were treated as described and freshly used with no further storage.

2.2.2. Preparation of plant

The *C. fistula* L. pods plant was collected from the zoo park of Alexandria, Egypt, washed with distilled water, air dried and then put in an open oven at 105˚ C and milled. About 1 kg of milled plant was extracted by boiling two times in 5 l of distilled water. The combined filtrates were concentrated under vacuum to dryness and further dried under vacuum in an oven at 55˚C to give a dark brown gummy solid.

2.2.3. Solutions

Double distilled water and analytical reagent-grade HCl, H_2SO_4, and NaCl were used for preparing the solutions. For experiments involving *o*-phenanthroline and water extract of *C. fistula* L. pods, the solids were added to 100 ml of the blank solution to reach final concentrations of 0.25, 0.50, 1.0, 2.5, and 5.0 mM and of 1, 2, 3, 4, and 5 g/l, respectively.

2.3. Gravimetric measurements

The specimens were weighed accurately then immersed in 125 ml of acidic solutions contained in a 250 ml beaker in the presence of different concentrations of inhibitors (*o*-phenanthroline or *Cassia festiula* L. pods) with or without the addition of 0.1 M NaCl. The aggressive acid solutions were maintained at 25 ± 1˚C in open air. After different time intervals (1–4 hand 2–36 h for 0.5 M HNO_3 and 2 M H_2SO_4, respectively), the specimens were taken out, washed, dried, and reweighed. The weight loss was taken as the difference between the weight at the given time and the original weight of the specimen.

2.4. Inhibition efficiency and degree of surface coverage

The inhibition efficiency (IE %) of *o*-phenanthroline and *Cassia festiula* L. on the corrosion of steel in sulfuric and nitric acids solutions and the degree of surface coverage (θ) were evaluated by comparing the weight losses in the presence and absence of inhibitor and 0.1 M NaCl were as follows [37,38]

$$\text{IE }\% = \left[1 - \frac{W_{\text{inh}}}{W_{\text{blank}}}\right] \times 100 \tag{1}$$

$$\theta = 1 - \frac{W_{\text{inh}}}{W_{\text{blank}}} \tag{2}$$

where W_{inh} and W_{blank} are the weight losses in the presence and absence of inhibitors, respectively.

2.5. Electrochemical tests

Polarization measurements were conducted at a scan rate of 20 mV/min starting from cathodic potential (E_{corr}–250 mV) going to anodic direction. The data was obtained in a three-electrode mode: platinum sheet and saturated calomel electrodes were used as counter and reference electrodes, respectively. Before polarization measurements, the working electrode was introduced into the test solution and left for 10 min to attain the open circuit potential (ocp) at which the change of ocp with time is 2 mV/min. To test the reliability and reproducibility of the measurements, duplicate experiments were performed in each case.

3. Results and discussion

3.1. GC-mass results

The GC-mass of the obtained dark brown solid extracted from *C. fistula* L. pods showed the presence of different organic compounds such as 3-acetoxy-2-aminopropanoic acid (**2**), 5-(hydroxymethyl) furan-2-carbaldehyde (**3**), 3,5-dihydroxy-6-methyl-2H-pyran-4(3H)-one (**4**), 4,5-dihydroxy-9,10-dioxo-9,10-di hydroanthracene-2-carboxylic acid (**5**),1,8-dihydroxy-3-methoxy-6-methylanthracene-9,10-dione (**6**), 3-formyl-1-hydroxy-8-methoxy anthaquinone (**7**), 1,8-dihydroxy-3-methylanthracene-9,10-dione (**8**), 3,5,7-trihydroxy-2-(4-hydroxyphenyl)-4H-chromen-4-one (**9**), 1,4,5-trihydroxy-6,7-dimethoxy-3-methyl-9,10-dioxo-9,10-dihydro anthracene-2-carboxylic acid or fistulic acid (**10**) 3,8,8´-trimethoxy-3´-(piperidin-1-yl)-2,2´-binaphthyl-1,1´,4,4´-tetraone (**11**), sennoside (**12**), and (6-acetoxy-7-methyl-5-(2-oxopropoxy)-1,3-dioxepan-4-yl)methyl acetate (**13**) (Fig. 1) [36]. Fig. 2 shows the GC-MS diagram of the water extracted mixture of *C. fistula* L. pods. From the previous structure, it can be seen that most of the compounds contain OCH_3, C=O, HC=O, $-CO_2H$ and/or ester groups and π-electrons which are important to make corrosion inhibition in acidic solution.

3.2. FTIR results

Fig. 3 shows the FTIR chart of the water extract mixture of *C. fistula* L. pods. IR spectra for compounds showed Si–OH stretching in the range at 3675.81–3711.71. A broad band in the range of 3,000–3,500 cm^{-1} can be assigned to the presence of superficially adsorbed water, stretching mode of an O–H and/or N–H (from plant extract). The wave numbers corresponding to amide −C=O, hydrogen bonded quinine C=O, and nonhydrogen bonded quinine C=O could be observed in the region 1,701–1,703, 1,665–1,668, and 1,643–1,645 cm^{-1}, respectively. In general the −C=O frequency for nonhydrogen bonded secondary amide carbonyl is observed in the range 1,680–1,630 cm^{-1}, in solid state. Higher wave numbers, 1,701–1,703 cm^{-1}, observed for the amide −C=O in compounds, show that the double bond character is further strengthened due to the influence of strong electron withdrawing nature of quinine function. In similar systems, it was reported that intramolecular hydrogen bonding was the reason for this kind of

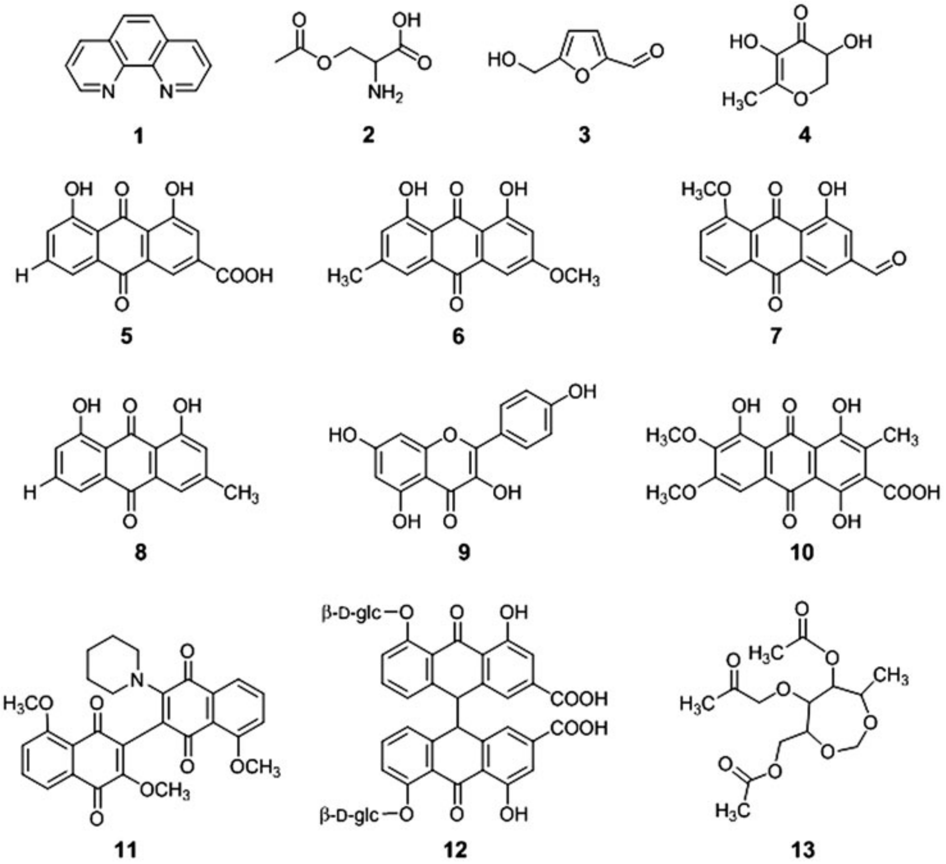

Fig. 1. Chemical structure of some organic compounds found in water extract of *C. fistula* L. pods and chemical structure of *o*-phenanthroline.

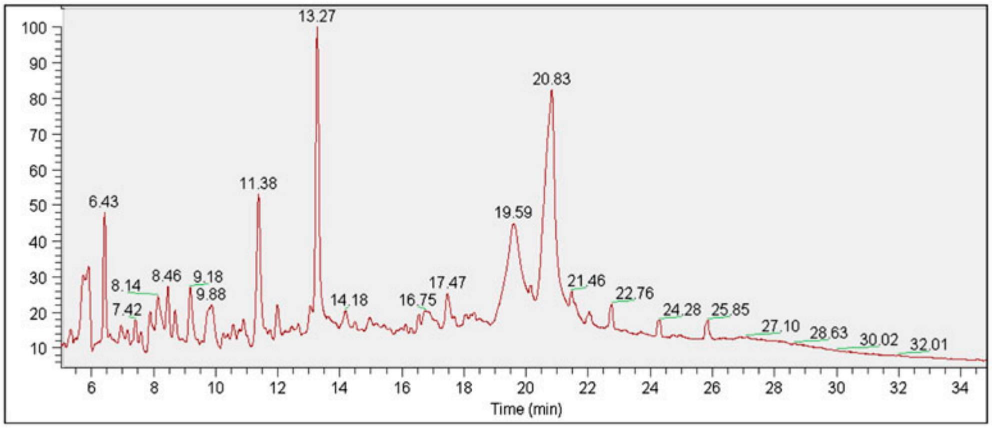

Fig. 2. GC-MS of water extract of *C. fistula* L. pods.

shift. Ranges between 1,635–1,653.56 cm^{-1} indicates the presence of primary and secondary amide stretching, and from 1,540.66–1,559.43 cm^{-1}, indicate the presences of secondary amide bending, and stretching aliphatic nitro compound. Also, aromatic nitro compound asymmetric stretching at 1,418–1,472 cm^{-1} represents the presence of azo compound and the presence of methyl asymmetrical bending (alkane), at 1,052 cm^{-1} in plane C–H bending (P–F stretching) aliphatic asymmetric P–O–C stretching [39–41].

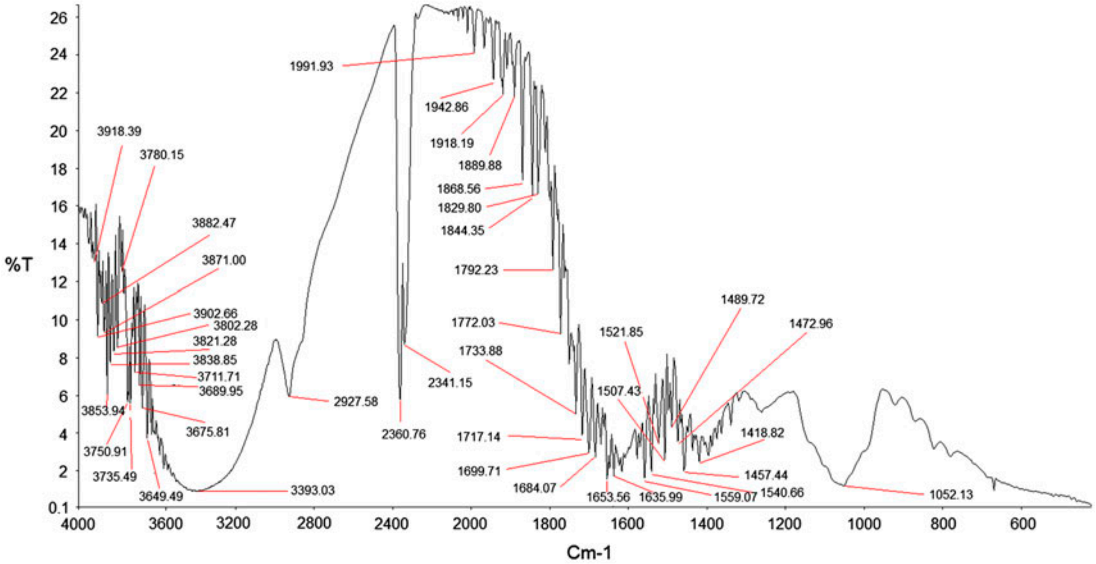

Fig. 3. FTIR of water extract of *C. fistula* L. pods.

3.3. Weight losses

The corrosion rate and inhibition efficiency IE (%) of mild steel exposed to 0.5 M nitric acid and 2.0 M sulfuric acid in the absence and presence of different concentrations of water extracted *C. fistula* L. pods and *o*-phenanthroline and 0.1 M NaCl at room temperature (25 ± 1˚C) are represented in (Figs. 4–7). The amount of weight loss is seen to decrease with an increasing additive concentration for both compounds. The highest inhibition efficiencies were 86.13 and 95.19% for *C. fistula* L. pods in0.5 M nitric acid and 2 M H_2SO_4 solutions, respectively. On the other hand, *o*-phenanthroline was recorded 72.76 and 86.09% in 0.5 M nitric acid and 2 M H_2SO_4 solutions, in respective order (Table 1). The corrosion rate values decrease when the inhibitor concentration increases due to the increase of the inhibition efficiencies (Figs. 8 and 9). Interestingly, water extract of *C. fistula* L. pods gave higher inhibition efficiencies for steel corrosion than *o*-phenanthroline in both acid solutions. HNO_3 solutions showed smaller IE %, which indicates a higher corrosion of iron specimens in 0.5 M HNO_3 than in 2 M H_2SO_4 solutions. This study showed that a single *o*-phenanthroline is not suitable enough as an inhibitor for steel corrosion in sulfuric acid. It has been reported by numerous authors that synergistic effects of halide ions have been utilized to improve the inhibition efficiency of *o*-phenanthroline [42–46]. Synergism between organic inhibitors and halide ions on metal corrosion in acidic solution has been reported by different authors [42,43,47,48]. The mechanism of synergistic inhibition between *o*-phenanthroline and chloride ion, might be due to an introduction of a chloride ion to a heterocyclic compound which improves its inhibitory effect by varying the disturbances and orbital energy configuration of electrons of the inhibitory compound [31,49].

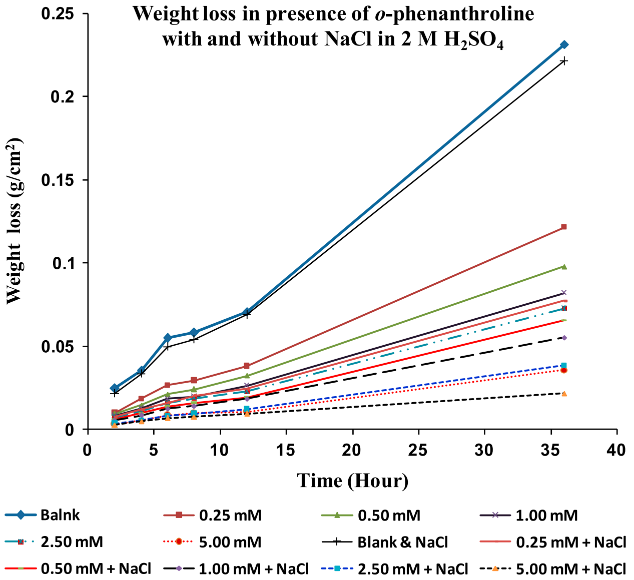

Fig. 4. Chart of the variation of weight loss with time of steel corrosion in 2 M H_2SO_4 solution in the absence and presence of different concentrations of *o*-phenanthroline with and without 0.1 M NaCl.

3.4. Langmuir adsorption isotherm

A given inhibitor functions by means of a specific mechanism that depends on the polarizability and

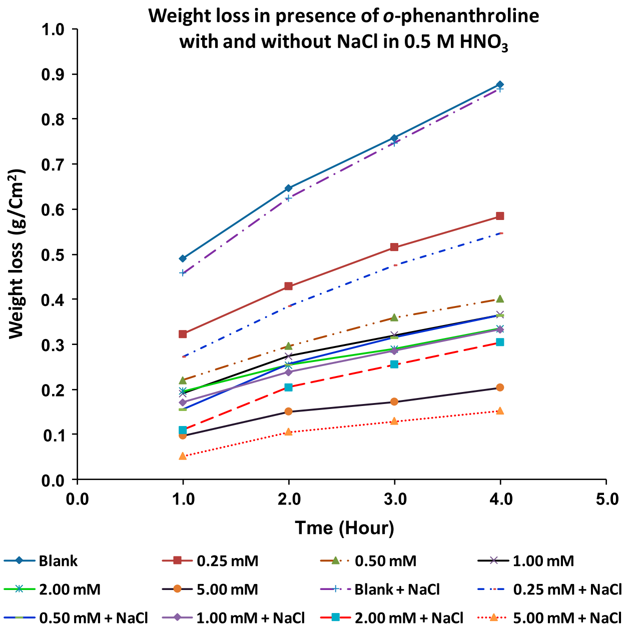

Fig. 5. Chart of the variation of weight loss with time for steel corrosion in 0.5 M HNO_3 solution in the absence and presence of different concentrations of *o*-phenanthroline and 0.1 M NaCl.

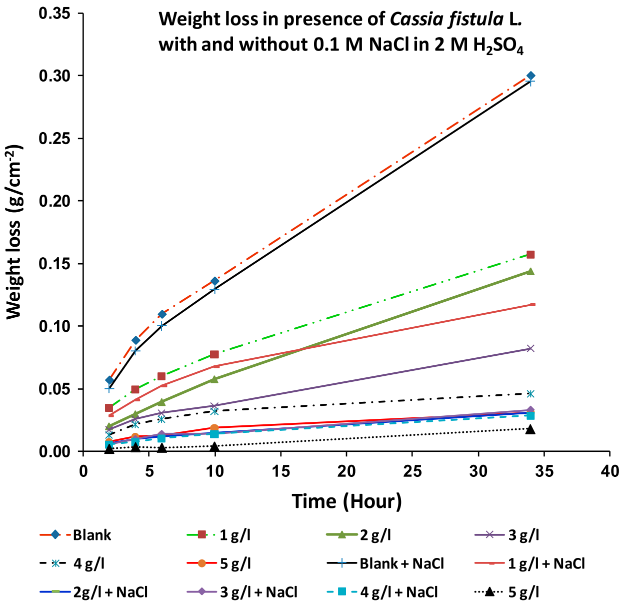

Fig. 6. Variation of weight loss with time for steel corrosion in 2 M H_2SO_4 solution in the absence and presence of different concentrations of water extract of *C. fistula* L. pods and 0.1 M NaCl.

electron density of the functional groups. Generally, the electron density is directly proportional to the strength of the adsorption bond. In heterocyclic compounds, adsorption normally occurs with the aromatic ring parallel to the metal surface. The degree of adsorption depends mainly on the electronic structure of the molecule [37,50]. Adsorption isotherms are very important in determining the mechanism of organic electrochemical reactions. The most frequently used adsorption isotherms are Langmuir and Temkin. The variation in efficiency depends not only on the type and nature of the constituents present but also on the structure of the inhibitor [35]. From the values of surface coverage (θ) (Table 1), it can be seen that the values increased with the increasing of the concentration of inhibitors in all solution systems at room temperature. Using these values of coverage, one can apply different adsorption isotherms to explain the experimental data. Assuming the adsorption of inhibitor molecule on steel surface is a monolayer adsorption, the lateral interaction between the inhibitor molecules is ignored, and then the Langmuir adsorption isotherm will be applied to investigate the adsorption mechanism by Eq. (3) [3,31]:

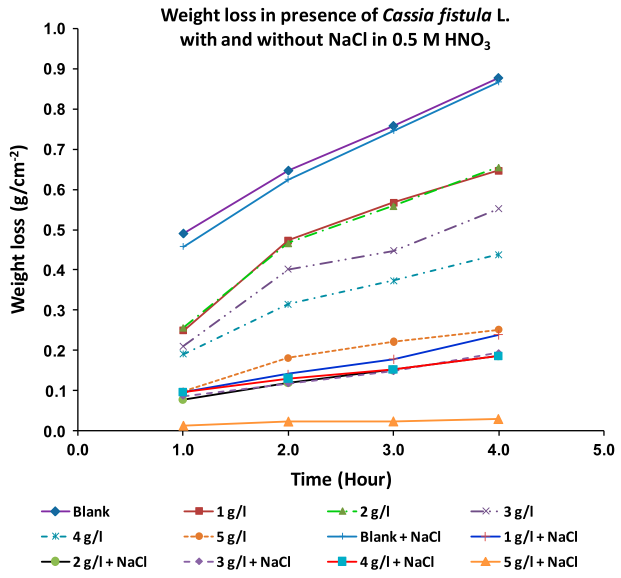

Fig. 7. Variation of weight loss with time for steel corrosion in 0.5 M HNO_3 solution in the absence and presence of different concentrations of water extract of *C. fistula* L. pods and 0.1 M NaCl.

$$\frac{c}{\theta} = \frac{1}{k} + c \tag{3}$$

which can also be written as Eq. (4):

$$\log\left(\frac{c}{\theta}\right) = \log c - \log k \tag{4}$$

where θ is the degree of surface coverage of the inhibitor; k is the equilibrium constant of adsorption of

Table 1
Calculated values of inhibition efficiency (IE %) and degree of surface coverage (θ) for steel in 2 M H_2SO_4 and 0.5 M HNO_3 solutions with inhibitors and 0.1 M NaCl mixtures at 25°C

Inhibitor conc. (mM)	Inhibition efficiency (% IE)		Surface coverage (θ)	
	o-phen (H_2SO_4)	*o*-phen (HNO_3)	*o*-phen (H_2SO_4)	*o*-phen (HNO_3)
Blank	0.00	0.00	0.00	0.00
0.25	46.84	32.45	0.47	0.32
0.50	56.33	53.35	0.56	0.53
1.00	62.28	57.14	0.62	0.57
2.50	66.41	60.57	0.66	0.61
5.00	**69.25**	**64.93**	**0.69**	**0.65**
0.1 M NaCl	0.00	0.00	0.00	0.00
0.25 + 0.1 M NaCl	64.80	37.15	0.65	0.37
0.50 + 0.1 M NaCl	71.40	57.92	0.71	0.58
1.00 + 0.1 M NaCl	74.78	61.82	0.75	0.62
2.50 + 0.1 M NaCl	83.06	65.93	0.83	0.66
5.00 + 0.1 M NaCl	**86.09**	**72.76**	**0.86**	**0.73**
Inhibitor conc. (g/l)	*C. Fistula* (H_2SO_4)	*C. Fistula* (HNO_3)	*C. Fistula* (H_2SO_4)	*C. Fistula* (HNO_3)
Blank	0.00	0.00	0.00	0.00
1.0	47.33	25.23	0.47	0.25
2.0	63.99	35.08	0.64	0.35
3.0	71.25	42.74	0.71	0.43
4.0	72.05	52.60	0.72	0.53
5.0	**75.48**	**61.15**	**0.75**	**0.61**
0.1 M NaCl	0.00	0.00	0.00	0.00
1.0 + 0.1 M NaCl	80.47	68.61	0.80	0.69
2.0 + 0.1 M NaCl	86.95	75.97	0.87	0.76
3.0 + 0.1 M NaCl	89.00	78.26	0.89	0.78
4.0 + 0.1 M NaCl	90.63	82.96	0.91	0.83
5.0 + 0.1 M NaCl	**95.19**	**86.13**	**0.95**	**0.86**

Note: Bold values represent the highest values.

inhibitor and c is the concentration of the inhibitor in the bulk electrolyte. The regressions between log (c/θ) and log c at different concentrations of inhibitors and in the presence and absence of 0.1 M NaCl in both the acid solutions have been computed and presented in Figs. 10 and 11, respectively. The straight lines obtained with high values of correlation coefficients (R^2) reflect the accuracy of the relationship, suggesting that the adsorption of inhibitor onto steel surface can be rigorously explained by the Langmuir adsorption isotherm. Values of free energy of adsorption, ΔG_{ads}, of water extract of *C. fistula* L. pods and *o*-phenanthroline on mild steel surface were calculated using Eq. (5) [19,51–55]:

$$\Delta G_{\mathrm{ads}} = -2.303RT \times \log(55.5k) \tag{5}$$

where R is the gas constant ($8.314 \times 10^{-3}\,\mathrm{kJ\,mol^{-1}\,K^{-1}}$), T (K) is the absolute temperature, and k is the equilibrium constant of adsorption of water extract of *C. fistula* L. pods and *o*-phenanthroline on the surface of mild steel. Values of ΔG_{ads} calculated from Eq. (5) are recorded in Table 2. These values are negative, indicating spontaneous adsorption of the inhibitor on the surface of mild steel [56,57]. Furthermore, the values of ΔG_{ads} also show the strong interaction of the inhibitor molecule onto the mild steel surface [58,59].

Generally, values of $\Delta G_{\mathrm{ads}} = -20\,\mathrm{kJ\,mol^{-1}}$ are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption). Those that are more negative than $-40\,\mathrm{kJ\,mol^{-1}}$ involve a charge sharing or a transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) [60,61]. For investigated water extract of *C. fistula* L.

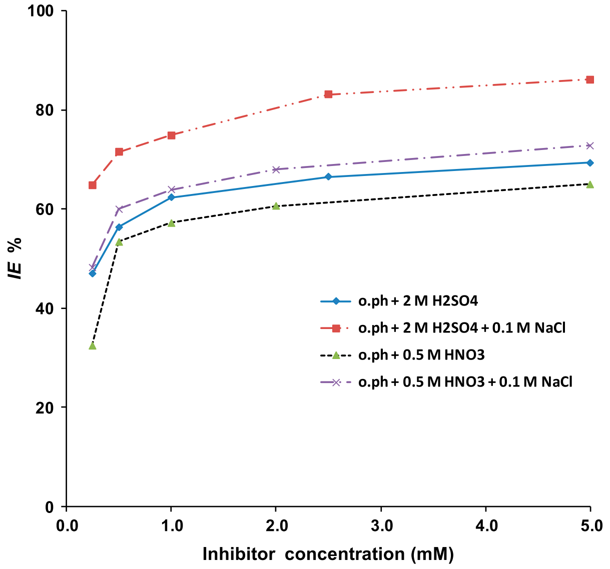

Fig. 8. Variation of percentage inhibition efficiency (IE %) with various concentrations of *o*-phenanthroline in 2.0 M H_2SO_4, 0.5 M HNO_3 and 0.1 M NaCl solutions.

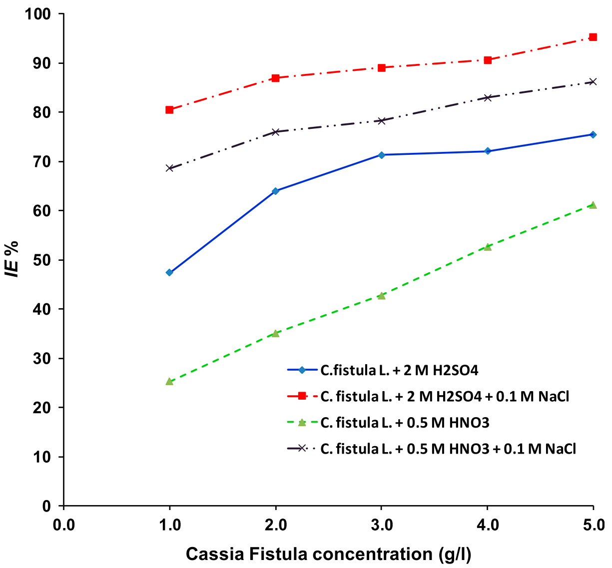

Fig. 9. Variation of percentage inhibition efficiency (IE %) with concentration of water extract of *C. fistula* L. pods in 2.0 M H_2SO_4, 0.5 M HNO_3 and 0.1 M NaCl solutions.

pods and *o*-phenanthroline inhibitors, one can see that the calculated ΔG_{ads} values, between -10.284 and $-16.834\,\mathrm{kJ\,mol^{-1}}$, indicate that the adsorption mechanism of both inhibitors on mild steel in 2 M H_2SO_4 and 0.5 M HNO_3 solution were typical of physisorption.

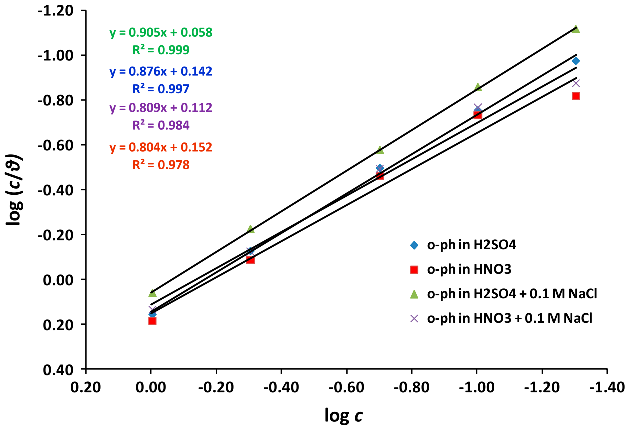

Fig. 10. Langmuir isotherm for *o*-phenanthroline in 2 M H_2SO_4 and 0.5 M HNO_3 at 25℃.

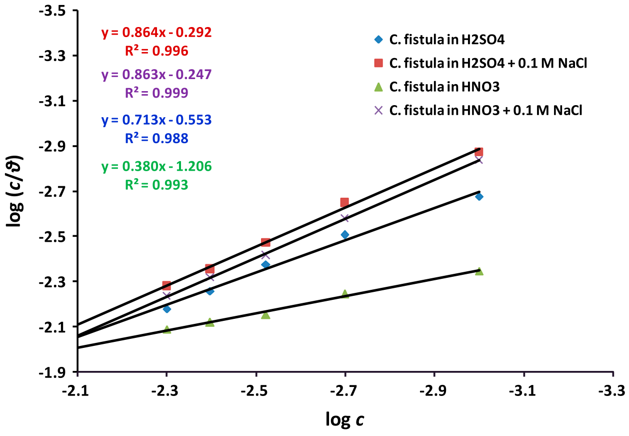

Fig. 11. Langmuir isotherm for water extract of *C. fistula* L. pods in 2 M H_2SO_4 and 0.5 M HNO_3 at 25℃.

3.5. Synergism mechanism

The data in Table 1 revealed that the presence of chloride ions increase the inhibition efficiency of *C. fistula* L. pods and *o*-phenanthroline. The *o*-phenanthroline is a nitrogen-containing organic compound, which contains unshared electron pair and π-electrons. The surface of iron is positively charged in sulfuric and nitric acid solutions [62] and chloride ions will be strongly adsorbed on the metallic part of the double layer, where they form intermediate bridges between the metal surface and the inhibitor [63]. In strong acidic solution (0.5 M HNO_3 and 2.0 M H_2SO_4), *o*-phenanthroline may be protonated, leading to positive charge in molecule. It is also wellknown that steel surface contains positive charge due to $E_{corr} - E_q = 0$ (zero charge potential) > 0 [31,32], thus, it is difficult for the positively charged

Table 2
Langmuir adsorption parameters for the adsorption of water extract of *C. fistula* L. pods and *o*-phenanthroline on the surface of mild steel

System	log *k*	*k*	Slope	ΔG_{ads} (kJ/mol)	R^2
o-phenanthroline + H_2SO_4	0.142	1.387	0.876	−10.763	0.997
+H_2SO_4 + 0.1 M NaCl	0.058	1.143	0.905	−10.284	0.999
+HNO_3	0.152	1.419	0.804	−10.820	0.978
+HNO_3 + 0.1 M NaCl	0.112	1.294	0.809	−10.591	0.984
Cassia Fistula L. + H_2SO_4	0.553	3.573	0.713	−13.108	0.988
+H_2SO_4 + 0.1 M NaCl	0.292	1.959	0.864	−11.619	0.996
+HNO_3	1.206	16.069	0.380	−16.834	0.993
+HNO_3 + 0.1 M NaCl	0.247	1.766	0.863	−11.362	0.999

o-phenanthroline to approach the positively charged steel surface because of the electrostatic repulsion, this is why single *o*-phenanthroline cannot act as an excellent inhibitor for steel corrosion in acidic solution without containing chloride ion. With the presence of chloride ion, the specific adsorption of chloride ion causes the negatively charged surface of steel, thus, by means of electrostatic attraction (physical adsorption), protonated *o*-phenanthroline easily reaches steel surface, followed by the transference of electron from nitrogen atom in *o*-phenanthroline to the d-orbital of iron atom at the steel/solution interface. The presence of the hydroxyl, carbonyl, and carboxylic groups in the compounds extracted from *C. fistula* L. pods may be protonated in acidic solution which explains the higher efficiencies of this extract over *o*-phenanthroline in the presence of NaCl due to the attraction between the positive charges on these compounds and the negative charges on the metal surface due to electrolyte barrier.

3.6. Electrochemical study

Fig. 12 presents the potentiodynamic polarization curves for steel in 0.5 N HNO_3 solution in the absence and presence of water extract of *C. fistula* L. pods and *o*-phenanthroline. The displayed curves show that the addition of *o*-phenanthroline and *C. fistula* L. pods extract shift the corrosion potential (E_{corr}) to less negative values indicating that the inhibitors behave as an anodic type inhibitor.

Potentiodynamic polarization curves for steel in 2 M H_2SO_4 solution in the absence and presence of NaCl, *C. fistula* L. pods and *o*-ph are presented in Fig. 13. As seen, the presence of chloride ions shifts the anodic part of the polarization curve to a more noble direction and corrosion potential (E_{corr}) into a more positive value, while the addition of *C. fistula* L. pods and *o*-phaffects both anodic dissolution of steel and cathodic reduction reactions in addition to a less negative shift of E_{corr} which indicates that the inhibi-

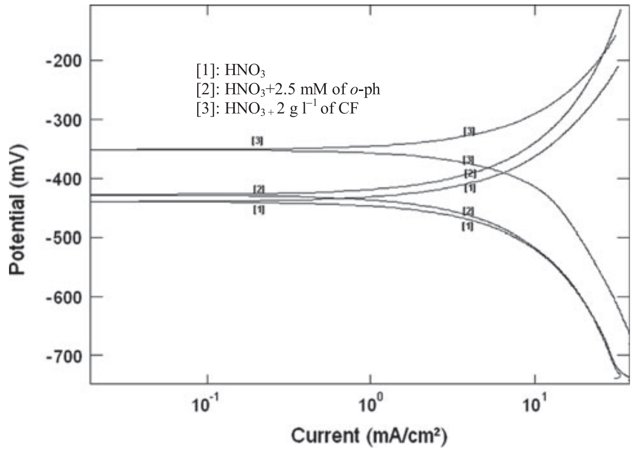

Fig. 12. Potoentiodynamic polarization curves for steel in 0.5 M HNO_3solution in absence and presence of FC and ph at 25°C.

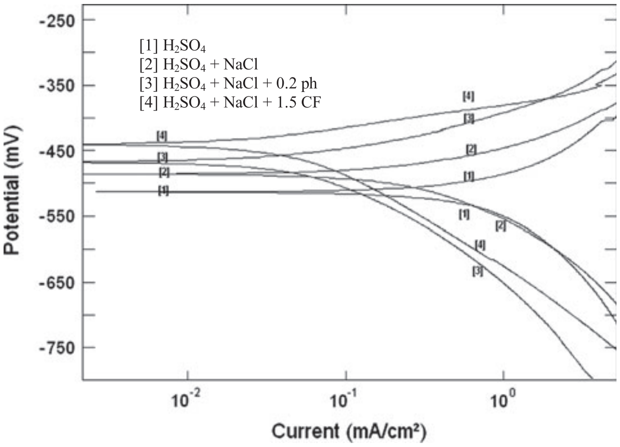

Fig. 13. Potoentiodynamic polarization curves for steel in 2 M H_2SO_4 solution in absence and presence of NaCl, *C. fistula* L. pods and *o*-ph at 25°C.

Table 3
Electrochemical polarization parameters of steel in 2 M H_2SO_4 and 0.5 M HNO_3 solutions in the absence and presence of 0.1 N NaCl and examined inhibitors at 25°C

Acid	NaCl Mol. l^{-1}	Inhibitor conc.	$-E_{corr.}$ mV	β_a	β_c	$i_{corr.}$ mV/cm^2	% P
				mV/decade			
H_2SO_4	00	00	520	13	163	0.71	00
		2.0 g l^{-1} (CF)	484	88	186	0.37	47.7
		2.5 mM (*o*-ph)	533	103	138	0.42	40.8
	0.1	00	497	91	112	0.31	00
		2.0 g l^{-1} (CF)	427	32	117	0.03	90.3
		2.5 mM (*o*-ph)	472	61	115	0.05	83.9
HNO_3	00	00	439	148	157	3.12	00
		3.0 g l^{-1} (CF)	430	152	140	2.58	17.3
		2.5 mM (*o*-ph)	392	151	159	2.17	30.5
	0.1	00	432	156	164	7.36	00
		3.0 g l^{-1} (CF)	451	133	267	1.04	85.6
		2.5 mM (*o*-ph)	403	114	126	1.80	75.5

tor acts as a mixed-type inhibitor with a predominant anodic effect.

The corrosion current density was calculated from the intersection of cathodic and anodic Tafel line. The values of the electrochemical parameters are given in Table 3. The displayed data shows that, in H_2SO_4, the presence of plant extract decreases the corrosion current density (i_{corr}) and shifts the corrosion potential (E_{corr}) to low negative values. On the other hand, the presence of *o*-phenanthroline slightly affects the values of corrosion potential (E_{corr}) indicating that it could act as a pickling inhibitor [64]. Moreover, in the presence of *o*-phenanthroline, the anodic and cathodic Tafel slopes (b_a and b_c) are slightly changed suggesting that the inhibiting action occurred by the simple blocking of the available cathodic and anodic sites on the metal surface, while the anodic Tafel slopes (β_a) have lower numerical values in the presence of *C. fistula* L. pods extract suggesting that the inhibiting action of the extract takes place by controlling the anodic processes. On the other hand, higher value of cathodic Tafel slopes (β_c) in HNO_3 and NaCl in the presence of plant extract indicates that the extract affects the cathodic process. The percentage of inhibition efficiency (IE %) was calculated from the polarization measurements using the relation:

$$\text{IE } \% = \left[\frac{i_o - i}{i_o}\right] \times 100 \tag{6}$$

where i_o and i are the corrosion current density, in the absence and presence of an inhibitor, respectively. As shown, plant extract is more efficient than *o*-phenanthroline. The data also proves that a higher inhibition efficiency of *o*-phenanthroline and plant extract is achieved in the presence of sodium chloride. This may be explained on the basis of cooperative mechanism of inhibition due to the strongly adsorbable chloride ion [65] which increases the adsorption of organic cations by creating oriented dipole [66].

4. Conclusion

- Water extract of *C. fistula* L. pods and *o*-phenanthroline effectively inhibit mild steel corrosion in 2 M H_2SO_4 and 0.5 M HNO_3 solutions and the inhibition efficiency increases in the presence of 0.1 M NaCl according to cooperative mechanism.
- The adsorptive behavior of water extract of *C. fistula* L. pods and *o*-phenanthroline were approximated by Langmuir isotherm. Calculated free energy of adsorption, ΔG_{ads}, values display that the adsorption mechanism of both inhibitors on mild steel in 2 M H_2SO_4 and 0.5 M HNO_3 solutions were typical of physisorption.
- In general, the addition of *C. fistula* L. pods and *o*-ph shift E_{corr} to a less negative direction indicates that the inhibitors have predominant anodic effect.
- FTIR and GC Mass indicated that *C. fistula* L. pods extract contains many functional groups and π electrons, which may be responsible for the inhibitive properties of this extract.

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